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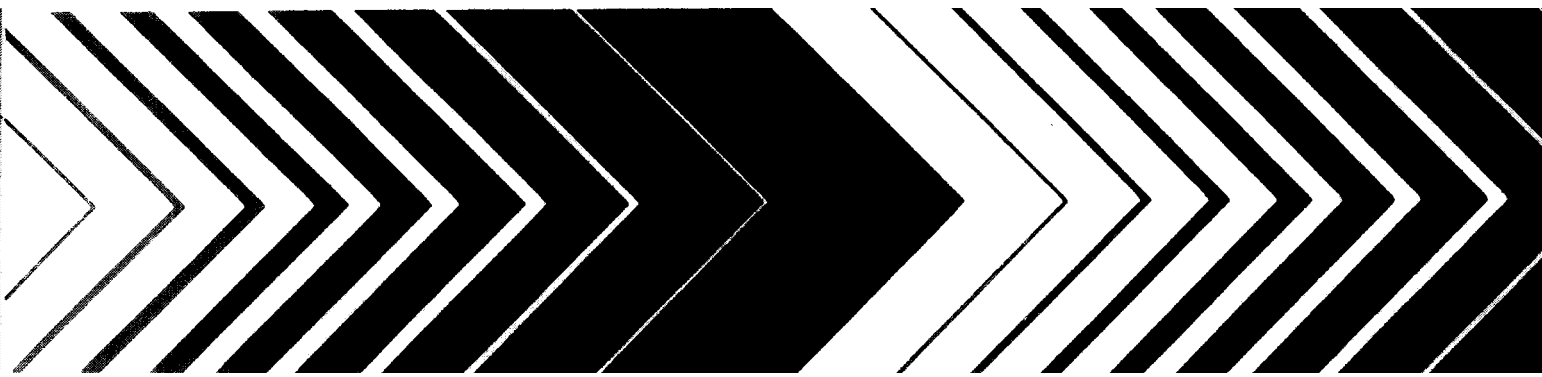
Methods for Monitoring Pump-and-Treat Performance



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METHODS FOR MONITORING PUMP-AND-TREAT PERFORMANCE

by

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FOREWORD

EPA is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

Since the 1980s, numerous pump-and-treat systems have been constructed to: (1) hydraulically contain contaminated ground water, and/or, (2) restore ground-water quality to meet a desired standard such as background quality or Maximum Contaminant Level (MCL) concentrations for drinking water. Although hydraulic containment is usually achievable, experience proves that aquifer restoration will be hindered at many sites due to Non-Aqueous Phase Liquid (NAPL) dissolution, contaminant desorption, inefficient hydraulic flushing of heterogeneous media, and other chemical and physical process limitations. Given the complexity and site-specific nature of ground-water remediation, pump-and-treat system objectives must be clearly identified and system operation carefully monitored to determine effectiveness. Typically, monitoring involves measuring hydraulic heads and contaminant concentrations to evaluate ground-water flow directions, recovery system capture zones, contaminant migration, and contaminant removal. This document was developed on behalf of the United States Environmental Protection Agency (EPA) to outline methods for evaluating the effectiveness and efficiency of pump-and- treat remediation systems.

Clinton W. Hall /s/
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EVALUATING GROUND-WATER PUMP-AND-TREAT SYSTEMS

Abstract

Since the 1980s, numerous pump-and-treat systems have been constructed to: (1) hydraulically contain contaminated ground water, and/or, (2) restore ground-water quality to meet a desired standard such as background quality or Maximum Contaminant Level (MCL) concentrations for drinking water. Although hydraulic containment is usually achievable, experience suggests that aquifer restoration can often be hindered at many sites due to the dissolution of Non-Aqueous Phase Liquids (NAPLs), contaminant desorption, inefficient hydraulic flushing of heterogeneous media, and other chemical and physical process limitations. Given the complexity and site-specific nature of ground-water remediation, pump-and-treat system objectives must be clearly identified and system operations carefully monitored to determine effectiveness. Typically, monitoring involves measuring hydraulic heads and contaminant concentrations to evaluate ground-water flow directions, recovery system capture zones, contaminant migration, and contaminant removal. This document was developed on behalf of the United States Environmental Protection Agency (EPA) to outline methods for evaluating the effectiveness and efficiency of pump-and-treat remediation systems.

1. INTRODUCTION

1.1 PUMP-AND-TREAT OBJECTIVES

Although this document focuses on the containment or remediation of contaminated ground water using pump and treat (P&T) systems, other technologies are discussed in a limited way, particularly as they are used in concert with P&T systems. It is important to note that in the selection and implementation of any remediation system, or consortia of systems which are designed to contain or remediate contaminated ground water, that the sources of contaminants must be removed from the site or sufficiently isolated to assure that they can no longer contribute contaminants to the ground water.

A common remedial strategy to deal with contaminated ground water is to extract the contaminated water and treat it at the surface prior to discharge or reinjection. This is referred to as conventional pump-and-treat (P&T) remediation. An overview of pump-and-treat ground-water remediation technology is provided by Mercer et al. (1990). Between 1982 and 1990, 72 percent (314) of all Superfund site Records of Decisions (RODs) addressing ground-water remediation specified P&T technology (Steimle, 1992).

P&T systems are designed to: (1) hydraulically contain and control the movement of contaminated ground water to prevent continued expansion of the contamination zone; (2) reduce dissolved contaminant concentrations to comply with clean-up standards and thereby "restore" the aquifer; or (3) a combination of these objectives.

Hydraulic containment of dissolved contaminants by pumping ground water from wells or drains has been demonstrated at numerous sites. The concept is illustrated in Figure 1-1. Fluid injection (using wells, drains, or surface application) and physical containment options (such as subsurface barrier walls and surface covers) can enhance hydraulic containment systems. Recovered und water is usually treated at the surface using methods selected to remove the contaminants of concern (Table 1-1). In many cases, hydraulic containment systems are designed to provide long-term containment of contaminated ground water at the lowest cost by optimizing well, drain, surface cover, and/or cut-off wall locations and by minimizing pumping rates.

P&T designed for aquifer restoration generally combines hydraulic containment with more active manipulation of ground water (i.e., higher pumping rates) to attain ground-water clean-up goals during a finite period. As described below, aquifer restoration is much more difficult to achieve than hydraulic containment.

Selection of P&T objectives depends on site conditions and remedial goals. Hydraulic containment is preferred where restoration is technically impracticable (e.g., not capable of being done or carried out) due to the presence of subsurface NAPL, buried waste, formation heterogeneity, or other factors (USEPA, 1993). Aquifer restoration may be an appropriate goal where these confounding factors are absent or minimal. At many sites, P&T systems can be used to contain contaminant sources areas and attempt restoration of downgradient dissolved contaminant plumes (Figure 1-2).

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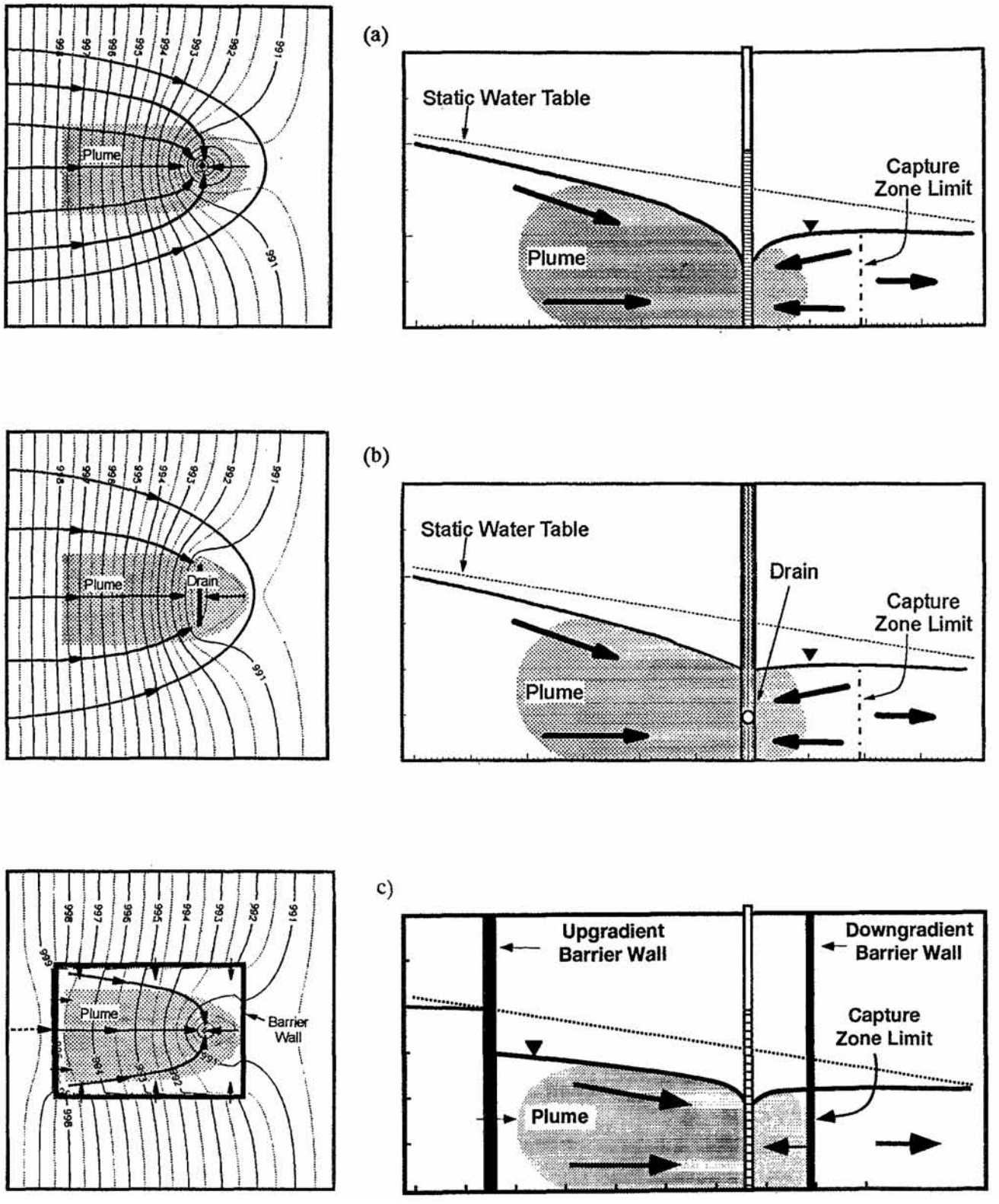

Figure 1-1. Examples of hydraulic containment in plan view and cross section using P&T technology: (a) pump well, (b) drain, and (c) well within a barrier wall system.

TABLE 1-1. SUMMARY OF SELECTED GROUND-WATER TREATMENT TECHNOLOGIES (FROM BOUWER ET AL., 1988).

Ground-Water Treatment Technology	*Representative Examples*	*Residual Streams*	*Status of Technology*
ORGANIC CONTAMINANTS:			
Air stripping	Packed towers, surface or diffused aeration removal of volatile compounds; soil venting	Air stream with VOCs	Commercial
Liquid-phase	GAC removal of broad spectrum of VOCs	GAC for regeneration or disposal	Commercial
Stream stripping	Packed tower with stream stripping, removal of low volatile organics	Recovered solvent	Some commercial
Membranes	Ultrafiltration for removal of selected organics	Concentrated brine side stream	Commercial
Oxidation	Ozone/UV, or ozone/H_2O_2, destruction of chlorinated organics	None	Some commercial in development stages
Activated sludge	Oxygen or air biological oxidation for removal/ destruction of degradable organics	Sludge	Commercial
Fixed-film biological reactors	Fixed-film fluidized bed, for oxidation of less degradable organics	Sludge	Commercial
Biophysical	Powdered carbon, with activated sludge, treatment of high strength wastewaters	Powdered carbon and bacterial	Commercial, PACT process
INORGANIC CONTAMINANTS:			
Alkaline precipitation	Heavy metals removal	Hazardous sludge	Commercial
Coagulation	Ferric sulfate or alum for heavy metals removal	Hazardous sludge	Commercial
Ion exchange	Heavy metals; nitrate	Regeneration stream	Commercial
Adsorption	Selenium removal on activated alumina	Regeneration stream	Commercial
Filtration	Removal of clays, other particulates	Backwash wastes	Commercial
Reduction	SO_2 reduction of CR (VI)	Chromium sludge	Commercial
Membranes	Reverse osmosis, ultrafiltration for removal or metals, other ions	Concentrated liquid waste	Commercial, new membranes under development
Oxidation	Fe(II) and Mn(II)	Sludge	Commercial

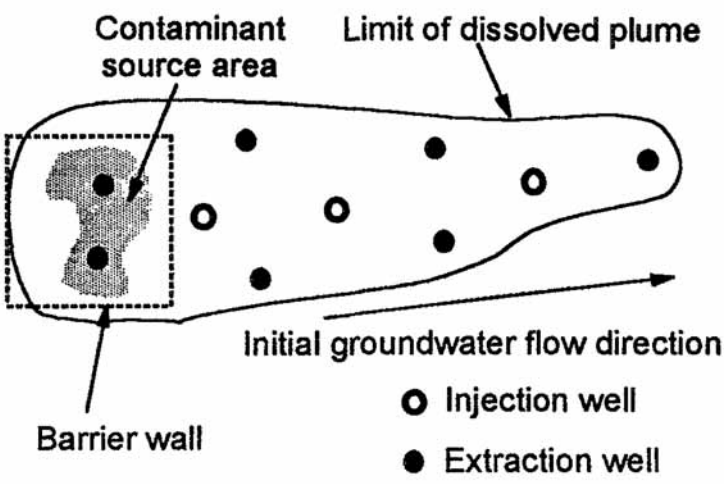

Figure 1-2. Plan view of the mixed containment-restoration strategy. P&T is used to contain ground-water contamination source areas (e.g., where NAPL or wastes may be present) and attempt aquifer restoration downgradient.

1.2 TAILING AND REBOUND CONSTRAINTS

Although P&T systems continue to be widely i4sed to reduce dissolved contaminants in ground water, experiences gained in recent years suggest that the efficiency of these systems can be compromised by a number of factors that are related to the contaminants of interest and characteristics of the site. As a result, it is often difficult to reduce dissolved contaminants to below drinking-water standards in reasonable time frames (e.g., less than 10 years) at many sites (Palmer and Fish, 1992; CH_2M Hill, 1992; Haley et al., 1991; Mercer et al., 1990; Mackay and Cherry, 1989; Keely, 1989; Harman et al., 1993; Doty and Travis, 1991). Monitoring contaminant concentrations in ground water with time at P&T sites reveals "tailing" and "rebound" phenomena. "Tailing" refers to the progressively slower rate of dissolved contaminant concentration decline observed with continued operation of a P&T system (Figure 1-3). At many sites, the asymptotic, apparent residual, contaminant concentration exceeds clean-up standards. Another problem is that dissolved contaminant concentrations may "rebound" if pumping is discontinued after temporarily attaining a clean-up standard (Figure 1-3).

Tailing and rebound may result from several physical and chemical processes that affect P&T remediation (Figure 1-4).

- *Non-Aqueous Phase Liquid (NAPL) dissolution* -- Subsurface NAPLs can be long-term sources of ground-water contamination due to their limited aqueous solubility that may greatly exceed drinking water standards (Cohen and Mercer, 1993). This long-term contamination potential is illustrated in Figure 1-4(d). If NAPLs are not removed (i.e., by excavation) or contained, tailing and rebound will occur during and after P&T operation, respectively, in and downgradient of the NAPL zone. The dissolution of a NAPL source may require the removal of thousands of equivalent pore volumes.

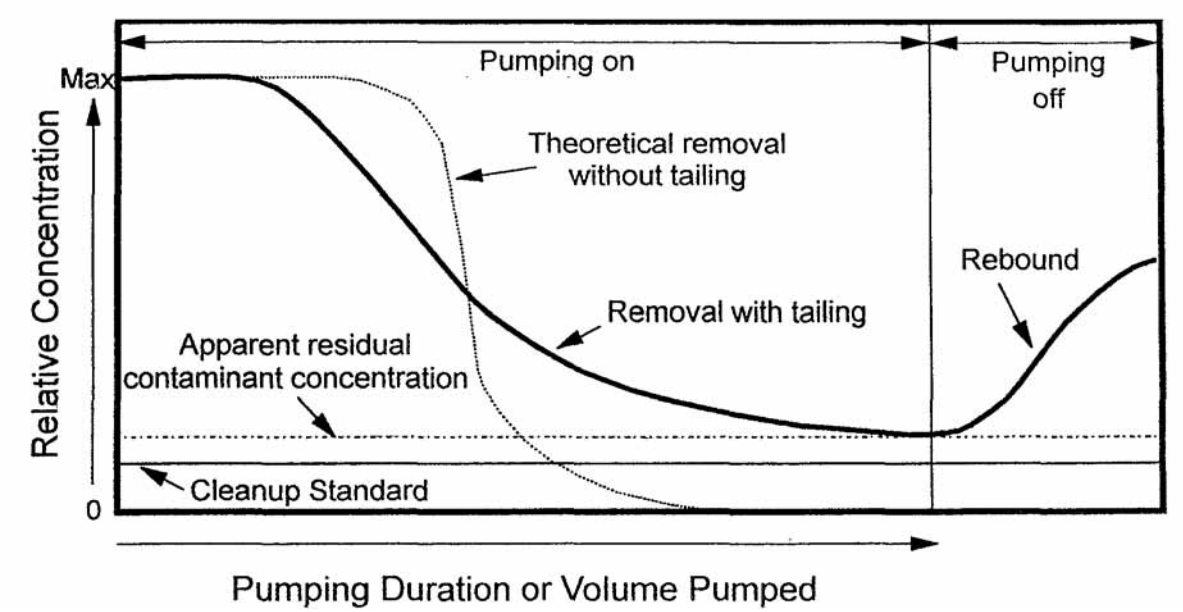

Figure 1-3. Concentration versus pumping duration or volume showing tailing and rebound effects (modified from Keely, 1989).

- *Contaminant desorption* -- As dissolved contaminant concentrations are reduced by P&T system operation, contaminants sorbed to subsurface media desorb from the matrix into ground water. This equilibrium partitioning process can be described by the Langmuir isotherm,

$$C_s = C_{smax} [K C_w) / (1 + K C_w)] \quad (1\text{-}1)$$

or the Freundlich sorption isotherm,

$$C_s = K C_w^{\,n} \quad (1\text{-}2)$$

where C_s and C_w are the contaminant concentrations associated with the solid and aqueous phases, respectively, K is the adsorption constant, C_{smax} is the maximum possible soil contaminant concentration, and n is a measure of nonlinearity (Figure 1-5). For the linear isotherms (n = 1) and for limited ranges of C_w, particularly at low concentration, where in the Freundlich constant can be identified as a distribution ratio, K_d, such that

$$K_d = C_s / C_w \quad (1\text{-}3)$$

The K_d values for hydrophobic, nonpolar organic contaminants are frequently represented as the product of the organic carbon content of the media, f_{oc} (mass of carbon/mass of soil), and the organic carbon partition coefficient, K_{oc} (mass of contaminant per unit mass of carbon/equilibrium concentration in soil) such that

$$K_d = K_{oc} \ f_{oc} \quad (1\text{-}4)$$

Values for f_{oc} and K_{oc} may be obtained from laboratory analyses of core material and literature sources (USEPA, 1990), respectively. By assuming a linear isotherm, these

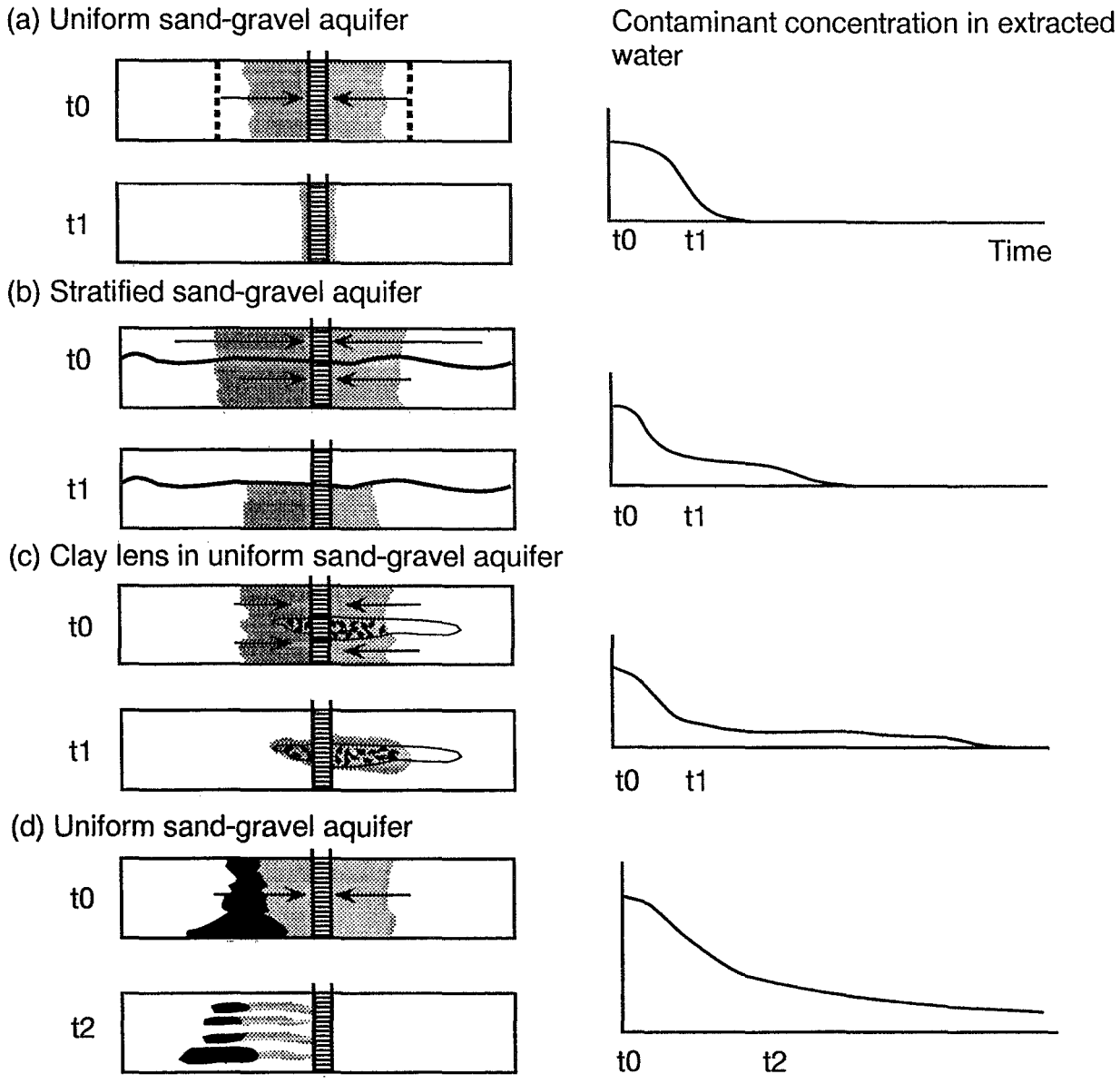

Figure 1-4. **Hypothetical examples of contaminant removal from ground water using P&T (modified from Mackay and Cherry, 1989). Black indicates NAPL presence; stippling indicates contaminant in dissolved and sorbed phases (with uniform initial distribution); and arrows indicate relative ground-water velocity. Ground water is pumped from the well at the same rate for each case. Note that the dotted lines in (a) represent the volume of ground water that would have to be pumped to flush slightly retarded contaminants from the uniform aquifer.**

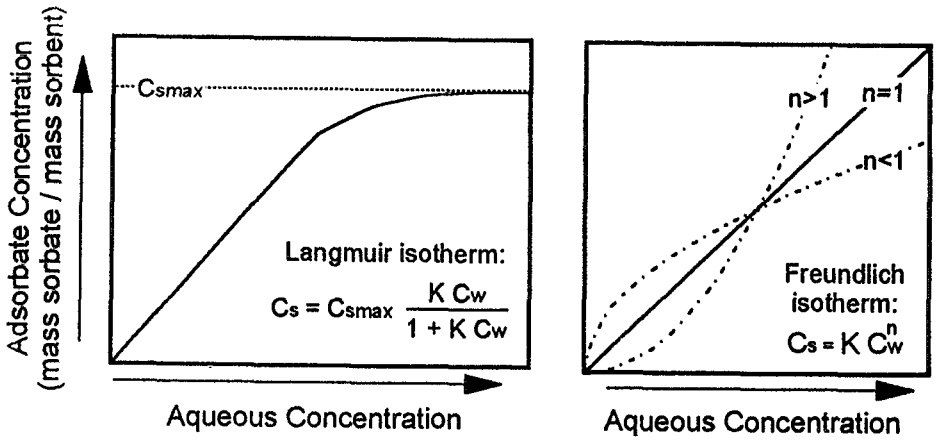

Figure 1-5. The Langmuir and Freundlich adsorption isotherms (modified from Palmer and Fish, 1992).

relationships can be used to estimate: (1) the retardation factor, R_f, or velocity of dissolved contaminant movement, v_c, relative to ground-water flow, v_{gw},

$$R_f = v_c/v_{gw} = 1/ [1 + (K_d\rho_b/n)] \quad (1\text{-}5)$$

(2) the retardation coefficient, R, which is the reciprocal of R_f,

$$R = 1 + (K_d\rho_b/n) \quad (1\text{-}6)$$

and (3) the equilibrium distribution of contaminant mass between the solid and aqueous phases

$$f_w = C_wV_w / [(C_wV_w)+(C_sM_s)] = V_w / (V_w +K_dM_s) \quad (1\text{-}7)$$

where ρ_b is the dry bulk density, n is the porosity, V_w is the volume of water in the total subject volume, M_s is the mass of solids in the total subject volume, and f_w is the fraction of mass residing in the aqueous phase.

Sorption and retardation are site-specific. Field retardation values vary between different contaminants at a given site and between different sites for a given contaminant (Mackay and Cherry, 1989). As illustrated in Figure 1-4, desorption and retardation increase the volume of ground water which must be pumped to attain dissolved contaminant concentration reductions. Tailing and rebound effects will be exacerbated where desorption is slow relative to ground-water flow and kinetic limitations prevent sustenance of equilibrium contaminant concentrations in ground water (Palmer and Fish, 1992; Haley et al., 1991; Brogan, 1991; Bahr, 1989). This concept is illustrated in Figure 1-6. Kinetic limitations to mass transfer are likely to be relatively significant in the high g round-water velocity zone in the vicinity of

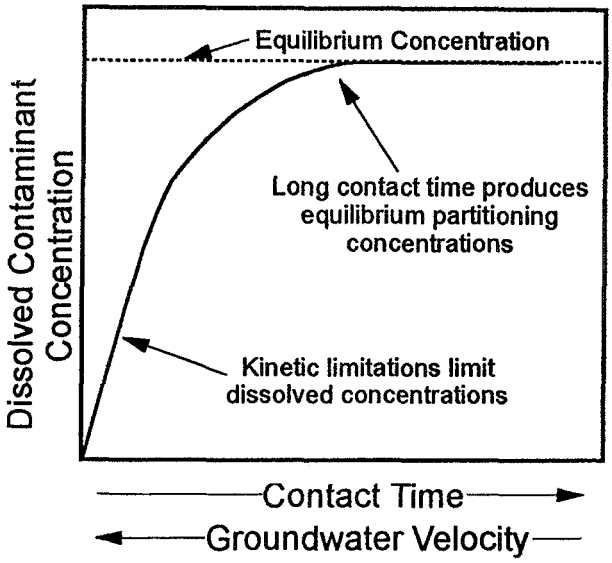

Figure 1-6. Relationship between ground-water velocity induced by pumping and the concentration of dissolved contaminants that (a) desorb from the porous media, (b) dissolve from precipitates, or (c) dissolve from NAPL (modified from Keely, 1989). Kinetic limitations to dissolution exacerbate tailing.

injection and extraction wells. Under such conditions, insufficient control time is available between the adsorbed contaminants and ground water to allow the development of maximum concentrations.

- *Precipitate dissolution* -- Large quantities of inorganic contaminants, such as chromate in $BaCrO_4$, may be bound with crystalline or amorphous precipitates on porous media (Palmer and Fish, 1992). Dissolution of contaminant precipitates may cause tailing (Figure 1-7) and rebound. These effects may increase due to mass transfer limitations where the dissolution rate is slow relative to ground-water flow.

- *Ground-water velocity variation* -- Tailing and rebound also result from the variable travel times associated with different flow paths taken by contaminants to an extraction well (Figures 1-4 and 1-8). Ground water at the edge of a capture zone travels a greater distance under a lower hydraulic gradient than ground water closer to the center of the capture zone. Additionally, contaminant-to-well travel times vary as a function of the initial contaminant distribution and differences in hydraulic conductivity. If pumping is stopped, rebound will occur wherever the resulting flow path modification causes the magnitude of contaminant dilution to be reduced.

- *Matrix diffusion* -- As contaminants advance through relatively permeable pathways in heterogeneous media, concentration gradients cause diffusion of contaminant mass into the less permeable media (Gillham et al., 1984). Where contamination persists for long periods, this diffusion may cease when contaminant concentrations equilibrate between the different strata. During a P&T operation, dissolved contaminant concentrations in the relatively permeable zones may be quickly reduced by advective flushing relative to the less permeable zones as illustrated in Figure 1-1 (c). This causes a reversal in the initial concentration

gradient and the slow diffusion of contaminants from the low to high permeability media. This slow process can cause long-term tailing, and rebound after the termination of pumping.

Tailing and rebound patterns associated with these different physical and chemical processes are similar. Multiple processes (i.e., dissolution, diffusion and desorption) will typically be active at a P&T site. Diagnosis of the cause of tailing and rebound, therefore, requires careful consideration of site conditions and usually cannot be made by examination of concentration versus time data alone.

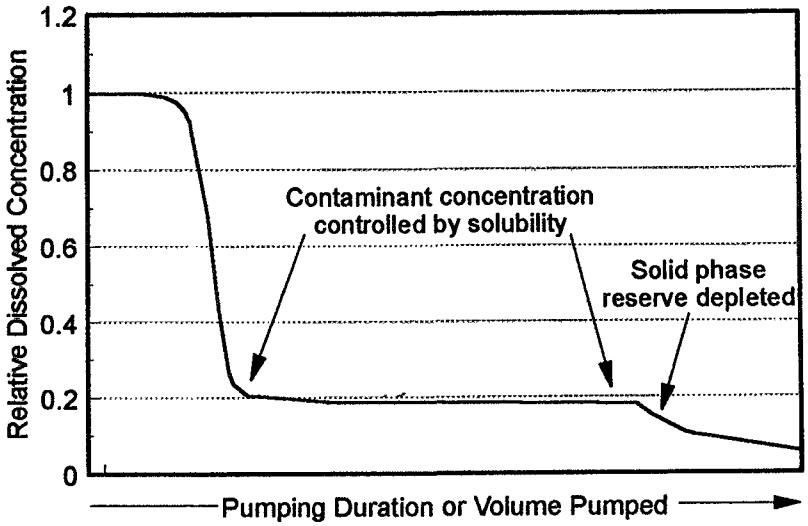

Figure 1-7. Dissolved contaminant concentration in ground water pumped from a recovery well versus time in a formation that contains a solid phase contaminant precipitate (from Palmer and Fish, 1992).

1.3 HOW IS SUCCESS MEASURED?

A successful P&T system is a design and implementation that has been determined capable of accomplishing the remedial action . objectives of containment and/or restoration in a desired time period. For containment, success is usually defined as the achievement of hydrodynamic control at the outer limits (horizontal and vertical) of the contaminant plume such that hydraulic gradients are inward to the pumping system. Measuring the effectiveness of a restoration program is generally more difficult due to: (1) limitations of methods used to estimate contaminant mass distribution prior to and during remediation, and (2) the inherent difficulty of aquifer restoration as discussed in the previous section.

Tracking the performance of a containment or restoration P&T system is achieved by setting performance criteria, monitoring to assess these criteria, and assessing operational efficiency. Performance measures such as induced hydraulic gradients and contaminant concentration reductions are monitored to verify that the system is operating as designed and achieving remediation goals. If the performance criteria have not been adequately formulated, perhaps due to a flawed site conceptual model,

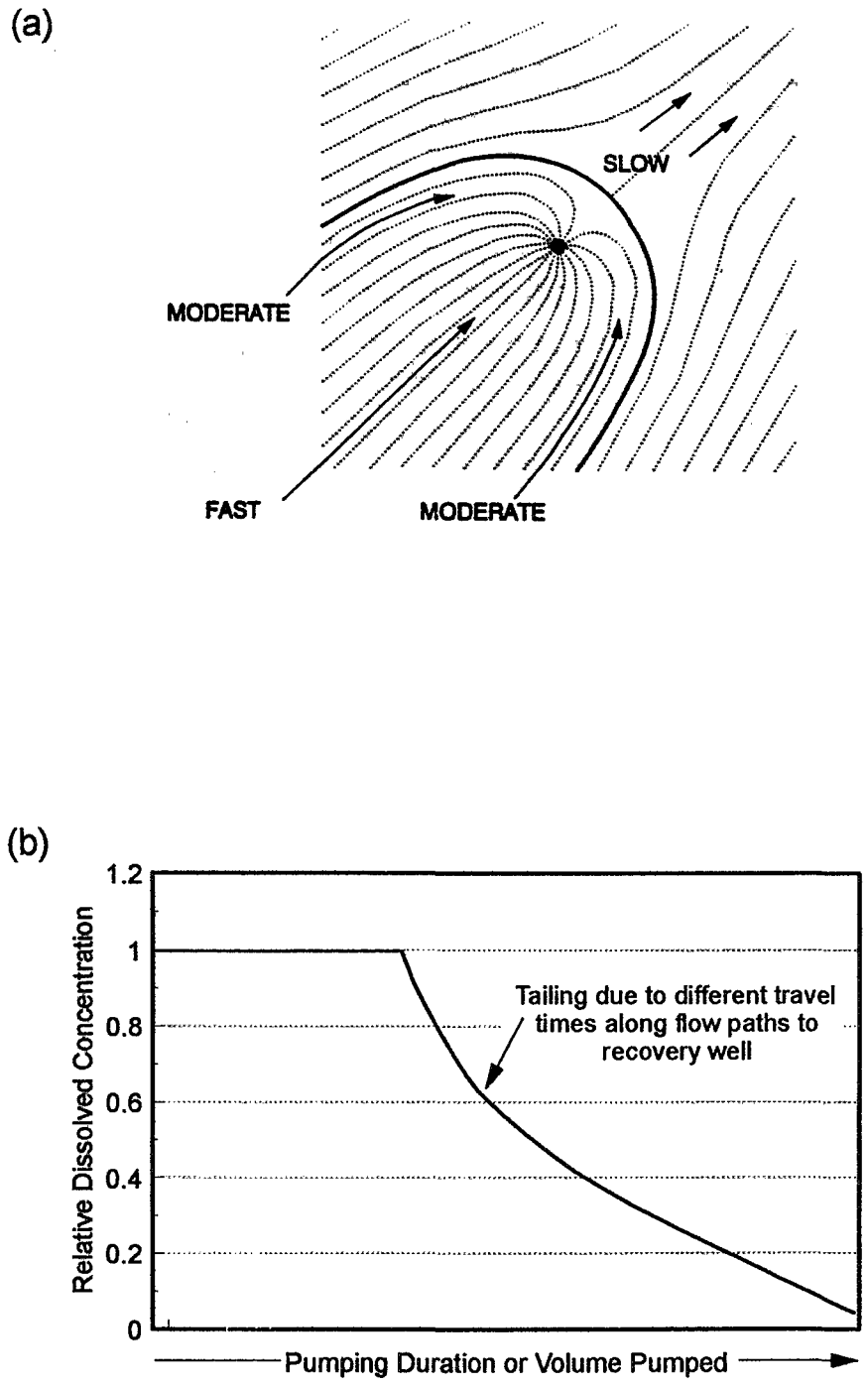

Figure 1-8. **Advective velocity, flowpath, and travel time variations (a) to a recovery well (from Keely, 1989) and (b) induce tailing (from Palmer and Fish, 1992).**

then meeting specified criteria may provide a misleading sense of system effectiveness. Operational efficiency is also a measure of success for a P&T system. It refers to the cost-effectiveness of a system, and can be measured by monitoring costs and assessing related environmental benefits. For example, a highly efficient and cost-effective hydraulic containment system may extract ground water at the minimum rate required to demonstrate attainment of hydraulic gradient objectives. Ideally, a phased remedial approach, whereby system improvements evolve from performance monitoring, will maximize both the performance effectiveness and efficiency of a P&T system.

1.4 PURPOSE AND FORMAT OF REPORT

The purpose of this report is to provide guidance for monitoring the effectiveness and efficiency of P&T systems. Related complementary guidance is given by USEPA (1992a). Emphasis herein is placed on the "pump" portion of P&T technology. Chemical enhancements to P&T remediation, such as injection of cosolvents or surfactants, are discussed by Palmer and Fish (1992). For details on ground-water treatment techniques and strategies, see AWWA (1990), Nyer (1992), and USEPA (1987), among others. It is assumed that the reader is familiar with basic concepts of hydrogeology and P&T technology.

The report is divided into six main sections: (1) Introduction, (2) Monitoring Hydraulic Containment, (3) Monitoring Ground-Water Restoration, (4) Evaluating Restoration Success/Closure, (5) A Case Study, and (6) References. Examples and illustrations are provided to convey concepts. This section provides an overview of P&T use, objectives, and limitations. Sections 2 and 3 describe performance criteria, monitoring objectives, data analysis, system enhancements, and protocols for evaluating the effectiveness of the P&T systems designed for containment and restoration, respectively. Methods for determining the timing of system closure are addressed in Section 4. In Section 5, monitoring data from the Chem-Dyne site in Hamilton, Ohio are presented as an example of a P&T system effectiveness evaluation.

2. MONITORING HYDRAULIC CONTAINMENT

2.1 OBJECTIVES AND PROCESS

Monitoring programs are designed to measure the effectiveness and efficiency of P&T system performance in achieving hydraulic containment objectives. For successful hydraulic containment, contaminants moving with ground water in the containment zone must follow pathlines that are captured by the P&T system (Figure 1-1). In addition to P&T systems designed to remove dissolved contaminants and contaminants that may be adsorbed to mobile colloids, remedial designs should be developed to preclude the migration of NAPLs, if present, beyond the containment perimeter.

In general, containment monitoring involves: (1) measuring hydraulic heads to determine if the P&T system affects hydraulic gradients in such a way as to prevent ground-water flow and dissolved contaminant migration across the containment zone boundary; and (2) ground-water quality monitoring to determine if temporal and spatial variations in contaminant distribution are consistent with hydraulic containment (i.e., no contaminant movement or increase of contaminant mass across the containment zone boundary). Containment monitoring activities, therefore, typically include some combination of hydraulic head measurement, ground-water sampling and analysis, tracer monitoring, and pumping rate measurement.

Containment monitoring plans are developed and revised during a phased remedial program. As outlined in Figure 2-1, the first step in establishing performance criteria, after characterizing pre-remedy ground-water flow patterns and contaminant distributions, is to determine the desired containment area (two-dimensional) and volume (three-dimensional). These should be clearly specified in site remedial action and monitoring plans.

At any particular site, there may be multiple separate containment areas, or a contaminant source containment area within a larger dissolved plume containment area (e.g., Figure 1-2), or a containment area that does not circumscribe the entire ground-water contamination zone. As shown in Figure 1-1, barrier walls are often used along the containment perimeter, while drains and recovery wells are located within the containment area. After defining the containment area, a capture zone analysis (Section 2.6) is conducted to design a P&T system and a performance monitoring plan is developed based on the predicted flow system (Figure 2-1). The monitoring plan may be revised as improvements to the site conceptual model and the P&T system evolve, and, if the containment area/volume is modified based on changes in contaminant distribution with P&T operation.

2.2 PERFORMANCE MONITORING MEASUREMENTS AND INTERPRETATION

Various hydraulic containment performance criteria are described in this section. Monitoring of these criteria is done to determine if the containment system is functioning as designed and to provide guidance for P&T system optimization. Performance is monitored by measuring hydraulic heads and determining gradients, ground-water flow directions, pumping rates, ground-water chemistry, and, possibly, tracer movement.

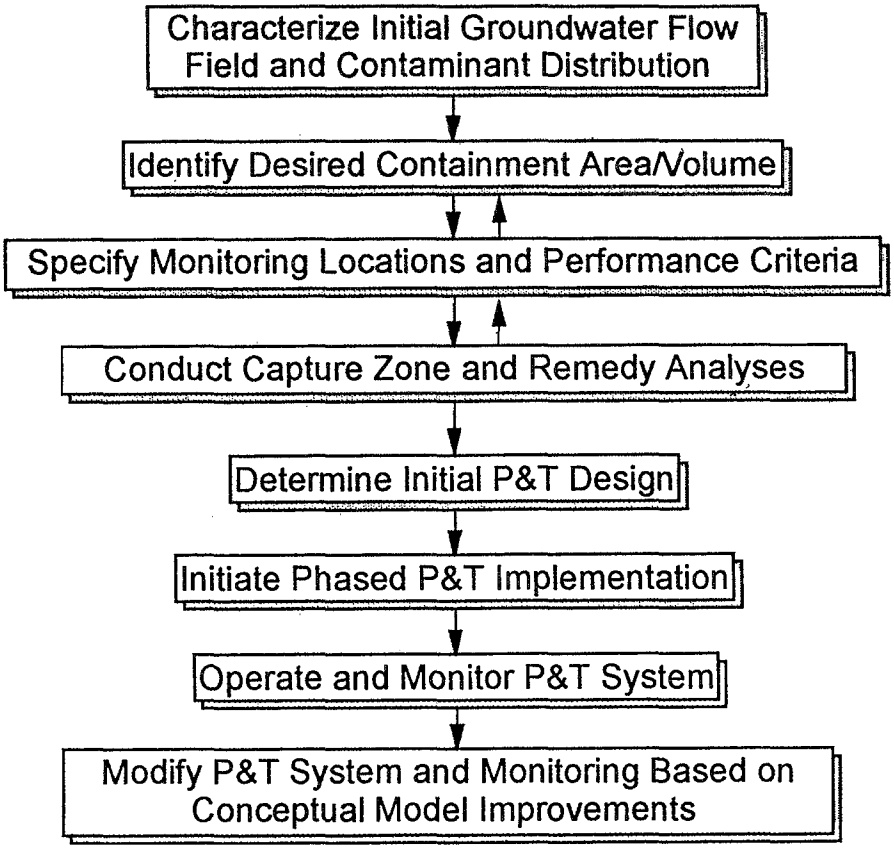

Figure 2-1. Components of a phased design and implementation of a P&T monitoring program.

2.2.1 Inward Hydraulic Gradients and Capture Zone Analysis

2.2.1.1 Performance Concept

Inward hydraulic gradients across the boundary of, and/or within, the desired containment may be specified as part of the performance standard. An inward gradient indicates that the ground-water flow is inward, thus allowing the capture of dissolved contaminants by the P&T system.

Hydraulic head and gradient data are interpreted within the context of capture zone analysis (Section 2.6). The capture zone concept is illustrated in Figure 2-2. Note that the capture zone of a well is not coincident with its zone of influence (ZOI) except in those incidences where the hydraulic gradient is negligible prior to pumping. Therefore, there can be locations in the vicinity of a pumping well where a drawdown within that well does not indicate that the ground water will be contained by the capture zone. It should also be noted that successful containment does not require the establishment of inward hydraulic gradients all around the containment zone when it is larger than the contaminated zone. In either case, the subsurface volume showing inward hydraulic gradients will not correspond to the actual capture volume (Larson et al., 1987).

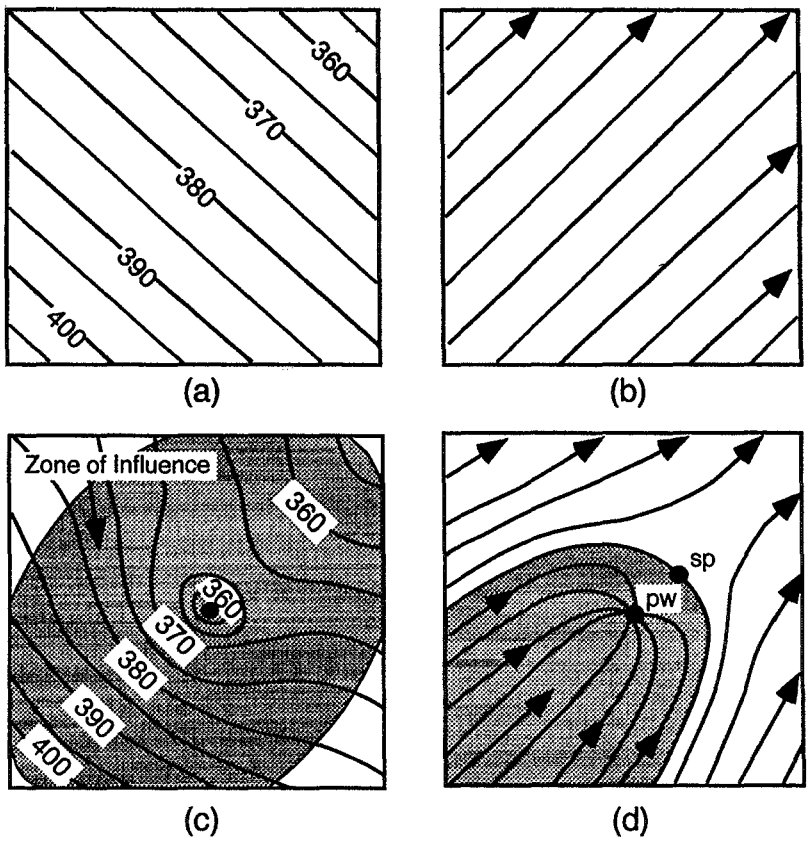

Figure 2-2. **In isotropic media, ground-water flow lines (b) are orthogonal to hydraulic head contours (a) (modified from Gorelick et al., 1993). Pumping causes drawdowns and a new steady-state potentiometric surface (c). Following the modified hydraulic gradients, ground water within the shaded capture zone flows to the pump well (d). The stagnation point is designated sp.**

2.2.1.2 Methods

Depth-to-water measurements can generally be made to +/- 0.01 or 0.02 ft. The accuracy of depth-to-water measurement methods is discussed by Thornhill (1989), USGS (1977), and Dalton et al. (1991). Well reference point elevations should be surveyed to +/- 0.01 ft and checked periodically due to the potential for settlement of surface materials, compaction of pumped strata, or physical damage to the well. This is particularly important when measuring small head differences because the flow direction may be misinterpreted due to slight elevation errors.

2.2.1.3 Measurement Locations

In relatively simple hydrogeologic settings inward hydraulic gradients can be estimated by comparing hydraulic heads in paired piezometers near the containment perimeter, primarily in the pre-pumping downgradient direction (Figure 2-3). For more complex flow systems, this may not always be true and gradients can only be determined by using three or more wells. Capture zone analysis incorporating aquifer tests and potentiometric surface data should be used to help select inward gradient control monitoring locations.

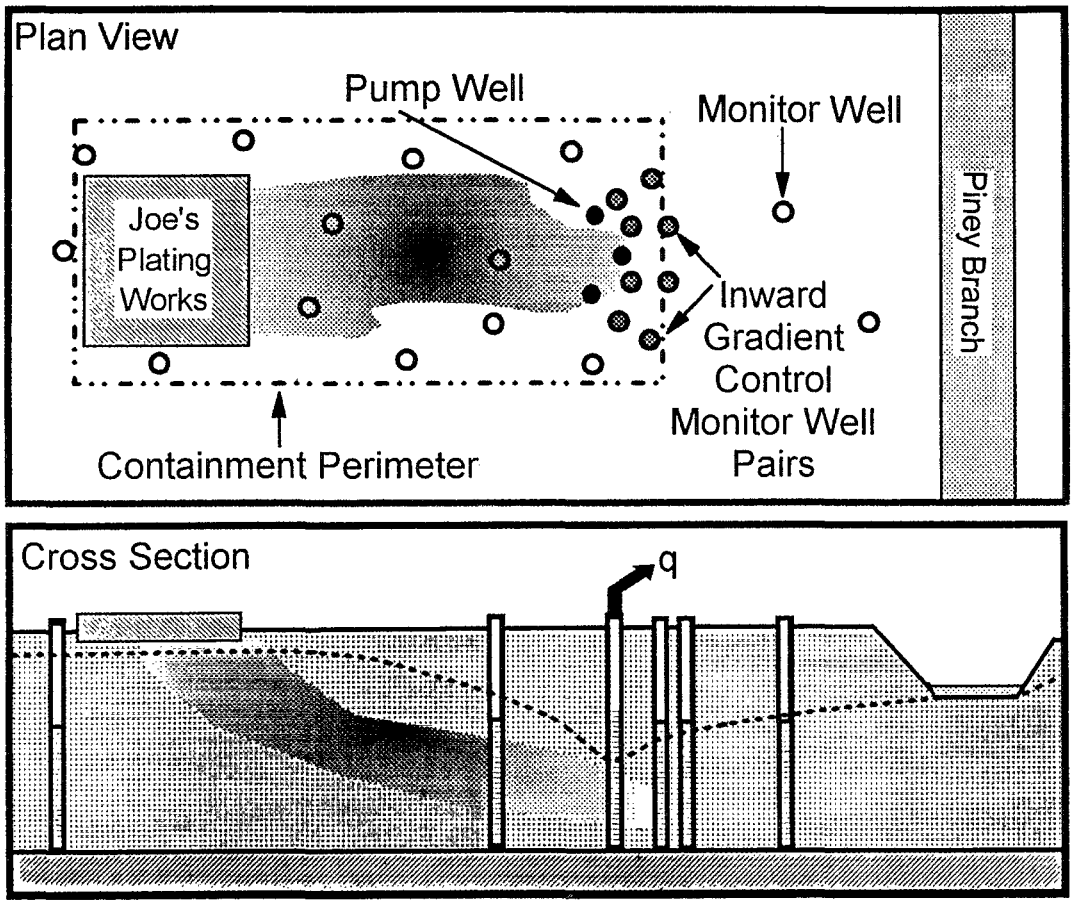

Figure 2-3. Inward gradients are often monitored by comparing hydraulic heads in paired piezometers near the containment perimeter and primarily in the pre-pumping downgradient direction.

Inward gradients can also be evaluated by interpreting potentiometric surface maps developed using all available and comparable hydraulic head data (measured in wells within and outside of the containment area). Since ground-water flow is perpendicular to the equipotential lines in the direction of decreasing potential, containment is inferred if flow lines at the containment boundary converge at extraction wells. However, it is critical that potentiometric surface maps be developed using hydraulic heads measured in comparable stratigraphic intervals to avoid misinterpreting horizontal flow directions, especially where significant vertical gradients are present. For this reason, care should be exercised with regard to incorporating measurements from wells with unknown or inconsistent completions. Potentiometric surface maps developed from wells completed in different geologic units may result in misleading interpretations and containment.

In addition to focusing on the downgradient side of the plume, containment boundary monitoring should also target the more permeable portions of the subsurface. Ground-water flow and contaminant migration occur preferentially in these zones. Ideally, the spatial distribution of preferential pathways will be identified during the remedial investigation. However, additional site characterization may be warranted to allow adequate performance monitoring.

Hydraulic gradients across the containment volume should be measured in three dimensions. This may be difficult to accomplish in areas lacking a sufficient number of observation wells to define the convoluted potentiometric surface that may develop due to complex site conditions (i.e., multiple pumping or injection wells, heterogeneity, anisotropy, transient effects, etc.). In addition to horizontal flow divides near pumping wells, flow divides also exist in the vertical dimension (Figure 2-4) because the hydraulic influence of each well extends only a limited depth (Larson et al., 1987; Keely, 1989). As shown in Figure 2-4, capture zone volume may be misinterpreted by neglecting vertical hydraulic gradients. Monitoring vertical hydraulic gradients is discussed further in Section 2.2.2.

In general, the number of observation wells needed to evaluate hydraulic containment increases with site complexity and with decreasing gradients along the containment perimeter. This latter factor is of particular concern with P&T systems that seek to minimize ground-water treatment and/or disposal costs by decreasing pumping to impose the smallest gradients needed for capture. In some cases, it may be practical (and necessary) to use a modeling analysis to interpret hydraulic head measurements and evaluate containment performance (Larson et al., 1987). In other cases, it will be cost-effective to overpump to achieve more demonstrable containment.

It is often easier to demonstrate that inward hydraulic gradients exist toward such systems as recovery drains than toward recovery wells (Figure 1-1). In some cases, this is a significant advantage of P&T systems that incorporate drains and walls.

2.2.1.4 Measurement Frequency

Inward gradients and hydraulic containment may be affected by hydraulic head fluctuations caused by the startup and cycling of P&T operations, offsite well pumping, tidal and stream stage variations, and seasonal factors. If the P&T site is located in an active hydrogeologic setting, hydraulic heads may rise and fall on the order of feet several times a day. To adequately monitor inward gradients and hydraulic containment, consider the following strategies.

(1) Monitor intensively during system startup and equilibration to help determine an appropriate measurement frequency. This may involve using pressure transducers and dataloggers to make near-continuous head measurements for a few days or weeks, then switching sequentially to daily, weekly, monthly, and possibly quarterly monitoring. Data collected during each phase is used to examine the significance of hydraulic head fluctuation and justify any subsequent decrease in monitoring frequency. An example of the use of frequent measurements to assess transient effects of daily pumping cycles on hydraulic gradients is shown in Figure 2-5.

(2) Make relatively frequent hydraulic head measurements when the P&T system pumping rates or locations are modified, or when the system is significantly perturbed in a manner that has not been evaluated previously. Significant new perturbations may arise from extraordinary recharge, flooding, drought, new offsite well pumping, improved land drainage, etc.

(3) Acquire temporally consistent hydraulic head data when measuring inward hydraulic gradients or a potentiometric surface so that differences in ground-water elevations within the well network represent spatial rather than temporal variations.

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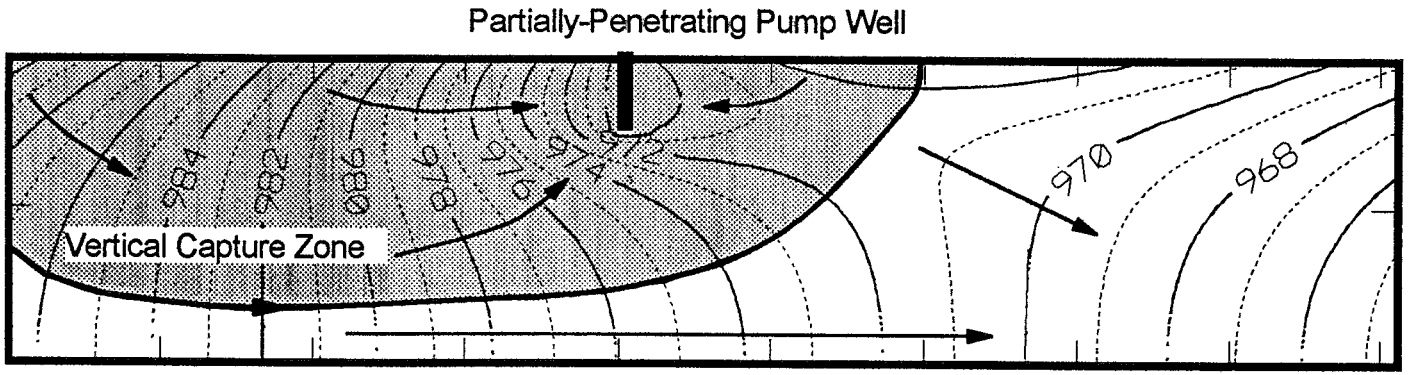


Figure 2-4. Cross-section showing equipotential contours and the vertical capture zone associated with ground-water withdrawal from a partially-penetrating well in isotropic media. Ground-water flow at depth beneath the well is not captured by pumping despite the presence of apparent upward gradients. In stratified, anisotropic media (e.g., Kx>Kz), the vertical hydraulic contro exerted by a partially-penetrating well will be further diminished.

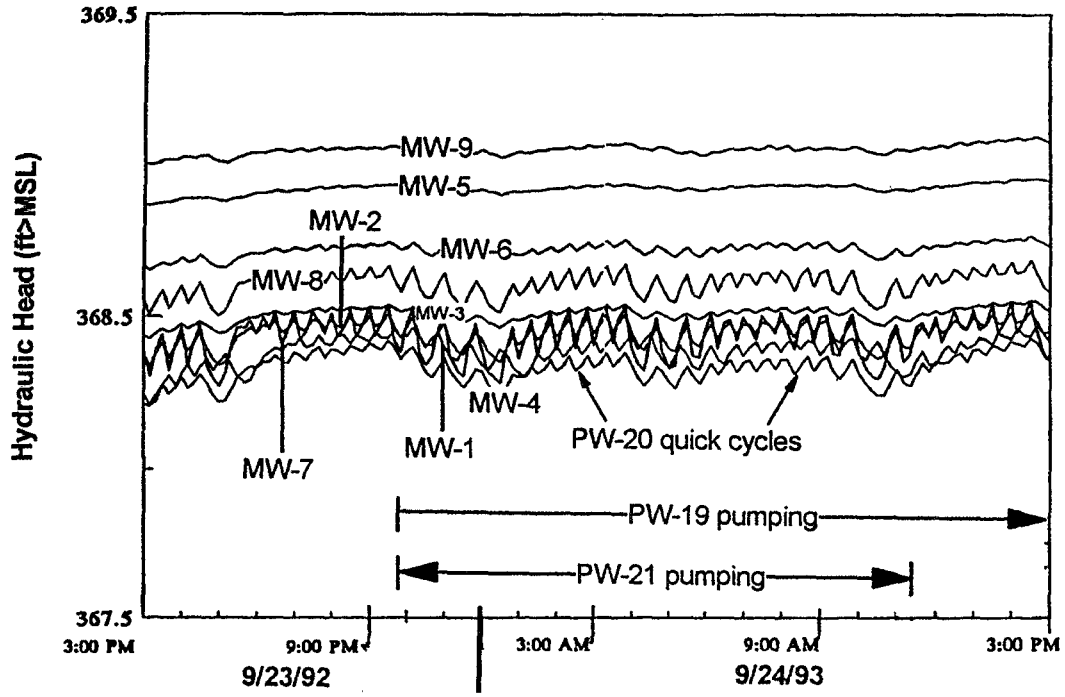


Figure 2-5. Near continuous hydraulic head measurements were made in several observation wells in the vicinity of a recovery well line to examine the transient water table response to pump cycles and recharge events (modified from ESE, 1992). The data reveal that ground-water flow directions are fairly constant during pump cycles. In conjunction with weekly data, it was determined that the frequency of hydraulic head surveys should be reduced to monthly.

If inward gradients are not maintained during P&T operation, an analysis should be made to determine if containment is threatened or lost. Rose diagrams can be prepared to display the variation over time of hydraulic gradient direction and magnitude based on data from at least three wells (Figure 2-6). Transient capture zone analysis, perhaps using a numerical model and particle tracking, may be required to assess containment effectiveness. Even where the time-averaged flow direction is toward the P&T system, containment can be compromised if contaminants escape from the larger capture zone during transient events or if there is a net component of migration away from the pumping wells over time.

2.2.1.5 Some Additional Considerations

Use of Pump Well Data -- Hydraulic heads and extraction rates associated with recovery wells should be factored into capture zone analysis. It is generally inappropriate, however, to interpret inward gradients by comparing the hydraulic head measured in a piezometer to that in a pump well (Figure 2-7). Rather, hydraulic gradients and flow patterns should be interpreted primarily based on head

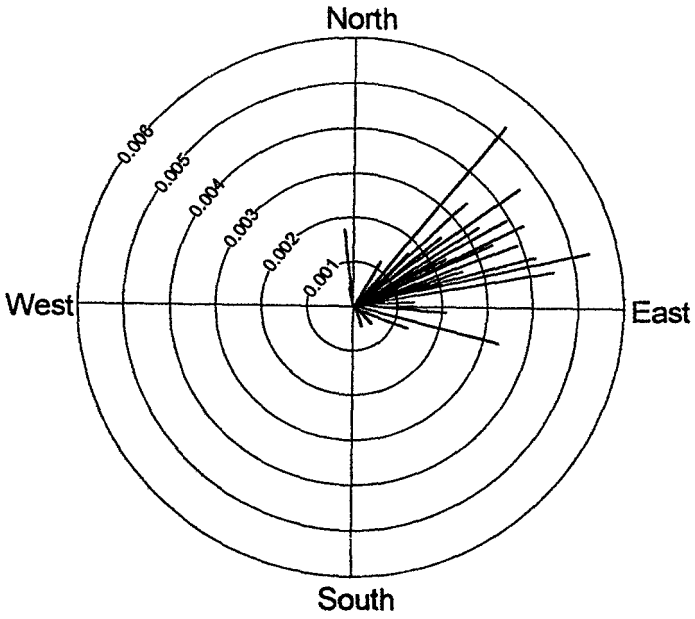


Figure 2-6. Example display of ground-water flow directions and hydraulic gradients determined between three observation wells.

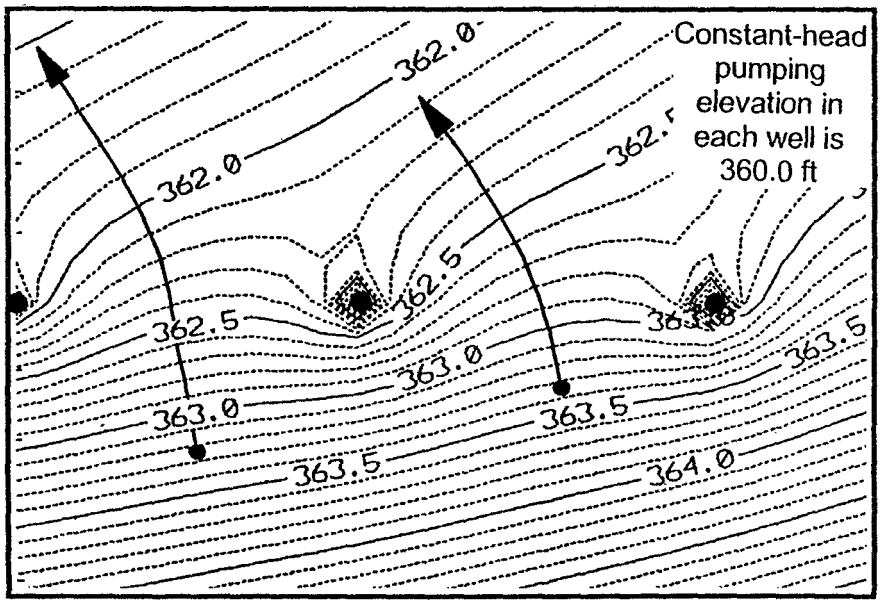


Figure 2-7. Ground water flows between and beyond the recovery wells even though hydraulic heads throughout the mapped aquifer are higher than the pumping level. Rely primarily on observation well data to determine flow directions.

measurements in observation wells or piezometers. Useful estimates of hydraulic heads in the vicinity of a pump well with a known pumping rate and level can be derived using well hydraulics equations (i.e., the Theis or Theim equations, Bear, 1979) or a ground-water flow model; but uncertainties associated with formation properties and well loss may confound the analysis.

Horizontal Anisotropy -- Where strata are inclined or dipping, particularly foliated media such as schist with high-angle dip, significant horizontal anisotropy may be present. The directions of maximum and minimum permeability are usually aligned parallel and perpendicular, respectively, to foliation or bedding plane fractures. In anisotropic media, the flow of ground water (and contaminants moving with ground water) is usually not perpendicular to the hydraulic gradient. This is demonstrated at a petroleum tank farm site in Virginia where the flow of leaked LNAPL and ground water is offset significantly from the hydraulic gradient toward the direction of maximum permeability (Figure 2-8). Interpretation of hydraulic head data and capture zone analysis must account for anisotropy to evaluate containment effectiveness. Various well hydraulics equations incorporate anisotropy (Papadopulos, 1965; Kruseman and deRidder, 1990) and many numerical models can treat anisotropic conditions.

Transient Loss of Capture during Early Pumping -- Given the steep initial hydraulic gradient induced by pumping, hydraulic containment provided by P&T operation may decrease with time due to the flattening of the drawdown cone(s) as illustrated by the computer simulations shown in Figure 2-9. Early demonstration of inward hydraulic gradients, therefore, does not ensure continued containment. Long-term monitoring must be relied upon to assess long-term P&T system performance.

Drawdown Limitations -- Under some conditions, inward hydraulic gradients cannot be maintained unless barrier walls are installed and/or water is injected (or infiltrated) downgradient of or within the contaminated zone. Limited aquifer saturated thickness, a relatively high initial hydraulic gradient, a sloping aquifer base, and low permeability are factors that can prevent hydraulic containment using wells or drains (Saroff et al., 1992). Where these conditions exist and hydraulic containment is planned, particular care should be taken during pilot tests to assess this limitation.

Injection/Extraction Cells -- Two prime objectives of aquifer restoration are to contain and/or remove contaminant plumes. Hydraulic controls provide an opportunity to concurrently accomplish both of these objectives. Recharging upgradient of the contaminant plume and flushing it toward downgradient collection points creates a ground-water recirculation cell that isolates the plume from the surrounding ground water. By properly adjusting recharge and extraction rates, these cells can minimize the volume of water requiring treatment, thereby reducing the flushing time. If permitted, water injection can greatly enhance hydraulic control of contaminated ground water. Options associated with selecting injection locations and rates provide great containment flexibility (e.g., Wilson, 1985).

Highly Permeable and Heterogeneous Media -- In highly permeable media, high pumping rates are usually required to attain hydraulic containment and performance monitoring can be complicated by flat hydraulic gradients. Barrier walls and containment area surface covers installed to reduce the rate of pumping needed for containment also facilitate demonstration of inward gradients (Figure 1-1). Complex heterogeneous media are difficult to characterize. Ideally, monitor wells are installed in the more

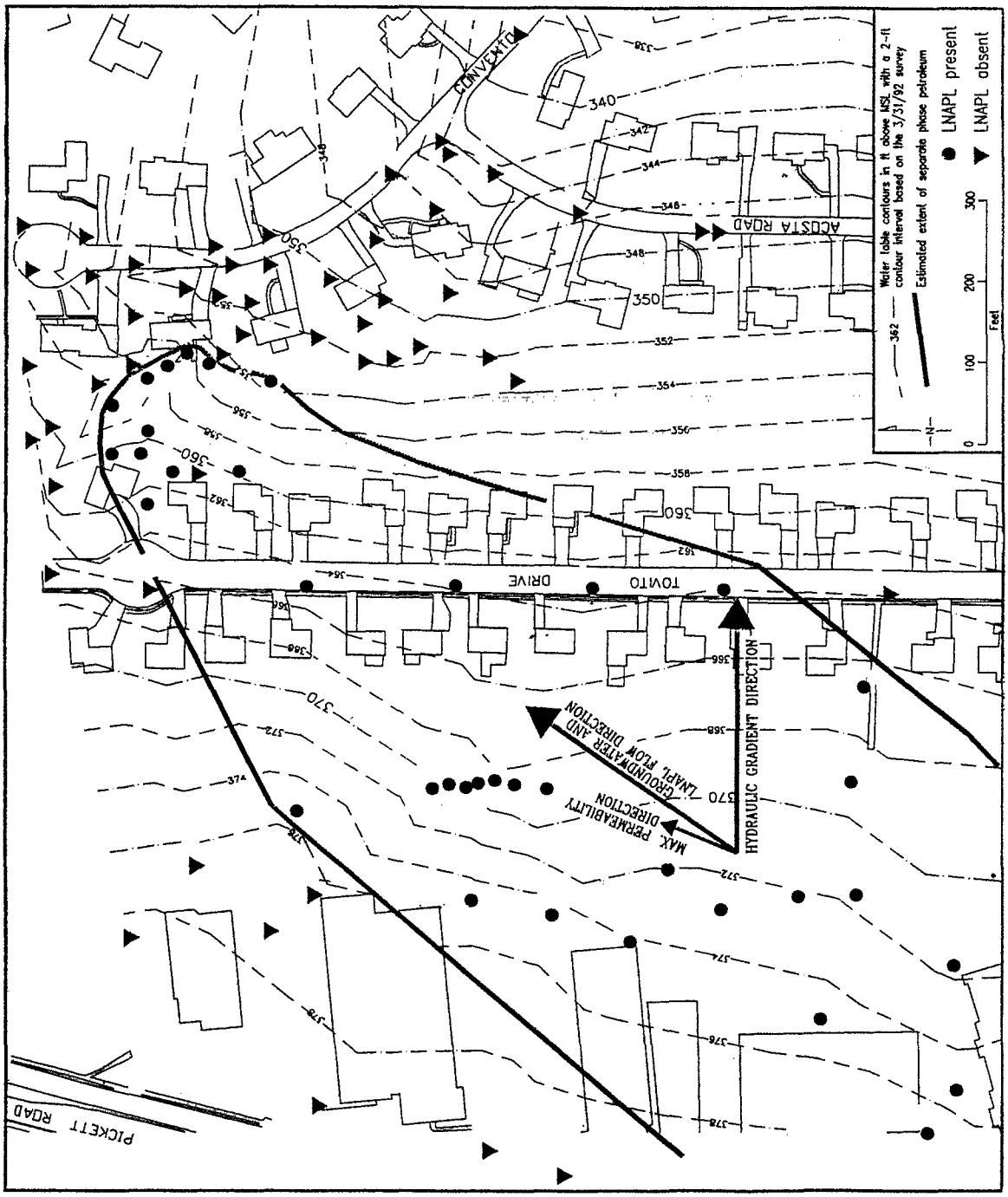


Figure 2-8. Ground-water and LNAPL flow in anisotropic saprolite soil from a petroleum-product tank farm in Fairfax, Virginia is offset from the hydraulic gradient toward the strike of saprolite foliation.

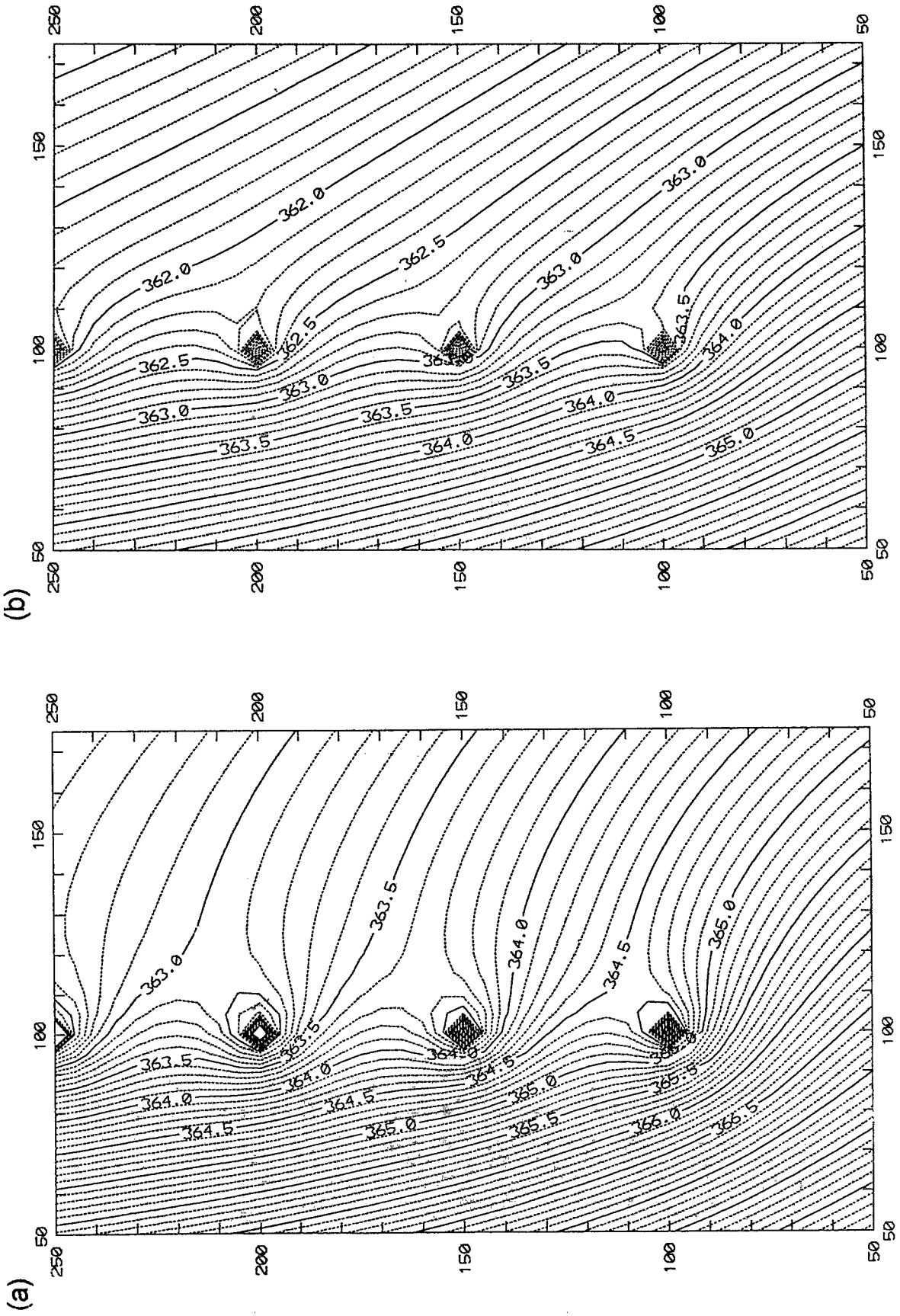


Figure 2-9. As this computer simulation illustrates, the initial steep drawdown induced by pumping flattens out with time, hydraulic containment may be diminished significantly as exemplified by the hydraulic head contours associated with a line of recovery wells after (a) 5 days of pumping and (b) after 30 days of pumping.

permeable strata to provide optimal chemical detection and gradient control monitoring capability. Hydraulic containment, inward gradient monitoring, and site characterization are also facilitated in heterogeneous media by installing barrier drains and walls, particularly if done in a manner that allows subsurface examination during construction.

NAPL Containment -- Inward hydraulic gradients will contain LNAPL migration. DNAPL, however, may migrate under the influence of gravity in directions that are counter to the hydraulic gradient. Unless of sufficient magnitude to overcome the gravitational force, therefore, inward hydraulic gradients cannot be relied upon to contain DNAPL movement. Cohen and Mercer (1993) describe several approaches for estimating hydraulic gradients required to arrest DNAPL migration.

Ambiguous Gradient Data -- At many P&T sites, interpretation of hydraulic gradients will provide an ambiguous measure of containment effectiveness. To raise confidence in the monitoring program, consider: (1) increasing the frequency and locations of hydraulic head measurements; (2) conducting more robust data analysis, perhaps using models; (3) relying more on chemistry monitoring; or (4) modifying the P&T system (e.g., by increasing the pumping rate) to provide more demonstrable containment.

2.2.2 Vertical Hydraulic Gradients

Inward gradients may also be specified as upward gradients at the base of the contaminant plume or containment volume. This is important because a P&T system may fail to prevent downward contaminant migration (e.g., where remediation wells are too shallow or have insufficient flow rates). For dissolved contaminants, in many cases, the magnitude of the upward gradient need only be measurable. For DNAPLs, the inward gradient must be large enough to overcome the potential for DNAPL to move via gravity and capillary pressure forces (Cohen and Mercer, 1993). At sites where upward hydraulic gradients sufficient to arrest DNAPL migration cannot be developed, consideration must be given to other containment strategies. For example, if DNAPL can be reduced to residual saturation by pumping, capillary forces may be sufficient to overcome gravitational forces and prevent downward migration.

Upward gradients across the bottom of the containment volume can be monitored by comparing (1) hydraulic head differences measured in adjacent nested wells that are screened at different depths and/ or (2) potentiometric surfaces developed for different elevations, stratigraphic units, or flow zones. Generally, a nested cluster of wells consists of three monitoring wells/piezometers completed at different depths. However, the required number of wells depends on site-specific monitoring objectives, contaminant distribution, P&T system design, and the degree of site complexity.

In a layered multiaquifer system, where the entire thickness of a contaminated upper aquifer is within the containment volume, upward gradient control wells can be completed above and below the underlying aquitard to determine the direction of flow across the aquitard (Figure 2-10). If, however, the containment volume bottom is within a flow zone of significant thickness, nested wells will generally be required at different elevations (above and below the containment volume bottom) within the flow zone. For this case, upward gradients may not ensure containment (Figure 2-4), and it may be necessary

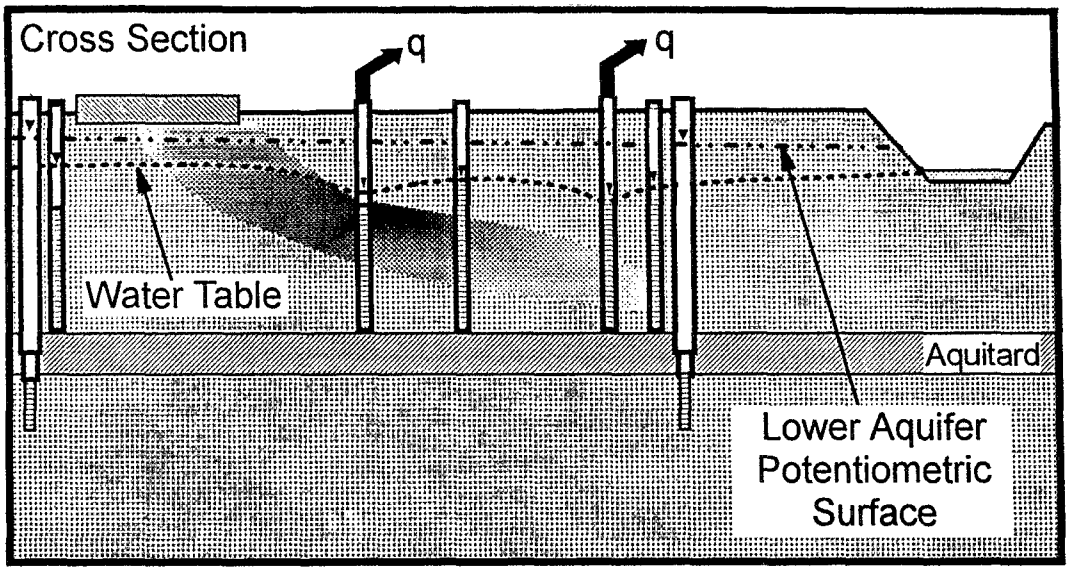


Figure 2-10. Vertical hydraulic gradients across an aquitard between aquifiers are typically measured using observation well nests.

to rely on a careful three-dimensional analysis of flow and chemical monitoring to evaluate containment effectiveness.

A more thorough analysis of upward hydraulic gradients can be made by comparing potentiometric surface maps for different elevations (or stratigraphic units) to develop a contour map of vertical hydraulic gradients. A vertical gradient contour map can be used to delineate areas of upward and downward flow components.

Special precautions should be taken when drilling monitor wells into and/or below a contaminated zone to minimize the potential for cross-contamination. Where DNAPL is present, it may be advisable to monitor potentially uncontaminated, deep units by installing wells beyond the DNAPL zone limit even though this will diminish the upward gradient monitoring capability.

2.2.3 Hydraulic Head Differences

True hydraulic gradients may be difficult to determine; therefore, the objective may revert to determining a measurable quantity, such as hydraulic head. Hydraulic head differences may be specified as performance criteria at pumping or observation wells as either differences in head between different locations at the same time or as time-dependent drawdown in particular wells. In any event, hydraulic head performance criteria must be developed within the context of capture zone analysis based on an understanding of the relationship between hydraulic heads at specific locations and local hydraulic gradients. Otherwise, they may be poor indicators of system performance.

2.2.4 Flow Meters

A few techniques and tools have been developed recently to measure horizontal ground-water flow directions directly in a single well. Such techniques include using a special flowmeter in a well to

measure horizontal flow direction (Kerfoot, 1984; Melville et al., 1985; Guthrie, 1986) and a colloidal borescope that measures the movement of naturally occurring colloids in ground water (Kearl and Case, 1992). If these tools are found to be reliable at a site, then flow directions (and hence inward hydraulic gradients) can be determined directly in wells placed along the containment boundary and elsewhere.

Technologies for measuring vertical flows within wells under ambient and pumping conditions hence also have been developed (Molz and Young, 1993). These tools allow better characterization of the relative permeability distributions and hence preferential flow paths.

2.2.5 Pumping Rates

For hydraulic containment, the placement and extraction or injection rates of wells are determined so that ground water in the containment area/volume follow pathlines to the P&T system. The initial design may be based on the results of ground-water modeling (Section 2.6) and may designate pumping rates, pump well drawdowns, or high-low pumping level ranges for the P&T system. However, it is not appropriate to specify model-determined pumping rates or levels as long-term performance criteria, because these may be too high or too low if the model is inaccurate. The feasibility of pumping rates and levels determined using a model must be verified during onsite aquifer testing, upon initiation of the P&T system, and by long-term monitoring.

Pumping rates and levels are monitored to: (1) demonstrate that the system is operational (or alert managers to make necessary repairs if pumps are found to be inoperable); (2) determine if pumping rates and levels are within specified tolerances; and, (3) provide data necessary for system optimization. Pumping rates must be maintained to control hydraulic gradients. As discussed in Section 2.2, if the rates are "optimized" to reduce P&T costs, it may become very difficult to demonstrate containment by measuring hydraulic gradients. When analyzing P&T system behavior, particularly where there are multiple pumping wells, it is important to monitor (and document) pumping rates, times, and levels on a well-specific basis (rather than simply monitoring totalized flows from multiple wells).

Well discharge rates can be determined by several methods, including the use of a pipe orifice weir, weirs and flumes, and flowmeters (Driscoll, 1986). During P&T system operation, however, pumping rates are usually monitored in a closed system using flowmeters which provide pumping rate and totalized discharge data. Several different types of flowmeters (e.g., rotameters, ultrasonic Doppler flowmeters, turbine/paddlewheel flowmeters, magnetic flowmeters, etc.) and automated data logging and alarm systems are available.

2.2.6 Ground-Water Chemistry

2.2.6.1 Performance Concept

Ground-water quality monitoring is performed at nearly all P&T operations to determine if temporal or spatial variations in contaminant distribution are consistent with effective hydraulic containment. If not, the monitoring identifies areas and temporal conditions of inadequate containment which should then be improved by a P&T system upgrade.

At sites where contamination is enclosed by the containment volume perimeter, a detection monitoring program can be implemented at or beyond this perimeter to evaluate P&T performance. Chemical analysis should target the most mobile site contaminants. Detection of contaminants above background concentrations (if any) indicates a lack of containment, unless the contaminant presence can be attributed to an alternate source.

Ground-water quality monitoring to assess containment may provide ambiguous results if some site contaminants are located beyond the containment volume perimeter prior to P&T system startup. Given this scenario, containment failure is suggested if: (1) the estimated total contaminant mass in ground water beyond the containment perimeter increases with time (see Section 3 and Appendix A); (2) contaminant concentrations change with time (e.g., increase) in perimeter or downgradient monitor wells in a manner that is inconsistent with effective containment; and/or (3) relatively retarded contaminants, that were previously restricted to the containment area, are detected in perimeter monitor wells. If the spatial distribution of contaminants or the ground-water flow field is ill-conceived, then each of these criteria is subject to misinterpretation. Where ground-water chemistry data limitations are significant, greater reliance is placed on hydraulic gradient monitoring.

Tracers can be injected within the plume and monitored outside the containment volume to discriminate between lack of containment, pre-existing contamination beyond the containment limit, and potential offsite contaminant sources. Detecting a unique tracer beyond the containment area indicates a lack of containment. The use of tracers is discussed in Section 2.2.8.

2.2.6.2 Ground-Water Quality Monitoring Locations

Monitor well locations and completion depths are selected to provide a high probability of detecting containment system leaks in a timely manner. Site characterization data and capture zone analysis are used to identify potential areas and pathways of contaminant migration across the containment volume perimeter during P&T operation and inoperation (due to mechanical failure or routine system maintenance). These potential migration routes may include the more permeable media, areas and depths subject to relatively weak ground-water flow control, and manmade or natural drainage features (e.g., sewers, streams, etc.). Using this hydrogeologic approach, site-specific conditions are evaluated to choose optimum ground-water sampling locations. Various geostatistical methods (e.g., Haug et al., 1990) and plume generation models (e.g., Wilson et al., 1992; Meyer and Brill, 1988) can also be used to help assess well spacing and depths. Loaiciga et al. (1992) present a review of the application of hydrogeologic and geostatistical approaches to ground-water quality network design. In general, as with mapping hydraulic gradients, the number of ground-water quality monitor wells needed to assess containment effectiveness increases with plume size and site complexity.

Ideally, P&T system failure will be detected before contaminants migrate far beyond the containment perimeter toward potential receptors. Consequently, monitor wells with a relatively close spacing are usually located along or near the potential downgradient containment boundary. Inward gradient control wells (discussed in Section 2.2.1) are frequently used for ground-water sampling. Public or private water supply wells located downgradient of the contamination may also be used to monitor

containment effectiveness and to determine the quality of ground water being consumed by local residents.

Modifications to monitoring locations and criteria may be needed to complement changes in P&T operation, ground-water flow directions, contaminant distributions, and/or the specified containment volume.

2.2.6.3 Ground-Water Quality Monitoring Frequency

Ground-water quality surveys are usually conducted less frequently than hydraulic head surveys because: (1) contaminant movement is a slower process than that controlling transient hydraulic head propagation; and (2) ground-water quality surveys are much more expensive to conduct than groundwater elevation surveys. Determining ground-water sampling frequency requires consideration of site-specific conditions. It should not be assumed that all wells must be sampled at the same time, for the same parameters, or during every sampling episode.

In general, it is good practice to sample at a higher frequency and perform more detailed chemical analyses in the early phase of the monitoring program, and then to use the information gained to optimize sampling efficiency and reduce the spatial density and temporal frequency of sampling in the later phases. For example, consider the following strategies.

(1) Monitor ground-water quality in perimeter and near-perimeter leak detection wells more frequently than in wells that are more distant from the contaminant plume limit.

(2) Specify sampling frequency based on potential containment failure migration rates that consider the hydraulic conductivity (k) and effective porosity (n) of the different media, and maximum plausible outward hydraulic gradients (i). If appropriate, account for the retardation factor, R_f (Section 1.2, Equation 1-4). Use modeling results or simple calculations of contaminant average linear velocity (v_c, where $v_c = R_f ki/n$) to estimate potential contaminant transport velocities. Consider sampling more permeable strata in which migration may occur relatively quickly more frequently than less permeable media.

(3) After performing detailed chemical analyses during the remedial investigation or the early phase of a monitoring program, increase monitoring cost-effectiveness by focusing chemical analyses on site contaminants of concern and indicator constituents. Conduct more detailed chemical analyses on a less frequent basis or when justified based on the results of the more limited analyses.

At sites with inorganic contamination or where organic site contaminants are present initially beyond the containment perimeter, it may be necessary to use statistical methods to: (1) distinguish contaminant detections from background concentrations; and (2) assess the influence of various temporal and spatial factors (e.g., recharge rate and heterogeneity, respectively) on contaminant concentration variability. Sampling locations and frequency, therefore, may be dictated by the requirements of

statistical analyses. Guidance on applying statistics to differentiate contamination from background and to identify concentration trends with statistical significance is provided by USEPA (1986, 1988a, 1989, 1992b, 1992c) and Gilbert (1987). At some sites, identifying background contaminant concentrations and trends may not be cost-effective given monitoring program objectives.

2.2.7 Perimeter Monitoring Using Noninvasive Methods

At sites where contaminants have not migrated beyond the containment perimeter, it may be cost-effective to enhance P&T monitoring by conducting surface geophysical or soil gas surveys along transects between monitor wells (Figure 2-11). Using this approach, an initial baseline survey is made along well-defined transects. Repeat surveys are then conducted periodically to detect changes from the baseline condition that evidence contaminant migration.

Electrical geophysical methods (EM-conductivity and resistivity) can be used to detect the migration of conductive contaminants in ground water. An application of this strategy using quarterly EM-conductivity surveys along transects between wells to augment a landfill leachate detection monitoring network is described by Rumbaugh et al. (1987). Similarly, under appropriate conditions, volatile organic contaminant movement in the upper saturated zone can be inferred by analysis of soil gas samples (Devitt et al., 1987; Cohen and Mercer, 1993).

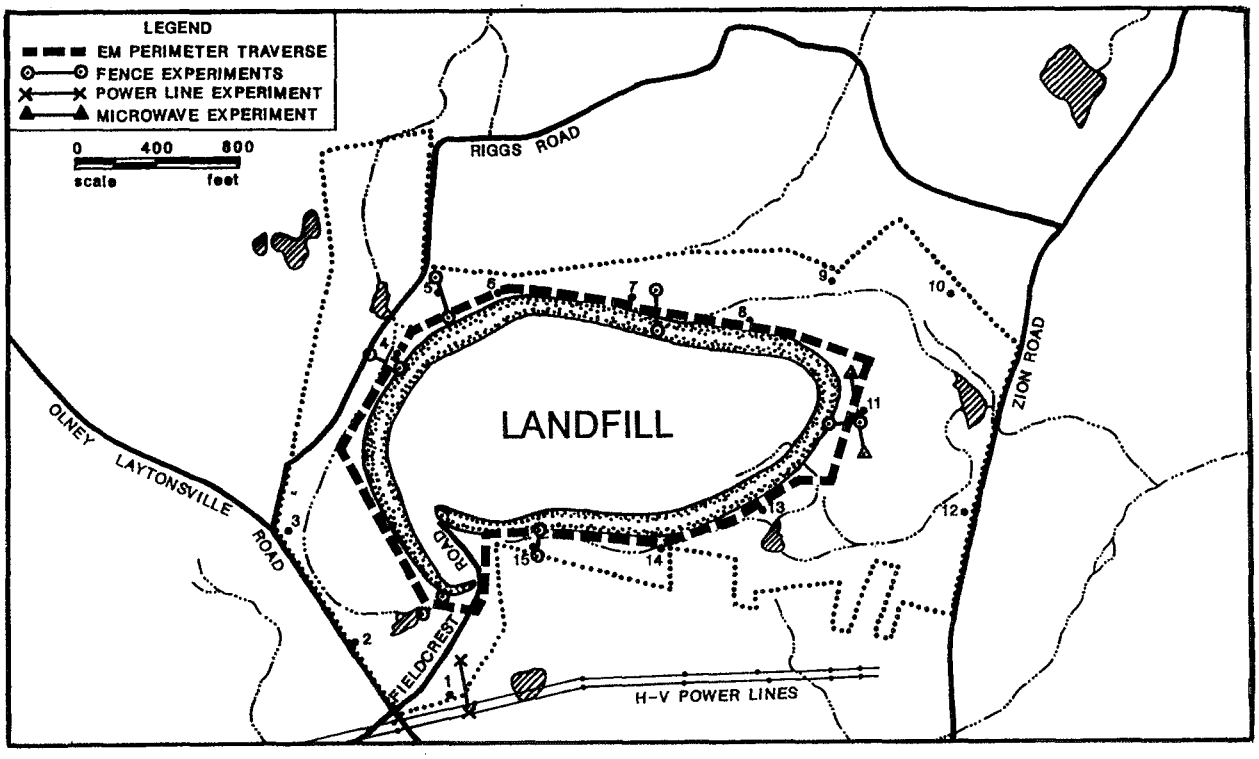


Figure 2-11. Surface geophysical EM-Conductivity) surveys were conducted periodically along transects between monitor wells encircling a sanitary landfill in Maryland to augment the leak detection monitoring network (from Rumbaugh et al., 1987).

Although often less costly, data acquired using noninvasive methods is also less definitive than direct ground-water sampling data. As a result, inferences derived from these techniques must be confirmed by ground-water sampling and analysis.

2.2.8 Tracers

Tracers are used in ground-water studies to determine flow path, velocity, solute residence time, and formation properties such as hydraulic conductivity, dispersivity, and effective porosity (Davis et al., 1985). At sites where contaminants are present beyond the containment zone, ground-water tracers can be used to enhance performance monitoring. A tracer can be released periodically into ground water inside the containment zone where hydraulic control is considered least effective. Subsequent tracer detection in ground water beyond the containment perimeter (e.g., during regular monitoring surveys) would indicate containment failure and possibly the general location of the failure. Tracers can also be used to help delineate the P&T capture zone by releasing tracer in areas of uncertain capture and monitoring for tracer presence in pumped ground water.

A detailed discussion of tracer selection and use for ground-water investigations is provided by Davis et al. (1985). Important ground-water tracers include particulates (spores, bacteria, and viruses), ions (chloride and bromide), dyes (Rhodamine WT and Fluorescein), radioactive tracers, fluorocarbons, and organic anions. Tracers are selected based on their properties (e.g., toxicity and mobility) and the availability of reliable analytical techniques. Determination of the amount of tracer to inject is based on its background concentration, the analytical detection limit, and the expected degree of tracer dilution at sampling locations. Tracer concentration should not be increased so much that density effects become a problem for the particular application.

2.3 MONITORING LOCATION SUMMARY

Hydraulic head and ground-water chemistry monitoring locations are discussed in Section 2.2 for each performance measure. In summary, monitoring is conducted within, at the perimeter, and downgradient of the containment zone to interpret ground-water flow, contaminant transport, and P&T system performance. Containment area monitoring is used particularly to assess extraction/injection impacts and hydraulic control at the containment volume bottom. Perimeter monitoring facilitates contaminant leak detection and evaluation of inward gradients. Downgradient monitoring provides additional containment failure detection capability and helps assess potential contaminant migration to water-supply wells and/or surface water.

2.4 OPERATIONS AND MAINTENANCE (O&M) MANUAL

Many P&T systems may be dysfunctional due to a lack of adequate monitoring and maintenance. O&M manuals should be prepared for each P&T system. Elements of an O&M plan should: (1) provide an introductory description of the P&T system; (2) identify and describe system components (e.g., pumps, controllers, piping, wiring, treatment system parts, alarms, etc.); (3) include detailed drawings of system layout, equipment schematic diagrams, and parts listings; (4) enumerate system installation, startup, and

operation procedures; (5) provide a troubleshooting guide and problem call-down or contact list; and (6) detail system monitoring, maintenance, and record-keeping requirements and schedules. Much of this information is available from equipment vendors.

2.5 P&T MONITORING PLAN

As noted in Section 2.1, a written monitoring plan should also be developed for P&T system operation. The plan should describe: (1) monitoring objectives; (2) the types of measurements to be made (e.g., pumping rates, hydraulic heads, ground-water chemistry, precipitation); (3) measurement locations; (4) measurement methods, equipment, and procedures; (5) measurement schedules; and (6) record-keeping and reporting requirements. It is important that the monitoring plan be revised as data is collected and improvements are realized with respect to the site conceptual model and knowledge of the distribution of contaminants is enhanced.

2.6 CAPTURE ZONE ANALYSIS AND OPTIMIZATION MODELING

In recent years, many mathematical models have been developed or applied to compute capture zones, ground-water pathlines, and associated travel times to extraction wells or drains (Javandel et al., 1984; Javandel and Tsang, 1986; Shafer, 1987a,b; Newsom and Wilson, 1988; Blandford and Huyakorn, 1989; Pollock, 1989; Strack, 1989; Bonn and Rounds, 1990; Bair et al., 1991; Rumbaugh, 1991; Bair and Roadcap, 1992; Fitts, 1993; Gorelick et al., 1993. These models provide insight to flow patterns generated by alternative P&T schemes and the selection of monitoring locations and frequency. Additionally, linear programming methods are being used to optimize P&T design (Ahlfeld and Sawyer, 1990; Hagemeyer et al., 1993; Gorelick et al., 1993) by specifying an objective function subject to various constraints (e.g., minimize pumping rates but maintain inward hydraulic gradients). Given their application to the design, evaluation, and monitoring of P&T systems, a brief overview of a few capture zone analysis and optimization techniques follows. It must be kept in mind, however, that the accuracy of modeling predictions is dependent on the availability and validity of the required input data.

Several semianalytical models employ complex potential theory to calculate stream functions, potential functions, specific discharge distribution, and/or velocity distribution by superposing the effects of multiple extraction/injection wells using the Thiem equation on an ambient uniform ground-water flow field in a two-dimensional, homogeneous, isotropic, confined, steady-state system (e.g., RESSQ, Javandel et al., 1984; DREAM, Bonn and Rounds, 1990; and, RESSQC, Blandford and Huyakorn, 1989). Based on this approach, the simple graphical method shown in Figure 2-12 can be used to locate the stagnation point and dividing streamlines, and then sketch the capture zone of a single well in a uniform flow field. The extent to which these results represent actual conditions depends on the extent to which the assumptions vary from actual site conditions.

This analysis is extended by Javandel and Tsang (1986) to determine the minimum uniform pumping rates and well spacings needed to maintain capture between two or three pumping wells along a line perpendicular to the regional direction of ground-water flow. Their capture zone design criteria and type curves given in Figure 2-13 can be used for capture zone analysis, but more efficient P&T systems

can be designed with nonuniform pump well orientations, spacings, and extraction rates. Streamlines and capture zones associated with irregular well spacings and variable pumping rates can be simulated by the complex potential flow models, RESSQ, RESSQC, and DREAM. Reverse particle tracking is implemented in RESSQC to derive steady-state capture zones by releasing particles from the stagnation point(s) of the system and tracking their advective pathlines in the reversed velocity field. Similarly, time-related captures zones (Figure 2-14) are obtained by tracing the reverse pathlines formed by particles released all around each pumping well (Blandford and Huyakorn, 1989; Shafer, 1987a).

Application of semianalytical models to field problems requires careful evaluation of their limiting assumptions (e.g., isotropic and homogeneous hydraulic conductivity, fully-penetrating wells, no recharge, no vertical flow component, and constant transmissivity). Several analytic models relax these restrictive assumptions by superposition of various functions to treat recharge, layering, inhomogeneity, three-dimensional flow, etc. (Fitts, 1989; Strack, 1989; Rumbaugh, 1991). Where field conditions do not conform sufficiently to model assumptions, the simulation results will be invalid (e.g., Springer and Bair, 1992).

Numerical models are generally used to simulate ground-water flow in complex hydrogeologic systems (e.g., MODFLOW, McDonald and Harbaugh, 1988; and SWIFF/486, Ward et al., 1993). For example, the benefits of using partially-penetrating recovery wells to minimize pumping rates and unnecessary vertical spreading of contaminants can be examined using a three-dimensional flow model.

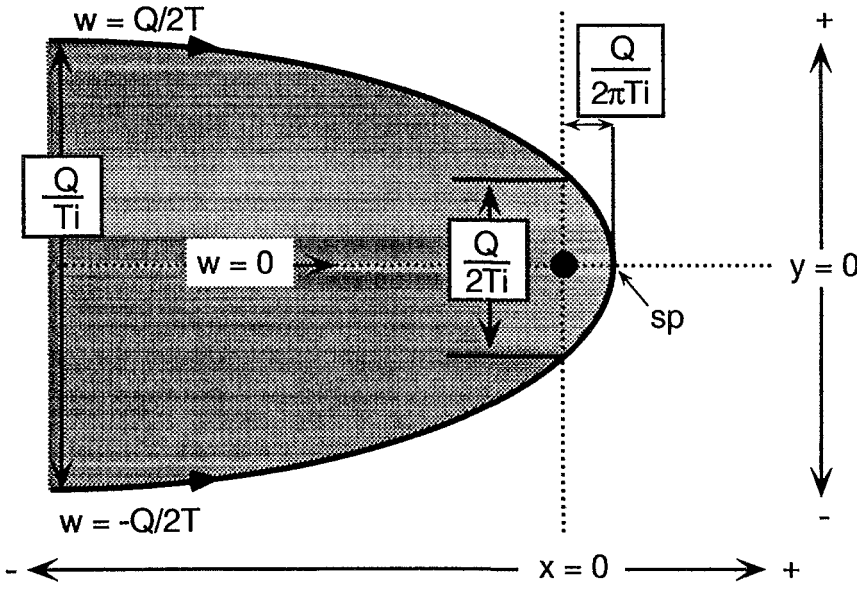
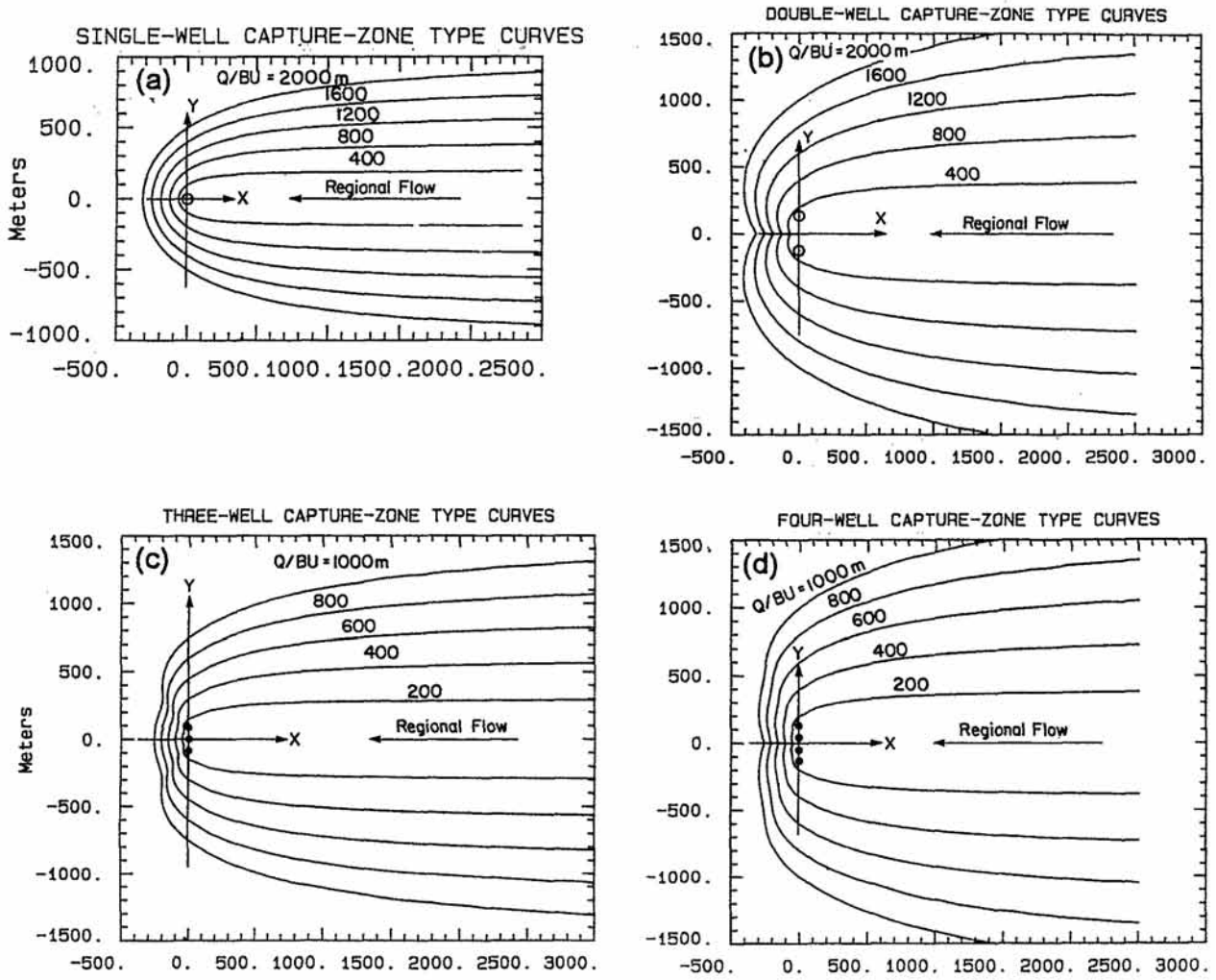


Figure 2-12. Equations for the dividing streamlines (w=Q/2T) that separate the capture zone of a single well from the rest of an isotropic, confined aquifer with a uniform regional hydraulic gradient (modified from Gorelick et al., 1993). Note that T=transmissivity (L^2/T), Q=pump rate (L^3/T), and i=initial uniform hydraulic gradient).



Number of Wells	*Recommended Distance between Each Pumping Well*	*Distance between Dividing Streamlines at Well Line*	*Distance between Dividing Streamlines Far Upstream from Well Line*	*Distance to Stagnation Point at the Center of the Capture Zone*
1	--	Q/(2Ti)	Q/Ti	Q/(2πTi)
2	Q/(πTi)	Q/Ti	2Q/Ti	Q/(2πTi)
3	1.26Q/(πTi)	3Q/(2Ti)	3QTi	3Q/(4πTi)

Figure 2-13. **Type curves showing the capture zones of 1 (a), 2 (b), 3 (c), and 4 (d) pump wells spaced evenly along the y-axis for several values of Q/BU (where Q = pumping rate (L^3/T), B = aquifer thickness (L), and U = Darcy velocity for regional flow (L/T) (from Javandel and Tsang, 1986). To assess the number of wells, pumping rates, and well spacings needed to capture a plume using evenly spaced recovery wells along a line: (1) Construct a plume map at the same scale as the type curves; (2) Superimpose the 1-well type curve over the plume with the x-axis parallel to the regional flow direction and overlying the center of the plume such that the plume is enclosed by one Q/BU curve; (3) Calculate the required single well pumping rate as Q=B*U*TCV where TCV is the bounding Type Curve Value of Q/BU; and, (4) If a single well cannot produce the calculated pump rate, repeat the steps using the 2, 3, and 4 well type curves until a feasible single well pump rate is calculated. Use the above equations to determine optimum well spacings. See Javendel and Tsang (1986) for details.**

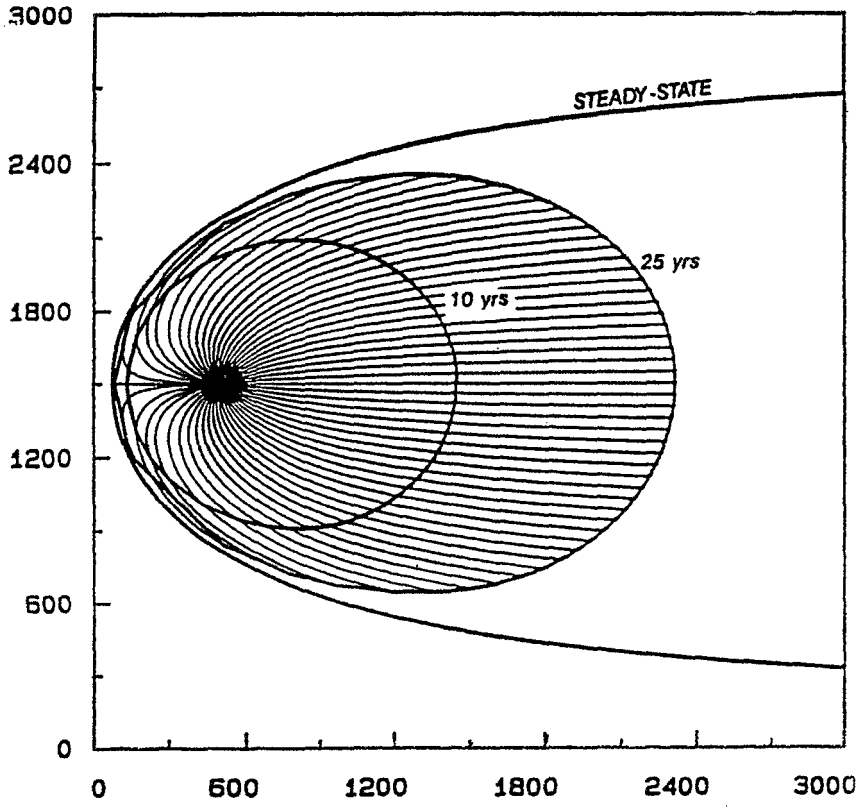


Figure 2-14. Example of steady-state, and 10-year and 25-year time-related capture zones delineated using reverse particle tracking (from Blandford and Huyakorn, 1989).

Numerical flow model output is processed using reverse or forward particle-tracking software such as MODPATH (Pollock, 1989), GWPATH (Shafer, 1987b), STLINE (Ward et al., 1993), FLOWPATH (Franz and Guiguer, 1990), PATH3D (Zheng, 1989), and the GPTRAC module of WHPA (Blandford and Huyakorn, 1989) to assess pathlines and capture zones associated with P&T systems at sites that cannot be accurately modeled using simpler techniques. Solute transport models are primarily run to address aquifer restoration issues such as changes in contaminant mass distribution with time due to P&T operation (e.g., Ward et al., 1987).

Ground-water flow models can be coupled with linear programming optimization schemes to determine the most effective well placements and pumping rates for hydraulic containment much more quickly than a trial-and-error approach. The optimal solution maximizes or minimizes a user-defined objective function subject to all user-defined constraints. In a P&T system, a typical objective function may be to minimize the pumping rate to reduce cost, while constraints may include specified inward gradients at key locations, and limits on drawdowns, pumping rates, and the number of pump wells. Gorelick et al. (1993) present a review of the use of optimization techniques in combination with groundwater models for P&T system design. Available codes include AQMAN (Lefkoff and Gorelick, 1987) an optimization code that employs the Trescott et al., (1976) two-dimensional ground-water flow model, and MODMAN (GeoTrans, 1992), which adds optimization capability to the three-dimensional USGS MODFLOW model (McDonald and Harbaugh, 1988) and others (USEPA, 1993a). A case study of the application of an optimization code to assist P&T design is given by Hagemeyer et al. (1993).

Coupled ground-water flow-optimization models can also be used to evaluate monitoring well network design (Meyer and Brill, 1988; Meyer, 1992). Objectives might be to (1) minimize the total number of monitor wells, (2) maximize the probability of detecting contaminant migration, and (3) minimize the area of expected contamination at the time of leak detection. The first two objectives are addressed using the Maximal Covering Location Problem method illustrated in Figure 2-15 to find well locations and depths that maximize the probability of future plume detection (Meyer, 1992). Another approach, the Extended P-Median Problem, addresses all three objectives by tracking plume size as it grows with time (Meyer, 1992).

Although P&T and monitoring design can be aided by the use of ground-water models, actual field monitoring must be carried out in order to provide information necessary to evaluate model predictions. As described in this Chapter, hydraulic containment effectiveness is determined by monitoring hydraulic heads and ground-water chemistry.

2.7 OPERATIONAL EFFICIENCY

Operational efficiency refers to the cost-effectiveness of actions taken to attain remedial objectives. These actions include P&T system design, operation, monitoring, and modification. Efficient P&T performance requires that there be a clear statement of remedial objectives.

For perpetual hydraulic containment, an appropriate objective might be to minimize the total cost required to maintain hydraulic containment and satisfy associated regulatory requirements. Given this objective, installing low permeability barriers to reduce pumping rates might be cost-effective. At sites with an economic incentive to remove contaminant mass (i.e., where the containment area size may be diminished or P&T discontinued if clean-up goals are met), a more complex cost-effectiveness trade-off exists between minimizing hydraulic containment costs and maximizing contaminant mass removal rates.

Comparative cost-benefit analysis requires evaluation of the benefits, costs, and risks of each design alternative based on P&T component and site specific factors. A framework for risk-based decision analysis applicable to P&T system design (Figure 2-16) is provided by Massmann and Freeze (1987), Freeze et al. (1990), and Massmann et al. (1991). Using this method, an objective function , $_j$, is defined for each remedial alternative, j = 1...N, as the net present value of the anticipated stream of benefits, costs, and risks taken over a remedial time period and discounted at the market interest rate. The goal is to maximize the objective function (Freeze et al., 1990):

$$\Phi_j = \sum_{t=0}^{T} \frac{[B_j(t) - C_j(t) - R_j(t)]}{(1+i)^t} \qquad (2\text{-}1)$$

where Φ_j = the objective function for alternative j [$]; $B_j(t)$ = benefits of alternative j in year t [$]; $C_j(t)$ = costs of alternative j in year t [$]; $R_j(t)$ = risks of alternative j in year t [$]; T = time horizon [years]; and i = discount rate [decimal fraction]. The probabilistic risk cost, R(t), is defined as (Freeze et al., 1990):

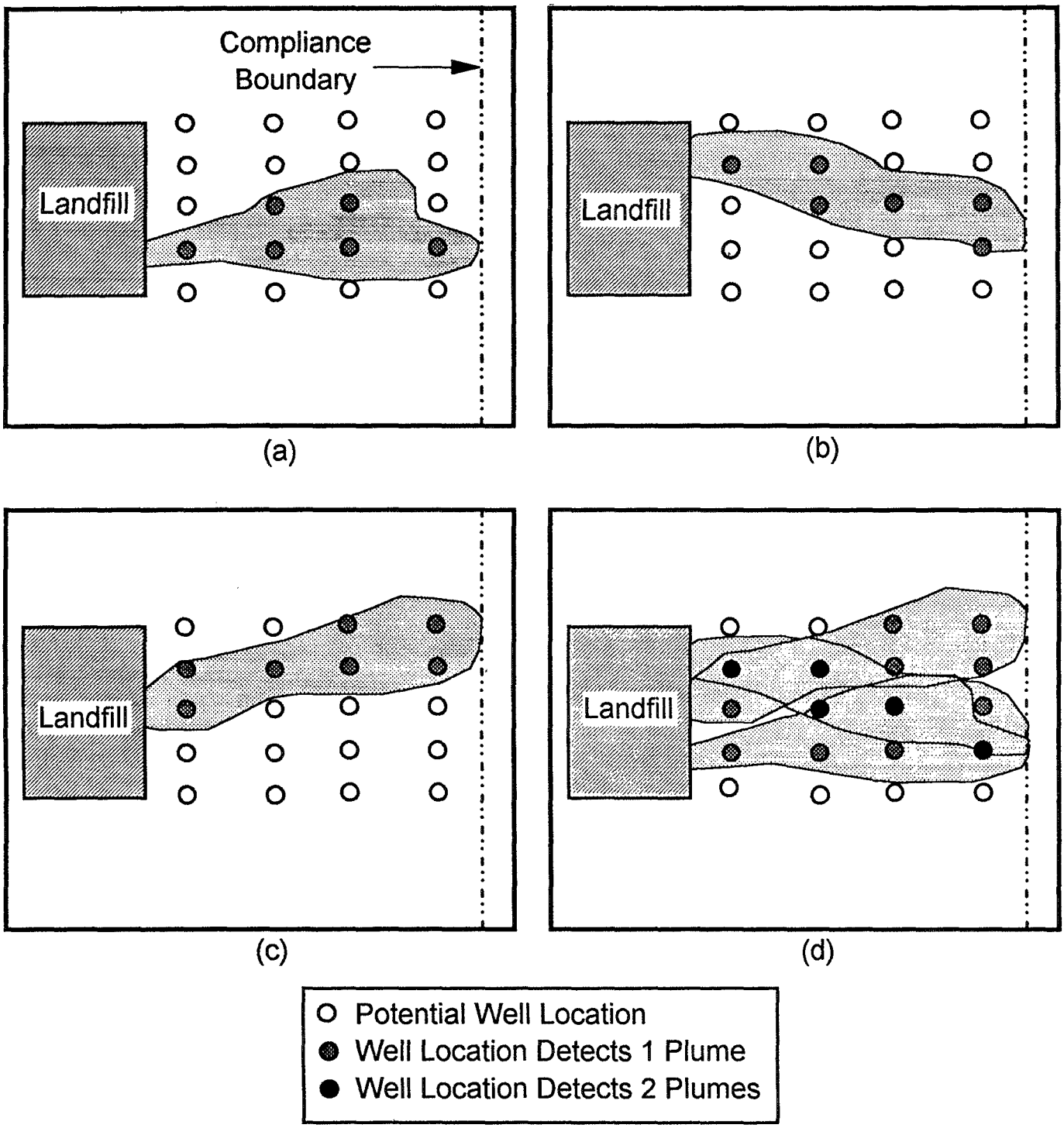


Figure 2-15. **An example of the Maximal Covering Location Problem applied to monitor well network design (from Meyer, 1992). The capability of different monitor well locations to detect random plumes generated using a Monte Carlo simulator in (a), (b), and (c) are combined to indicate optimum well locations in (d).**

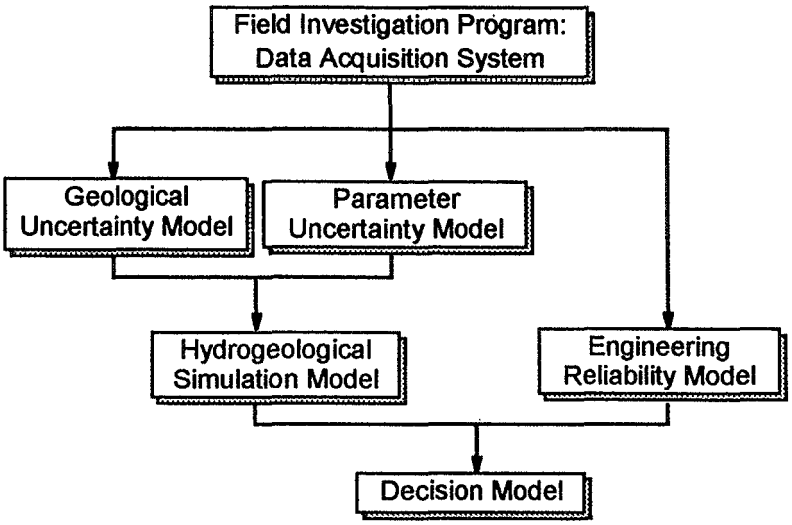


Figure 2-16. A framework for risk-based decision making regarding P&T system design and monitoring (modified from Freeze et al., 1990.)

$$R(t) = Pr(t)\ Cr(t)\ \gamma(Cr) \qquad (2\text{-}3)$$

where Pr(t) = the probability of failure in year t [decimal fraction] $C_f(t)$ = costs associated with failure in year t [$]; and $\gamma(Cr)$ = the normalized utility function [decimal fraction, ? $ 1] which can be used to account for possible risk-averse tendencies of decision makers. The benefits of an alternative, B(t), can similarly be formulated as probabilistic benefits. Trade-offs between cost and risk and the concept of optimal risk are illustrated in Figure 2-17. Note that acceptable risk, from a societal or regulatory perspective, may be less than an owner-operator's optimal risk.

Example applications of this risk-based decision analysis approach to P&T system design are given by Massmann et al. (1991) and Evans et al. (1993). Variables pertaining to P&T monitoring design, such as well spacing and sampling frequency, can also be evaluated using this methodology, as can proposed modifications to system design that might be derived from monitoring data. Monitoring contributes to the objective function by reducing the probability of failure, or equivalently, increasing the probability of detection (Meyer and Brill, 1988).

Remedial efficiency can be also be enhanced by applying total quality management practices to P&T operation. Hoffman (1993) recommends nine steps to increase the efficiency of a P&T system designed for hydraulic containment and contaminant mass removal: (1) perform a thorough site characterization; (2) establish a decision support system that allows rapid interpretation and integration of new data; (3) locate and remove or contain shallow sources of ground-water contamination; (4) design the

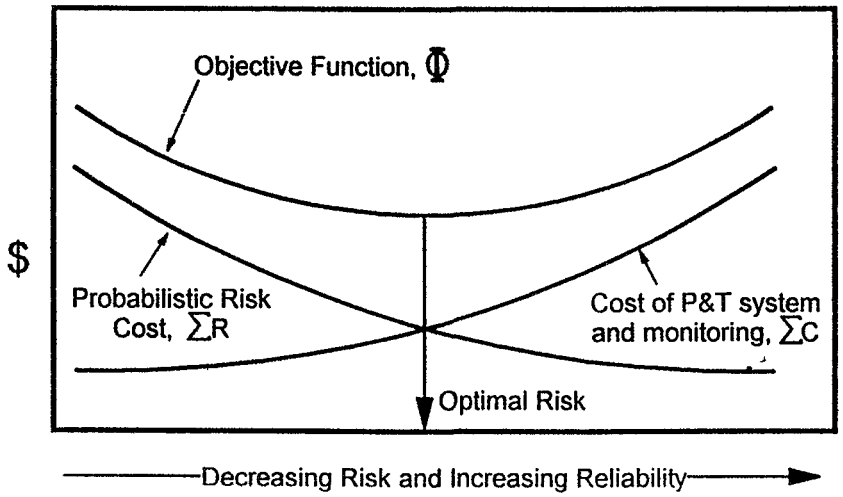


Figure 2-17. The concept of optimal risk (from Freeze et al., 1990).

P&T system to contain and remove contaminant mass; (5) phase in the remedial program to take advantage of ongoing conceptual model improvements; (6) maintain extensive monitoring of the P&T system; (7) design the well field such that extraction and injection rates and locations can be varied to minimize ground-water stagnation; (8) use reinjection of treated ground water and other techniques to enhance contaminant mass removal; and (9) set contaminant concentration goals (e.g., at the containment area perimeter) that will allow appropriate water standards to be met at the downgradient point of use. Although the applicability of various monitoring and remedial measures depends on site-specific conditions, active P&T system management will usually be cost-effective and lead to enhanced operational efficiency.

3. MONITORING AQUIFER RESTORATION

3.1 INTRODUCTION

The challenge of aquifer restoration is presented in Chapter 1. Restoration P&T design will typically reflect a compromise between objectives that seek to: (1) reduce contaminant concentrations to clean-up standards, (2) maximize contaminant mass removal, (3) minimize clean-up time, and (4) minimize cost. At many sites, P&T systems cannot be relied upon to reduce ground-water contaminant concentrations to comply with clean-up standards within a short time frame. Aquifer restoration efforts are made more difficult by concentration tailing and rebound caused by NAPL dissolution, contaminant desorption, precipitate dissolution, ground-water velocity variations, and/or matrix diffusion (Section 1.2). Consequently, P&T for aquifer restoration requires a high degree of performance monitoring and management to identify problem areas and improve system operation.

Hydraulic containment generally is a prerequisite for aquifer restoration. Reference, therefore, should be made to discussions of hydraulic containment design, monitoring, and management in Chapter 2. This chapter focuses on managing and monitoring P&T technology to clean up ground water in the containment area/volume. Statistical analysis of monitoring data is discussed in Chapter 4.

3.2 PERFORMANCE MEASUREMENTS AND INTERPRETATION

Various restoration performance criteria are described in this section. These criteria are monitored to determine if the P&T system is functioning as designed and to provide guidance for system optimization. Performance is monitored by measuring hydraulic heads and gradients, ground-water flow directions and rates, pumping rates, pumped water quality, contaminant distributions in ground water and porous media, and, possibly, tracer movement.

3.2.1 Hydraulic Containment

Hydraulic containment is a design objective of nearly all restoration P&T systems. That is, the plume is contained to prevent further spread during restoration efforts. In addition, as shown in Figure 1.2, for some ground-water contamination problems, restoration and containment are used for different sections of the aquifer. Refer to Chapter 2 for guidance on hydraulic containment performance monitoring.

3.2.2 Managing Ground-Water Flow

Restoration P&T ground-water flow management typically involves optimizing well locations, depths, and injection/extraction rates to maintain an effective hydraulic sweep through the contamination zone, minimize stagnation zones, and flush pore volumes through the system. Wells are installed in lines or five-spot patterns to enhance hydraulic flushing efficiency; drains are installed to effect line sweeps. In the following sections, various aspects of ground-water flow management are discussed including

(1) pore volume flushing, (2) stagnation zone control, (3) pulsed pumping, and (4) pumping in the presence of NAPL.

3.2.2.1 Pore Volume Flushing

Restoration requires that sufficient ground water be flushed through the contaminated zone to remove both existing dissolved contaminants and those that will continue to desorb from porous media, dissolve from precipitates or NAPL, and/or diffuse from low permeability zones until the sum of these processes and dilution in the flow field yields persistent acceptable ground-water quality at compliance point locations.

The volume of ground water within a contamination plume is known as the pore volume (PV), which is defined as

$$PV = \int_A bn \, dA \qquad (3\text{-}1)$$

where b is the plume thickness, n is the formation porosity, and A is the area of the plume. If the thickness is relatively uniform, then

$$PV = BnA \qquad (3\text{-}2)$$

where B is the average thickness of the plume.

The number of pore volumes (NPV) which must be extracted for restoration is a function of the clean-up standard, the initial contaminant distribution, and the chemical/media complexities discussed in Section 1.2. Estimates of the NPV required for clean up can be made by modeling analysis and by assessing the trend of contaminant concentration versus the NPV removed. At many sites, many PVs (e.g., 10 to 100) will have to be flushed through the contamination zone to attain clean-up standards.

The NPV withdrawn per year is a useful measure of the aggressiveness of a P&T operation. It is calculated as

$$NPV_{yr} = Q_{yr}/PV \qquad (3\text{-}3)$$

where Q_{yr} is the total annual pumping rate. Systems are typically designed to remove between 0.3 and 2.0 PVs annually. Low permeability conditions or competing uses for ground water may restrict the ability to pump at higher rates. Additionally, kinetic limitations to mass transfer (Figure 1-7) may diminish the benefit of higher pumping rates. If limiting factors are not present, pumping rates may be increased to improve P&T performance.

Water flushing will be limited to infiltration rates where P&T operation has dewatered contaminated media. As a result, dissolved contaminant concentrations may rebound as the water table rises when pumping is reduced or terminated. Water can be injected or infiltrated to both minimize this potential problem and increase the rate of flushing. Where injection is not feasible, soil vapor extraction or other vadose zone remedial measures might be needed to remove contaminant mass above the water table.

Where the P&T design is appropriate, but concentration reduction is very slow, monitoring data should be evaluated to determine if it is technically impracticable to meet remedial action objectives (Section 3.4). In order to demonstrate technical impracticability, it must be shown that poor or inappropriate remedial design is not responsible for tailing. Additional information on technical impracticability is provided in U.S. EPA, 1993.

Poor design factors include low pumping rates and improper location of pump wells and completion depths. A simple check on the total pumping rate is to calculate the NPV_{yr}. Inadequate location or completion of pump wells (or drains) may lead to poor P&T performance even if the total pumping rate is appropriate. For example, wells placed at the containment area perimeter may withdraw a large volume of clean ground water from beyond the plume via flowlines that do not flush the contaminated zone. Similarly, pumping from the entire thickness of a formation in which the contamination is limited vertically will reduce the fraction of Q_{yr} that flushes the contaminated zone. In general, restoration pump wells or drains should be placed in areas of relatively high contaminant concentration.

Well placement can be evaluated by: (1) applying expert knowledge linked to a proper conceptual model of the hydrogeologic system and contaminant distribution; (2) comparing contaminant mass removed to contaminant mass dissolved in ground water; and (3) using ground-water flow and transport models. P&T system modifications should be considered if any of these methods indicate that different pumping locations or rates will improve system effectiveness.

3.2.2.2 Minimize Ground-Water Stagnation

Ground-water flow patterns need to be managed to minimize stagnation zones during P&T operation. Stagnation zones develop in areas where the P&T operation affects low hydraulic gradients (e.g., downgradient of a pump well and upgradient of an injection well) and in low permeability zones regardless of hydraulic gradient. Stagnation zones caused by low hydraulic gradients can be identified by measuring hydraulic gradients, tracer movement, ground-water flow rates (e.g., with a downhole flowmeter), and by modeling analysis. Low permeability heterogeneities should be delineated as practicable during the site characterization study and during ongoing P&T operation. Flow modeling results can be used to generate either Darcy or interstitial velocities. These can then be contoured or used with particle tracking to help identify and locate potential stagnation zones. Examples of stagnation zones associated with different pumping schemes simulated by a ground-water model are given in Figure 3-1, and the distribution of potential stagnation zones at a complex field site is shown in Figure 3-2.

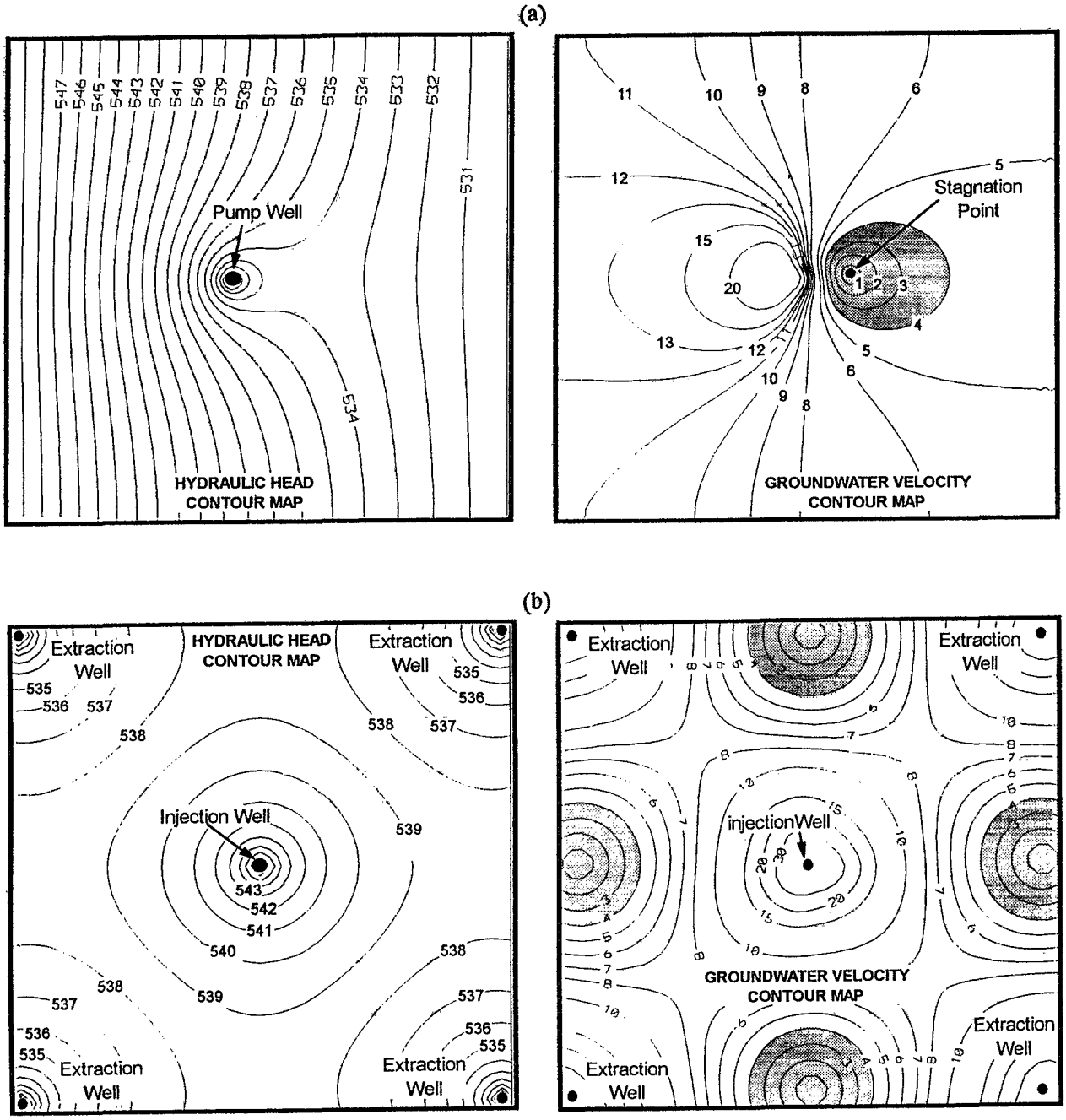


Figure 3-1. Examples of stagnation zones (shaded where the ground-water velocity is less than 4 L/T) associated with single-well and five-spot pumping schemes.

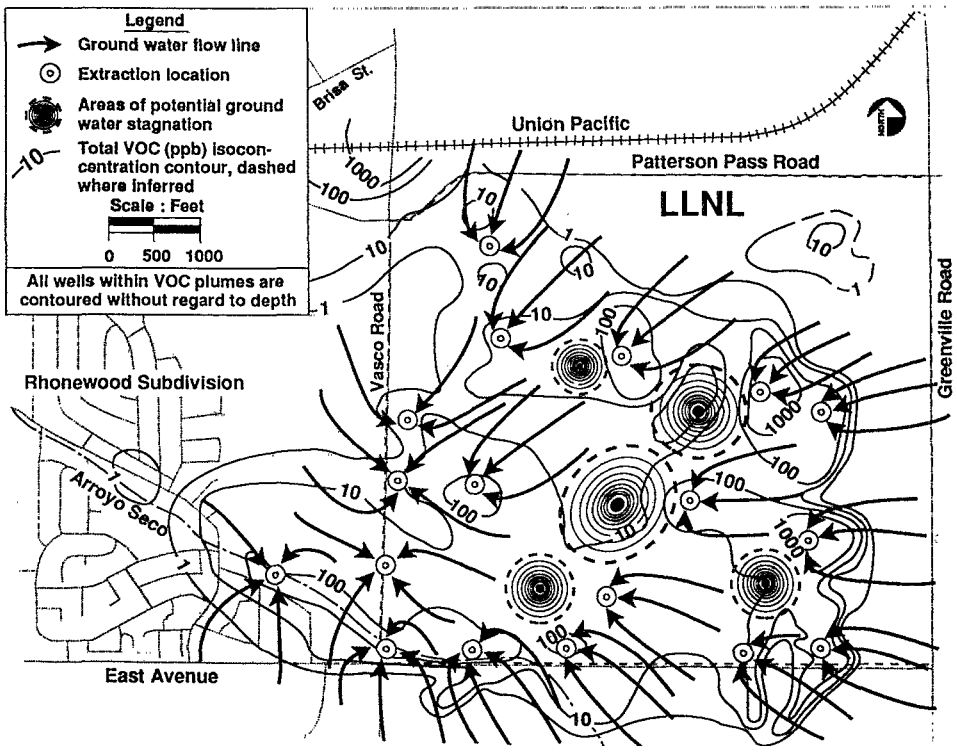


Figure 3-2. Conceptualized ground-water flow patterns and stagnation zones superimposed on a total VOC isoconcentration contour map at the Lawrence Livermore National Laboratory site in California (from Hoffman, 1993).

Once identified, the size, magnitude, and duration of stagnation zones can be diminished by changing pumping (extraction and/or injection) schedules, locations, and rates. Again, flow modeling based on field data may be used to estimate optimum pumping locations and rates to limit ground-water stagnation. An adaptive pumping scheme, whereby extraction/injection pumping is modified based on analysis of field data, should result in more expedient cleanup (Figure 3-3).

3.2.2.3 Pulsed Pumping

Pulsed pumping can be used to increase the ratio of contaminant mass removed to pumped ground-water volume where mass transfer limitations restrict dissolved contaminant concentrations (Figure 1-7). The concept of pulsed pumping is illustrated in Figure 3-4. Dissolved contaminant concentrations increase due to diffusion, desorption, and dissolution in slower-moving ground water during the resting phase of pulsed pumping. Once pumping is resumed, ground water with higher concentrations of contaminants is removed, thus increasing mass removal during pumping. Pulsed pumping may also help remediate stagnation zones by cycling certain well schemes and altering flow paths. Detailed information can be obtained from Keely, 1989.

Pulsed pumping schedules can be developed based on highly monitored pilot tests, modeling analysis, or ongoing performance monitoring of hydraulic heads and contaminant concentrations. Special care must be taken to ensure that the hydraulic containment objective is met during pump rest periods.

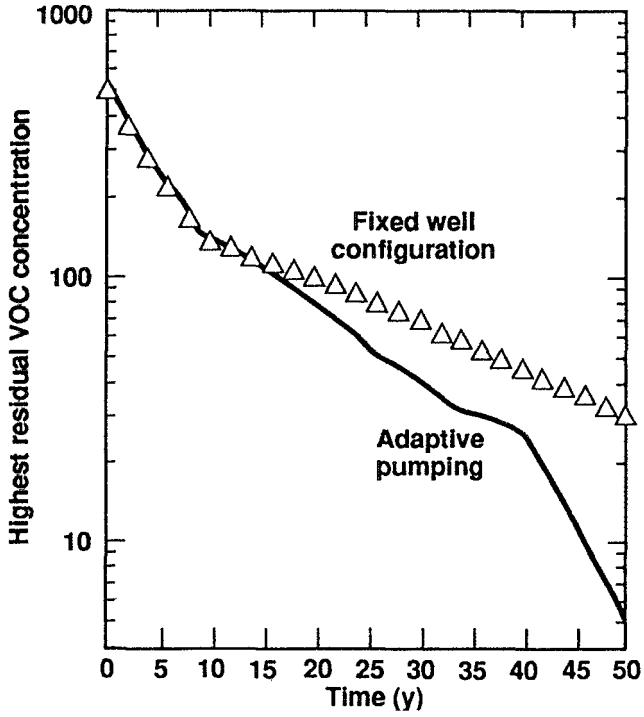


Figure 3-3. Adaptive modifications to P&T design and operation can reduce clean-up time (from Hoffman, 1993).

3.2.2.4 Contain the NAPL Zone

Subsurface NAPL can be a long-term source of ground-water contamination (Figure 1-5) due to: (1) its low aqueous solubility (that may greatly exceed clean-up standards); and, (2) the inability to remove all NAPL that is trapped at residual saturation by capillary forces and in dead-end pores. The mixed containment-restoration strategy shown in Figure 1-2 should be used to contain the NAPL zone and prevent NAPL migration (that may, perhaps, be induced by pumping) into the P&T restoration area. Within the NAPL zone, pumping may be used to reduce NAPL mobility by lowering NAPL saturation to residual. An overview of NAPL pumping techniques is provided by Mercer and Cohen (1990).

3.2.3 Contaminant Monitoring

Samples of ground water taken from wells, soil (or rock) from borings in the contaminated zone, and treatment plant influent and effluent should be analyzed periodically for contaminant presence to monitor restoration P&T performance. Sampling locations and frequencies depend on the distribution of ground-water and contaminant flow velocities within the study area. Mathematical models can be used to help determine appropriate locations and schedules for sampling ground water and formation solids. Treatment plant influent and effluent are generally analyzed on a relatively frequent basis to ensure proper treatment system performance. The degree of monitoring should increase with site complexity. Various contaminant monitoring considerations are discussed below. Additional relevant information is provided in Chapter 2.

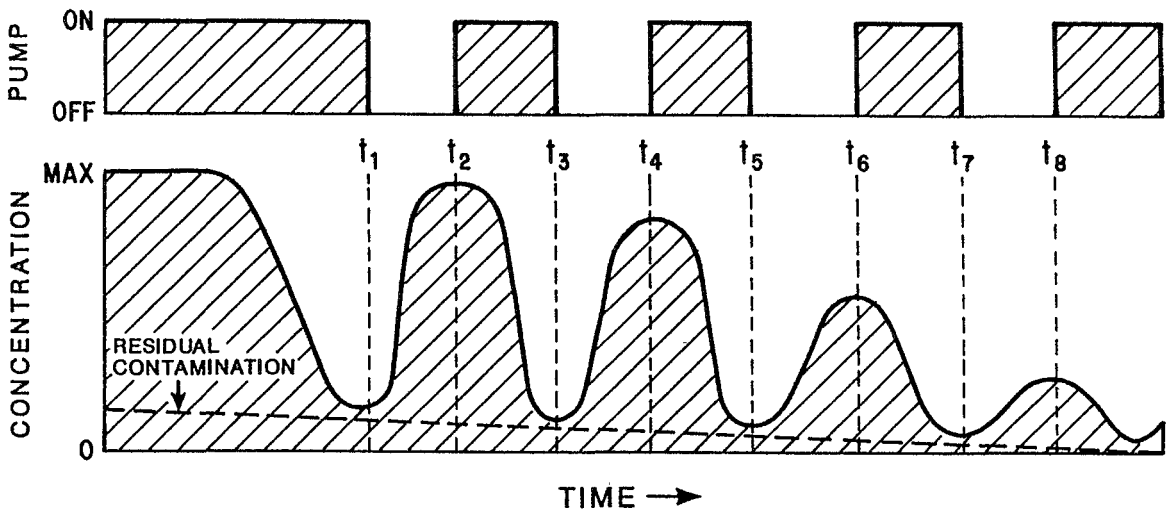


Figure 3-4. The pulsed pumping concept (modified from Keely, 1989).

3.2.3.1 Ground-Water Sampling and Analysis

Ground-water sampling is performed to monitor changes in the contaminant concentration and distribution during remediation. As described in Section 2.2.6, ground-water samples taken from beyond the restoration area are analyzed to assess hydraulic containment. For restoration P&T, samples should also be taken from all pump wells and selected observation wells within the contaminant plume to interpret clean-up progress. An example of a restoration monitoring well network is shown in Figure 3-5. The number of observation wells at which samples are taken (in addition to all pump wells) and sampling frequency depends on site-specific conditions and cost-benefit trade-offs (Section 2.7). In general, greater sampling density and frequency allows for more adaptive and effective P&T remediation (Figure 3-3). Turning off pumping wells that produce clean water or do not significantly contribute to hydraulic containment allows greater resources to be allocated to more highly contaminated zones.

Parameters analyzed should include: (1) the chemicals of concern (or indicator chemicals), (2) chemicals that could affect the treatment system (such as iron which may precipitate and clog treatment units if ground water is aerated), and (3) chemicals that may indicate the occurrence of other processes of interest (e.g., dissolved oxygen, carbon dioxide, nutrients, and degradation products; where biodegradation is considered). As described in Section 2.2.6, relatively detailed analyses should be performed during the early phase of P&T and sampling frequency should account for probable contaminant velocities.

Background wells located upgradient or cross-gradient of contaminated ground water should be monitored to indicate if contaminants have migrated beyond the containment zone (e.g., as might occur where injected water drives contaminated ground water outward). These wells should also be monitored

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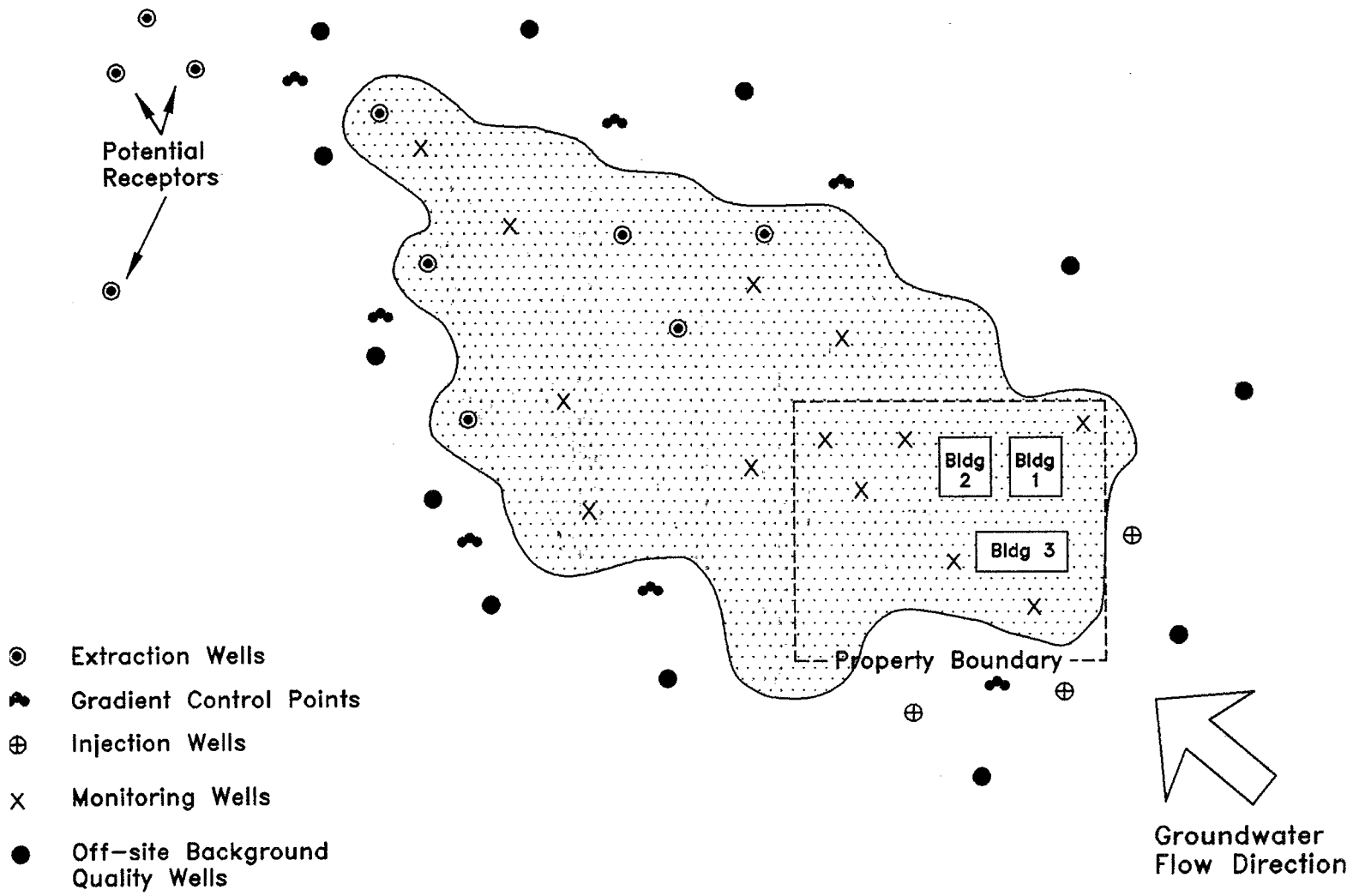

Figure 3-5. Example of a ground-water monitoring well network at a P&T remediation site (modified from USEPA, 1992a).

to detect offsite contamination that may be confused with onsite data. Additional guidance on monitoring ground-water quality beyond the restoration area is given in Section 2.2.6.

Increasing or decreasing contaminant concentration trends in individual wells may not directly reflect overall clean-up performance. A heterogeneous initial contaminant distribution and flow pattern changes caused by pumping will result in different portions of the restoration area becoming more or less contaminated with system operation (e.g., Figure 3-6). For example, contaminant concentrations in restoration pump wells near the plume perimeter will generally decrease quickly as clean water from beyond the perimeter flows inward to these wells. Conversely, concentrations may increase at locations along the flowpath of highly contaminated ground water to pumped wells.

Projections of concentration trends from individual wells can be used to assess clean-up times. The first indication of contaminant tailing is usually revealed by concentration histories of individual wells. The statistical methods discussed in Chapter 4 can be applied to evaluate trends and test for an asymptote (near zero-slope) on an individual well basis. In many cases, individual well results will show contradictory trends due to plume movement and/or statistical errors associated with sampling and analysis. The difficulty with variable projections from individual wells can partially be overcome by evaluating the total restoration P&T performance as described in Sections 3.2.3.3 and 3.2.4.

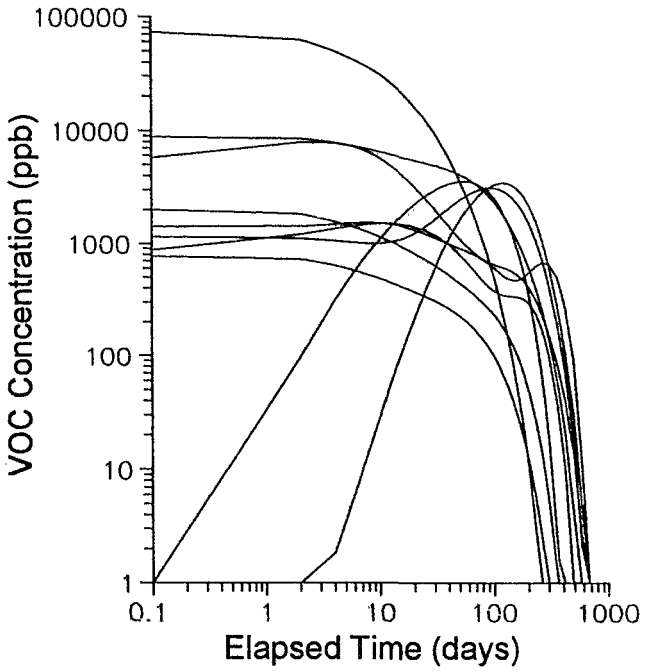

Figure 3-6. Simulated trends of VOC concentration in ground water pumped from ten extraction wells during a P&T operation.

3.2.3.2 Sampling Aquifer Material

Periodic sampling and chemical analysis of aquifer materials from representative locations in the contamination zone provides a measure of contaminant removal during P&T operation. The heterogeneous distribution of subsurface materials, including contaminants, must be considered when determining sampling requirements, selecting sample locations, and interpreting contaminant mass data. Unfortunately, high costs will usually preclude acquiring sufficient data to reliably estimate the magnitude of trends when dealing with sorbed and residual phase contaminants. At most sites, it will be preferable to analyze soil samples from many locations infrequently (e.g., at intervals needed to sweep at least two PVs through a formation) than to analyze fewer samples more frequently. Even where mass-in-place cannot be reliably estimated, a consistency check can be performed by comparing contaminant mass data with other P&T monitoring data.

Measuring natural organic carbon content in the formation can also provide useful information for estimating sorption of hydrophobic contaminants (see Section 1.2). Determining natural total organic carbon, however, is confounded where the porous media are contaminated with anthropogenic organic contaminants. Methods and considerations for collecting total organic carbon data are provided by Powell (1990). Retardation of hydrophobic contaminants migrating toward recovery wells and desorption of hydrophobic contaminants from organic carbon can greatly extend the time required for aquifer restoration using P&T (see Section 3.3).

3.2.3.3 Treatment System Influent and Effluent

Sampling and analysis of treatment system influent and effluent must be performed regularly to assess: (1) treatment, system performance, (2) changes in influent chemistry that may affect treatment effectiveness, and (3) dissolved contaminant concentration trends. The performance of individual treatment units within a treatment train (e.g., where water is pumped through a clarifier to remove metal hydroxides, and then into an air stripper followed by an activated carbon filter to remove VOCs) are similarly monitored by periodic analysis of samples taken between units. Such monitoring will provide data necessary to: (1) estimate total mass removed from system, individual treatment unit loadings, and estimated breakthrough times; (2) document compliance with discharge requirements; and (3) identify the need to modify, replace, or regenerate system components. Treatment system monitoring criteria should be specified in the O&M manual (Section 2.4).

The concentration of influent to the treatment plant can be plotted versus time to evaluate the trend of ground-water cleanup. Careful consideration, however, must be given to the contaminant distribution and ground-water flow patterns to the pump wells when interpreting this data. A variation of this analysis involves computing the trend of contaminant concentration versus the NPV extracted, rather than concentration versus time. This approach accounts for variations in pumping rates. A limitation of focusing on treatment plant influent data is that it may not be representative of clean-up progress throughout the plume.

3.2.4 Restoration Measurement Frequency Summary

The hydraulic head and chemical sampling frequency recommendations for containment discussed in Sections 2.2.1.4 and 2.2.6.3 apply to restoration P&T. Some additional aspects of measurement frequency, however, need to be considered for restoration monitoring. As described above, detennining the frequency and density of sampling for chemical analysis depends on site-specific conditions (including the distribution of contaminant velocities and pore volume sweep rates induced by P&T operation) and cost-benefit trade-offs. Adaptive modification of pumping locations and rates means that it may also be beneficial to revise sampling locations and frequency.

Minimum restoration measurement frequencies cannot be reasonably specified due to the site-specific nature of P&T remediation. Typical measurement frequencies, however, include: (1) daily to monthly analyses of contaminant concentrations (or indicator parameters) in treatment system influent and effluent; (2) monthly to yearly analysis of contaminant concentrations in ground water sampled from all pump wells and specified observation wells; (3) infrequent analyses of aquifer solids (e.g., at intervals needed to sweep at least two PVs through a formation volume); (4) weekly to monthly hydraulic head surveys to monitor flow directions and rates; (5) continuous (using flowmeters) to weekly monitoring of individual well pumping rates; and, (6) continuous flowmeter measurement of the combined inflow to treatment units.

3.2.5 Evaluating Contaminant Concentration and Distribution Trends

Contaminant distribution trends in ground water and aquifer materials should be examined to assess restoration progress. Performance measures based on concentration decreases are discussed in Chapter 4. Other performance measures are based on mass removal rates and contaminant mass-in-place trends. Specifically, these include: (1) the rate of contaminant mass removed by pumping (mass/year); (2) the rate of reduction of contaminant mass-in-place (mass/year); and (3) the rate of reduction of the volume of aquifer contaminated above MCLs or other standards (volume/year). A determination of contaminant mass-in-place, both dissolved and total, is necessary to apply these performance criteria.

3.2.5.1 Estimating Contaminant Mass-in-Place

A meaningful analysis of P&T performance can be obtained by comparing the contaminant mass removed versus dissolved contaminant mass-in-place. The dissolved mass-in-place (M_W) of a contaminant at a specific time is given by:

$$\mathbf{M_W} = \int_{\mathbf{A}} nC_W b \, dxdy \qquad (3\text{-}4)$$

where n is the formation porosity, C_w is the dissolved contaminant concentration, b is the plume thickness, and A is area of the plume.

The total contaminant mass-in-place (M_T) in the saturated zone, discounting NAPL presence, is more difficult to estimate than dissolved contaminant mass-in-place because of the additional data requirements. M_T can be estimated based on chemical analyses of ground water and solid samples as:

$$\mathbf{M_T} = \int_A (nC_W + \rho_b C_s) b \, dxdy \qquad (3\text{-}5)$$

where C_s is contaminant concentration in the solid media, and P_b is the formation bulk density. Alternatively, M_T can be approximated using the partition coefficient, K_d (See Section 1.2), as:

$$\mathbf{M_T} = \int_A (nC_W + \rho_b C_W) b \, dxdy \qquad (3\text{-}6)$$

Determining mass-in-place prior to and during remediation is frequently complicated by a paucity of available data, particularly with regard to estimating K_d, and C_S distributions, and therefore, M_T. The presence of NAPL can also confound application of mass-in-place performance measures. Where present, NAPLs will usually account for a dominant portion of the M_T, but estimation of NAPL mass is subject to a very high level of uncertainty. If undetected, NAPL presence may cause misinterpretation of mass removed versus mass-in-place trends.

Determining mass-in-place necessitates defining the "plume". This is generally not straightforward because it involves interpolating sparse data to develop a continuous plume distribution. There are several means to interpolate sparse data (Jones et al., 1986), including hand contouring which takes into account the experience, knowledge, and bias of the individual performing the contouring.

Computer software packages are used to contour large amounts of data (Hamilton and Jones, 1992). To determine mass-in-place, interpolation is usually performed on contaminant concentration values or the logarithm of these values. It is especially important that a log transformation be made for "spiked" plumes to improve data fitting without significant loss of peak values. Ground-water quality analyses at contamination sites determine "detect" and "non-detect" values. Whereas significant detects are the basis for interpolation, the non-detects pose problems. Although non-detect sample locations may clearly indicate the outermost possible extent of the plume, it is often difficult to delineate the true extent of contamination. Additionally there are often areas lacking any data. In these areas, the contouring packages are unbounded and may extrapolate data poorly. It may be necessary to provide boundary clarification with "dummy" zero concentration points.

Even computer-based contouring is subjective in that different contouring methods produce different results. Most applications are based on contouring two-dimensional isopleths, although contouring of three-dimensional isopleths is possible. Numerous contouring software products, many of which were developed in the mining, petroleum and civil engineering fields, are available commercially. Contouring routines are also incorporated as modules of Geographical Information Systems.

Several interpolation techniques are available for estimating mass-in-place including:

- Graphical methods based on contoured concentration data (e.g., inverse distance raised to a power of 2, 4, 6, or higher);
- Kriging (universal and unique variograms); and
- Triangulated Irregular Network (TIN).

A brief introduction to these methods follows.

The graphical method involves calculating the mass within each interval of a concentration contour map by measuring the interval area and multiplying it by the plume thickness, porosity, and contour concentration (or mean of the contour values bounding the interval area). This method cannot easily account for nonuniform porosity or plume thickness. Kriging is an advanced geostatistical technique that potentially can provide the best estimate of mass-in-place. Kriging, however, requires considerable experience for proper application. The TIN method is a simple numerical integration approach commonly used to estimate volumes in civil engineering applications. The procedure involves determining the optimum network of triangles to connect monitor and extraction wells and then evaluating a mass-in-place equation (such as 3-4) for each triangle. Different numerical approximations are obtained using different interpolation functions. Appendix A is the documentation of a TIN computer program that assumes linear interpolation over the triangle area. The program is included on a computer disk with this document. The TIN method can account for nonuniform plume thickness and porosity.

3.2.5.2 Determining Rate of Contaminant Mass Removal

The rate of contaminant mass removal (M_{Ri}) can be determined by sampling treatment plant influent for the constituents of concern and then multiplying the dissolved concentration (C_{wi}) of contaminant (i) by the total flow rate (Q_T):

$$M_{Ri} = Q_T C_{wi} \qquad (3\text{-}7)$$

This estimate can be compared to a calculation of M_{Ri} using data collected at each extraction well (j):

$$M_{Ri} = \sum_{j=1}^{n} q_j C_{wij} \qquad (3\text{-}8)$$

where n is the number of extraction wells, q_j is the pumping rate of well (j), and C_{wij} is the dissolved concentration of contaminant (i) pumped from well (j). These two estimates of mass removal rate should be comparable, but not necessarily identical, due to (1) variability of analytical results and (2) difference in the sum of individual well flow measurements and the measurement of treatment plant inflow.

3.2.5.3 Comparing Mass Removal and Mass-in-Place Trends

Restoration progress can be assessed by comparing the rate of contaminant mass removal (e.g., plotted as cumulative mass removed) to the dissolved and/or total contaminant mass-in-place. If the rate of contaminant mass extracted approximates the rate of dissolved mass-in-place reduction, then the contaminants removed by pumping are primarily derived from the dissolved phase. This is illustrated for trichloroethene in Figure 3-7, which shows mass removed as a mirror image of mass-in-place. Conversely, a contaminant source is indicated where the mass removal rate greatly exceeds the rate of dissolved mass-in-place reduction. The source may be NAPLs, contaminants sorbed to formation solids, an uncontained disposal area, or dissolved contaminants diffusing from low-permeability strata. Site hydrogeology and contaminant properties should be evaluated to determine if source removal and/or containment, and/or system modifications could improve P&T performance.

The time needed to remove dissolved contaminants can be projected by extrapolating the trend of the mass removal rate curve or the cumulative mass removed curve. If the mass removal trend indicates a significantly greater clean-up duration than estimated originally, the conceptual model of contaminant distribution may need to be reevaluated, and system modifications may be necessary. The effect (or lack of effect) of P&T system modifications will be evidenced by the continuing mass removal rate and cumulative mass removed trends.

Progress inferred from mass removal rates can be misleading, however, where NAPL and sorbed contaminants are present (e.g., the mass removed will exceed the initial estimate of dissolved mass-in-place). Interpretation suffers from the high degree of uncertainty associated with estimating NAPL or sorbed contaminant mass-in-place. Stabilization of dissolved contaminant concentrations while mass removal continues is an indication of NAPL or solid phase contaminant presence. Methods for evaluating the potential presence of NAPL are provided by Cohen and Mercer (1993), Feenstra et al. (1991), and Newell and Ross (1992).

Mass removal rates are also subject to misinterpretation where dissolved contaminant concentrations decline rapidly due to: (1) mass transfer rate limitations to desorption, NAPL or precipitate dissolution, or matrix diffusion; (2) dewatering a portion or all of the contaminated zone; (3) dilution of contaminated ground water with clean ground water flowing to extraction wells from beyond the plume perimeter; or (4) the removal of a slug of highly contaminated ground water. Contaminant concentration rebound will occur if pumping is terminated prematurely in response to these conditions.

3.3 PROJECTED RESTORATION TIME

The projected restoration or clean-up time is site specific and varies widely depending on contaminant and hydrogeologic conditions and the clean-up concentration goal. For example, clean-up time in homogeneous transmissive aquifers contaminated with mobile dissolved chemicals may be on the order of several years. NAPL sites or sites with sorbed contaminants in heterogeneous aquifers, however, may require decades or centuries of P&T operation to reach clean-up levels with currently available

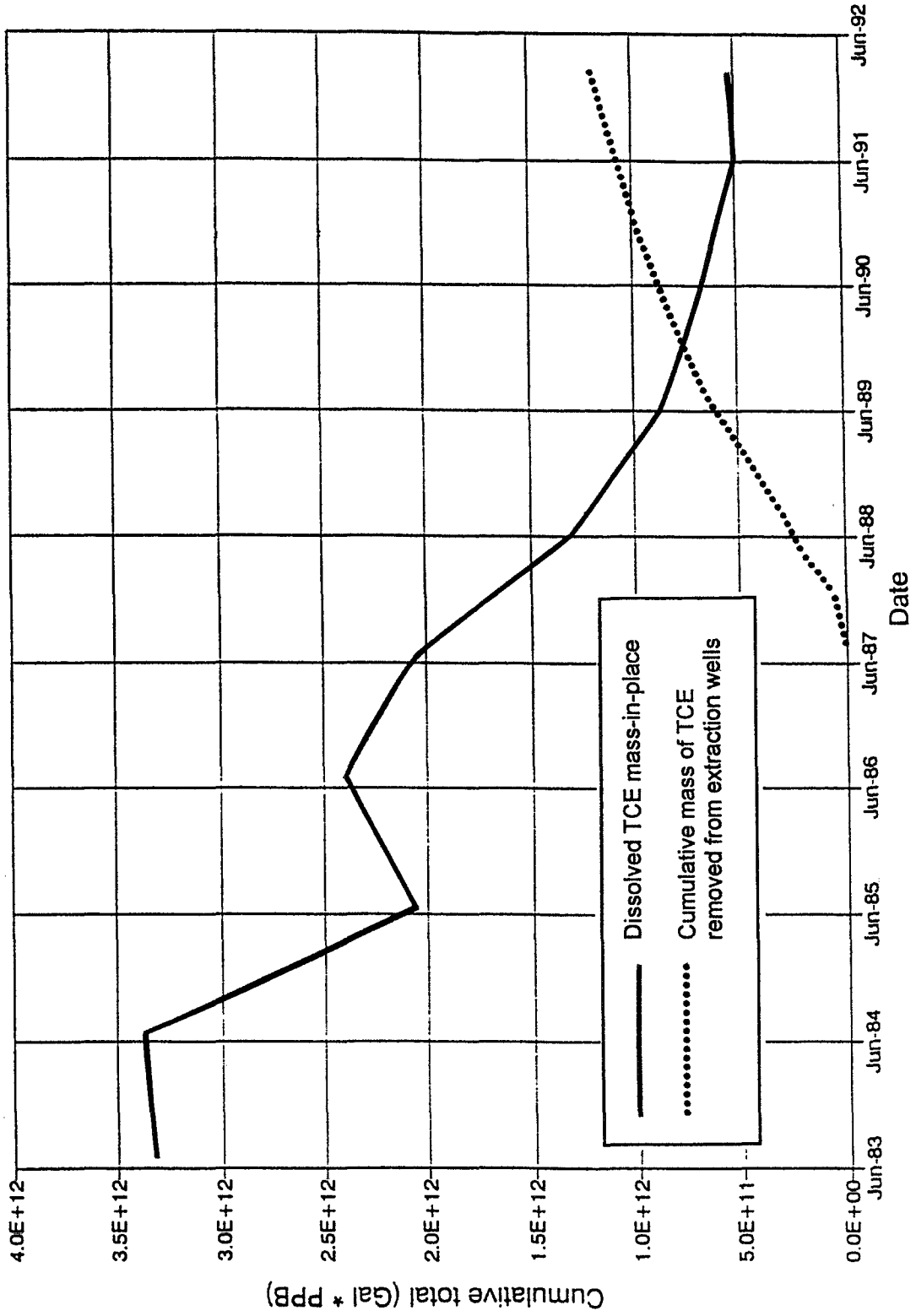

Figure 3-7. Comparison of cumulative mass of TCE removed versus dissolved TCE mass-in-place during P&T operation at the Air Force Plant 44 in Tucson, Arizona.

technology. Further, the length of time for restoration is usually difficult to estimate due to complications associated with characterization of the processes that limit cleanup (see Section 1.2).

The determination of restoration time is necessary to evaluate whether clean-up goals are practical and for choosing the most efficient remediation system. To demonstrate the magnitude of clean- up time variation at sites with different conditions, several examples are included herein. The first example illustrates a simple method to estimate the time required to extract mobile dissolved contaminants in a homogeneous aquifer (Hall, 1988). Assume that ground water in a 55-ft thick aquifer with a 0.3 storage coefficient is contaminated by conservative solutes throughout a ten acre area. The pore volume of the contamination zone is approximately 54,000,000 gallons, which, under ideal conditions, could be removed after one year of pumping at approximately 100 gpm. In reality, however, actual sites are not this simple and P&T hydraulics cannot be managed to prevent inflow of ground water from beyond the plume perimeter. To remove one pore volume from the plume requires pumping a greater volume of ground water. Geologic and chemical complexities can add years, decades, or longer to clean-up time due to processes described in Chapter 1 that cause tailing.

Diffusion also complicates clean-up time calculation. Conservative contaminants that have migrated (by any process) into less permeable strata in heterogeneous media will slowly diffuse into the more permeable zones during P&T operation. This diffusion may dictate the time necessary for complete remediation. For example, consider an aquifer with clay lenses that was contaminated for a long time before P&T operation reduced dissolved concentrations in the permeable strata, but not in the clay, to below clean-up standards. The areal extent of the clay is such that an approximation of one-dimensional diffusion out of each lens can be used to help estimate the time needed to deplete contaminants in the clay. The concentration gradient from the center to the edge of each clay lens can be approximated as unity if we assume relative dissolved contaminant concentrations of one (maximum concentration) in the center of each clay lens and zero (clean) in the permeable strata. The time for conservative contaminants to diffuse out from the clay center under these circumstances is:

$$t = m^2/D_a$$

where m is half of the clay lens thickness, D_a is the contaminant's apparent diffusion coefficient, and where

$$D_a = D/\alpha R$$

where R is the retardation coefficient, α is tortuosity (usually = 1.3 to 1.5), and D is the aqueous diffusion coefficient. D_a is the water diffusion coefficient modified to reflect tortuosity of the porous medium and sorption of the contaminant. The water diffusion coefficient for tetrachloroethene (a nonconservative contaminant), for example, is 7.5×10^{-6} cm^2/sec (Lucius et al., 1990), yielding a corresponding D_a value of 1×10^{-6} cm/sec. Using this value, for clay lenses that are 0.2, 1, 2, and 4 ft thick, the times for contaminants to diffuse from the center of the clay lenses are 0.29, 7.36, 29, and 118 years. In reality, the time required to reduce contaminant concentrations to very low levels may be much longer because the concentration within the clay will decline slowly and the concentration gradient will be less than unity.

Sorption and desorption also cause tailing, concentration rebound, and slow ground water restoration. The number of pore volumes which must be passed through a contamination zone to attain clean-up standards increases with the sorptive tendencies of a contaminant and kinetic limitations to the rate of desorption (Keely, 1989). An example of this process is demonstrated by a numerical model to evaluate a proposed P&T configuration for the Chem-Dyne site in Hamilton, Ohio (Ward et al., 1987; see Chapter 5). Due to the simulation of linear contaminant partitioning between soil and water, a nearly linear relationship was found to exist between retardation and the duration of P&T operation (or the NPV pumped) needed to attain a specific ground-water clean-up standard. Other investigators have concluded that nonlinear sorption may further increase the time required for ground-water-cleanup using P&T technology. For example, Stephanatos et al. (1991) recommend using site-specific leaching tests to assess sorption, and that, in lieu of such tests, they suggest using USEPA's Organic Leachate Model (OLM) (51 Fed. Reg. 21,653, June 13, 1986; 51 Fed. Reg. 27,062, July 29, 1986; 51 Fed. Reg. 41,088, November 13, 1986) as a more realistic approach to setting ground-water based soil clean-up goals. To illustrate their point, Stephanatos et al. (1991) present data from the Whitmoyer Laboratories CERCLA site. Nonlinear sorption for an iron-arsenic compound was determined from soil leaching tests. Based on these results, an estimated clean-up time of 50,000 years would be required to reduce arsenic concentrations in ground water to below 0.05 mg/l using conventional P&T technology. Assuming linear sorption, the restoration time was underestimated to be about 160 years.

Another complexity in estimating clean-up times for P&T systems involves the presence of NAPL. Where NAPL is present, it will slowly dissolve, creating a continuing source to ground-water contamination until the NAPL mass is depleted. Flow rates during P&T may be too rapid to allow residual NAPL to dissolve to its effective aqueous solubility limits. As such, the contaminated water is advected away from the NAPL residuals prior to reaching chemical equilibrium and is replaced by fresh water from upgradient. This has the same ramifications as other processes that cause tailing in that large volumes of water with low concentrations may be pumped during P&T operation. Several relationships have been derived to predict dissolved concentrations and time required to deplete residual and pooled NAPL sources (Cohen and Mercer, 1993). These indicate that NAPL can persist as a source of ground-water contamination for decades or longer.

Guidance for estimating ground-water restoration times using batch and continuous flushing models is provided by USEPA (1988b). The batch flushing model is based on a series of consecutive discrete flushing periods during which contaminated water in equilibrium with adsorbed contaminants is displaced from the aquifer pore space by clean water. Values of contaminant concentration in soil and water are calculated after each flush. An example of an analogous method (and corrections) to this batch flushing model are provided by Zheng et al. (1991, 1992). The batch and continuous models assume that: (1) zero-concentration influent water displaces contaminated ground water from the contamination zone by simple advection with no dispersion; (2) the clean ground water equilibrates instantaneously with the remaining adsorbed contaminant mass; (3) the sorption isotherm is linear; and (4) chemical reactions do not affect the sorption process. Care must be taken to avoid relying on misleading estimates of restoration time that may be obtained by using these simplified models.

The relatively simple calculations provided in this section demonstrate some of the difficulty in estimating clean-up time. It is obvious that long periods of P&T operation will be required to attain drinking water clean-up standards at many sites. Although more sophisticated modeling techniques are available (NRC, 1990), their application usually suffers from data limitations, resulting in uncertain predictions. Nevertheless, clean-up time analyses are needed to assess alternative remedial options and to determine whether or not clean-up goals are feasible.

3.4 ADDITIONAL CONSIDERATIONS

Pilot tests and phased implementation of restoration P&T are recommended to improve understanding of site conditions and thereby address complex and costly remediation in an effective and efficient manner. Discussions of modeling and operational efficiency provided in Sections 2.6 and 2.7 are very relevant to restoration P&T. Similarly, O&M and monitoring plans noted in Sections 2.4 and 2.5, respectively, should be developed for restoration P&T systems.

4. EVALUATING RESTORATION SUCCESS/CLOSURE

4.1 INTRODUCTION

Ground-water restoration (as operationally defined) is achieved when a predefined clean-up standard is attained and sustained. To ensure that these conditions are met, the procedure as outlined in Figure 4-1 should be followed. To protect human health and the environment, clean-up standards and/or containment objectives first must be set to define the goals of the remediation. Clean-up standards are site-specific and depend on the contaminants present, the risk imposed by those contaminants, and the fate of those contaminants in the subsurface. Clean-up standards include Maximum Contaminant Levels (MCLs), Alternate Concentration Limits (ACLs), detection limits, and natural water quality. Guidelines for selection of clean-up standards are provided in Guidance on Remedial Actions for Contaminated Ground Water at Superfund Sites (USEPA, 1988).

Much of the information in this chapter follows closely material in USEPA (1992c), with an attempt to minimize duplication. Figure 4-2 is provided to show the stages (indicated by the circled numbers) of remediation using water quality data from a single well. During the first stage, the site is evaluated to determine the need for and conditions of a remedial action. Once the remediation system is started, concentrations at most wells will decrease as shown for stage 2 in Figure 4-2. Concentrations will fluctuate around the trend due to seasonal changes, fluctuations due to the heterogeneous distribution of chemicals in the subsurface, changes in pumping schedules, variations in sample collection, and lab measurement error.

Based on both expert knowledge of the ground-water system and data collected during P&T, the time to terminate treatment will be determined (stage 3). For system termination, all wells on the site should be monitored and analyzed individually for compliance unless site-specific conditions dictate otherwise. Data analysis may indicate that clean-up standards will not be achieved, and other technologies and/or goals may be assessed. For remediation systems that have terminated, the transient effects resulting from remediation will take time to dissipate (stage 4). Monitoring during this time period is referred to as post-termination monitoring. After the ground-water flow system has reached a post-remediation equilibrium, sampling to assess attainment of the clean-up standards begins (stage 5). At stage 6, data collected during stage 5 is used to determine if the clean-up standard has been attained.

Due to fluctuating concentrations over time, the average concentration over a short period of time may be different from the average over a long period of time. Statistical decisions and estimates that only apply to the sampling period of approximately one year or less, are referred to as short-term estimates (USEPA, 1992c). Decisions and estimates that apply to the foreseeable future are called long-term estimates, and assume that ground-water processes can be described in a predictable manner. Long-term estimates are used to assess attainment, whereas short-term estimates are used to make interim management decisions.

Short-term analyses as applied to the P&T system operation (stage 2) are presented in Section 4.2. The methods described include both parametric and nonparametric analyses. Long-term analyses

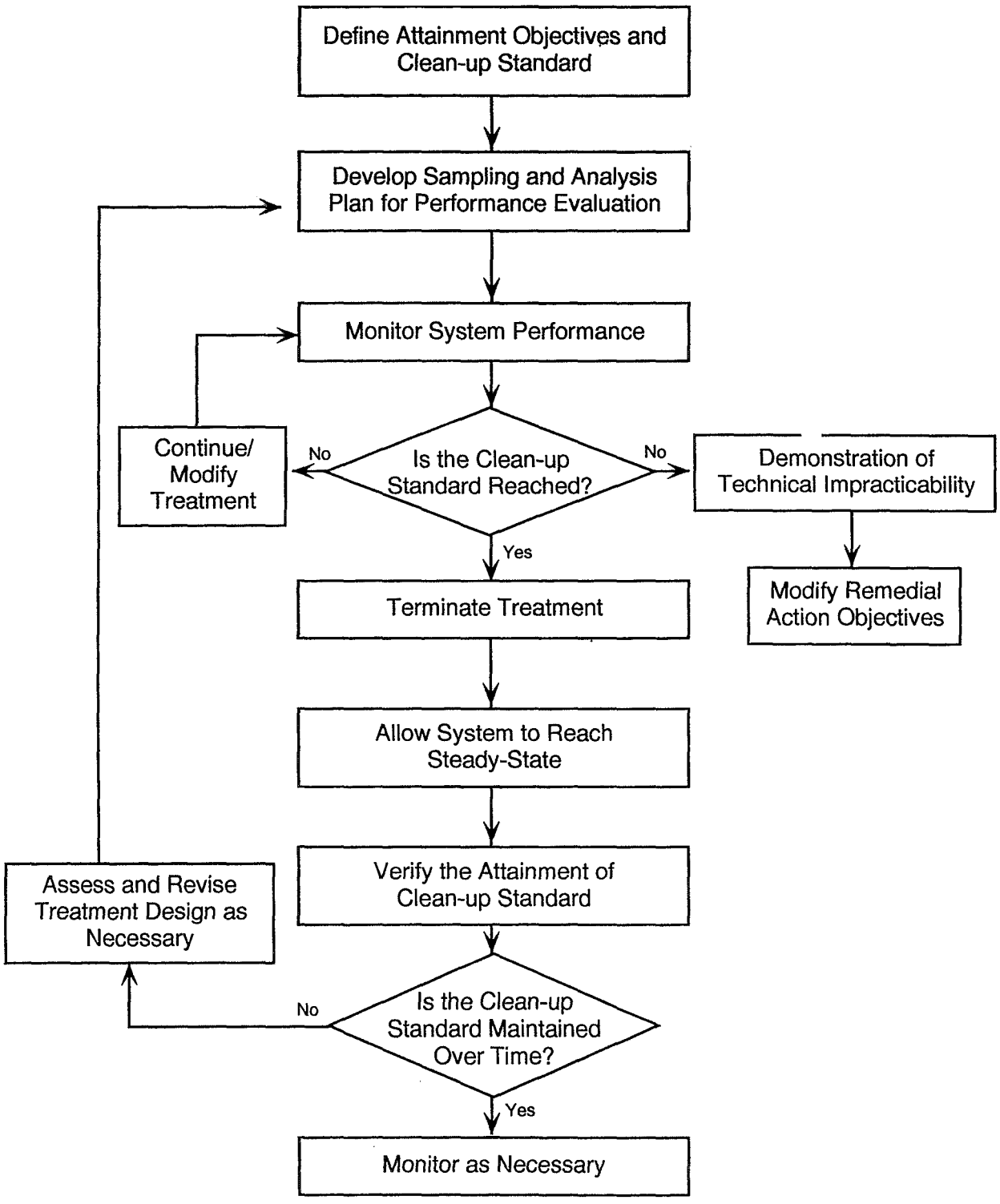

Figure 4-1. Determining the success and/or closure of a P&T system.

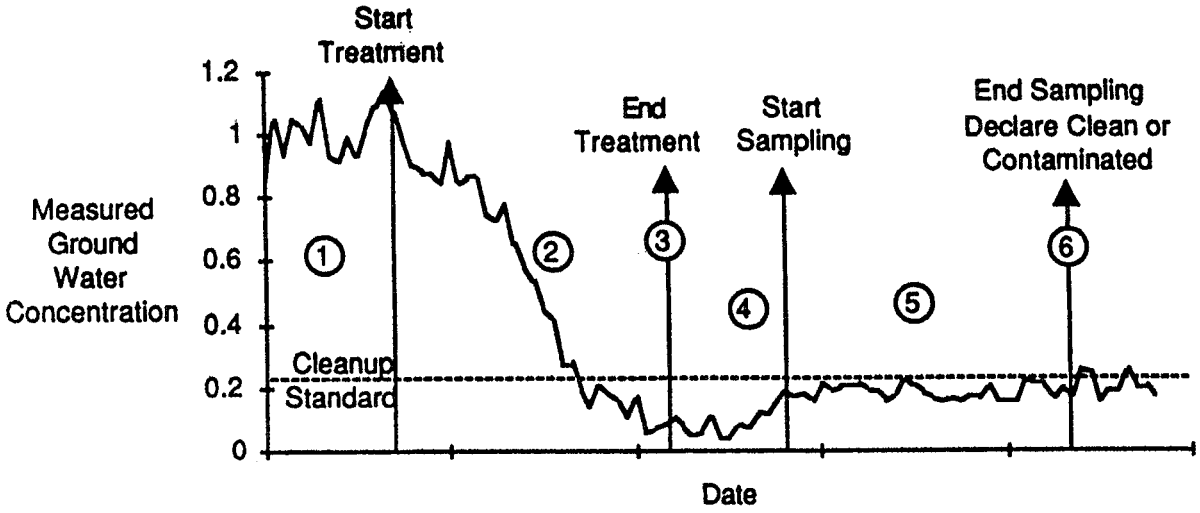

Figure 4-2. Example contaminant concentrations in a well at P&T site (USEPA, 1992c).

used to determine the time of treatment termination (stage 3) are presented in Section 4.3. Long-term analyses include parametric trend analyses, nonparametric trend analyses, and time-series analyses. Post-remediation monitoring of ground-water concentrations and water levels (stage 4) is discussed in Section 4.4. Section 4.5 discusses the general statistical methods used to determine if ground-water conditions after P&T system termination will remain below the site clean-up standard (stage 5 and 6).

4.2 SYSTEM OPERATION: SHORT-TERM ANALYSES

Statistical methods for analyzing short-term trends (stage 2) answer questions of the following nature:

- Are concentrations in individual wells at the site currently below the clean-up standard? To what degree of confidence is this true?
- Is the average sitewide concentration currently below the clean-up standard? To what degree of confidence is this true?
- Is the current sampling program sufficient to make inferences about concentration trends?
- Are there sections of the plume where clean-up standards have been met with confidence?

Short-term analyses consist of parametric and non-parametric techniques; i.e., those statistical analyses that can be performed on data that has a known distribution, and those data whose distribution is unknown or non-normal, respectively.

A set of concentration measurements taken over a year (short-term) can be described through simple sample statistics such as sample mean, standard deviation, standard error and percentile. The sample mean for this population characterizes the average concentration for all wells over the year. Sample-based comparisons can be made using hypothesis testing of differences between the sample mean and the site clean-up goal or other standards. Statisticians use the standard error, or sample variability to characterize the precision of samples-based comparisons through confidence intervals. Confidence intervals delineate a range of values within which the true value is expected to exist within a specified level of confidence. The standard error of the mean concentration provides a measure of the precision of the mean concentration obtained from ground-water samples taken over the year. The appropriate method used to calculate the standard error of the mean for a short-term analysis depends on the behavior of contaminant measurements over time, and the sampling design used for sample collection. Corrections to the standard error of the mean must be made if the data are collected systematically (at specified intervals), if there are seasonal patterns, if the data are serially correlated, and if there are trends in the data (see USEPA, 1992c).

4.2.1 Parametric Tests

Once sample statistics have been developed, simple hypothesis testing can be used to determine if the mean of the sample population (ground-water concentrations) is less than the clean-up standard. The following procedure describes simple hypothesis testing (USEPA, 1992c).

(1) Assume that the mean concentration of the collected data is greater than the clean-up standard as the null hypothesis. The clean-up standard therefore represents the null hypothesis of the analysis.

(2) Collect a set of data representing a random sample from the population of interest (e.g., concentrations over the year).

(3) Develop a statistical test from the sample data. Assuming that the null hypothesis is true, calculate the expected distribution of the statistic.

(4) If the value of the statistic is consistent with the null hypothesis, conclude that the null hypothesis provides an acceptable description of the analyses made.

(5) If the value of the statistic is highly unlikely given the assumed null hypothesis, conclude that the null hypothesis is incorrect.

If the chance of obtaining a value of a test statistic beyond a specified limit is, for example, 5 percent, and the null hypothesis is true, then if the sample value is beyond this limit, substantial evidence exists that the null hypothesis is not true and the mean concentration is less than or equal to the clean-up standard. An example of simple hypothesis testing for a short-term concentration mean of the data provided in Table 4-1 is presented in Box 4-1. If comparisons of means to clean-up standards are repeated periodically, a general evaluation of the remediation can be made. With time, the variance of

concentration, as measured by standard deviation, should decrease as the system reaches "steady-state" and concentrations are reduced by dispersion effects and remediation. For this reason, confidence levels about the mean concentration may be increased. Hypothesis testing of this nature assumes the data roughly represent a normal distribution. If the sample data set is limited, and the sample distribution is unknown, then nonparametric analyses must be performed.

4.2.2. Nonparametric Tests

A nonparametric analysis is used when the raw concentration data have been found to violate the normality assumption (based on a chi-squared or other normality test), a log-transformation fails to normalize the data, and no other specific distribution is assumed (USEPA, 1989). Similar to the parametric analysis, a nonparametric analysis produces a simple confidence interval that is designed to contain the true or population median concentration with specified confidence. If this confidence interval contains the clean-up standard, it is concluded that the median concentration does not differ significantly from the clean-up standard. If the interval's lower limit exceeds the clean-up standard, this is statistically significant evidence that the concentration exceeds the clean-up standard.

To compare the median site concentration to the site clean-up standard using a nonparametric analysis, an approach outlined in USEPA (1989) for compliance at RCRA facilities can be applied.

TABLE 4-1. DISTRIBUTION OF MONOCHLOROBENZENE.

Well ID	*Concentration of Monochlorobenzene in ppb*	*Well ID*	*Concentration of Monochlorobenzene in ppb*
MW-1	86	MW-14	76
MW-2	109	MW-15	55
MW-3	85	MW-16	87
MW-4	84	MW-17	105
MW-5	91	MW-18	75
MW-6	65	MW-19	53
MW-7	99	MW-20	135
MW-8	107	MW-21	113
MW-9	115	MW-22	84
MW-10	167	MW-23	83
MW-11	58	MW-24	19
MW-12	66	MW-25	118
MW-13	89	MW-26	21

Box 4-1. Short-term Hypothesis Testing

Table 4-1 represents the distribution of monochlorobenzene at 26 wells at a site. Wells at the site were sampled at approximately the same time. The data are assumed to be normally distributed, not affected by seasonal effects, and not serially correlated. The mean concentration value of these data is 86.3 ppb. The standard deviation of these data is 32 ppb. The standard error of the mean concentration is 6.3 ppb and is given by the following equation:

$$S_{\bar{X}} = \frac{S}{\sqrt{N}}$$

where s is standard deviation, s_0 is the standard error of the mean, and N represents the number of samples taken.

A one-sided confidence interval can be calculated by

$$\bar{x} + t_{1-\alpha;N-1}S_{\bar{X}}$$

where 0 is the mean value of the sample population, and $t_{1-\alpha;\ N-1}$ is the t statistic for N-1 degrees of freedom at an a level of significance.

The clean-up standard for monochlorobenzene at the site is 100 ppb. For 25 degrees of freedom (N-1) and a 95 percent confidence level ($\alpha = 0.05$), $t_{1-\alpha;\ N-1}$ is 1.671 (USEPA, 1992c; Appendix A.1). The one-sided confidence interval yields 96.8 ppb. If, in the null hypothesis, the mean concentration was assumed to be greater than 100 ppb, then the null hypothesis is incorrect to a 95 percent confidence level; i.e., 96.8 ppb is less than 100 ppb. The site mean concentration is highly likely (to a 95 percent confidence level) to be less than the clean-up standard.

This method requires a minimum of seven observations. This procedure as outlined is as follows (USEPA, 1989):

(1) Order the n data from least to greatest, denoting the ordered data by X(l),...,X(n), where X(i) is the ith value in the ordered data.

(2) Determine the critical values of the order statistics. If the minimum seven observations are used, the critical values are 1 and 7. Otherwise, find the smallest integer, M, such that the

cumulative binomial distribution (see Conover, 1980) with parameters n (the sample size) and p = 0.5 (0.5 quantile) is at least 0.99. For sample sizes from 4 to 11 values of M and the n+1-M together with the exact confidence coefficient can be found in Table 6.3 of USEPA (1989). For larger sample sizes, take as an approximation the nearest integer value to

$$M = n/2 + 1 + Z_{0.99}\sqrt{(n/4)} \qquad (4\text{-}1)$$

where $Z_{0.99}$ is the 99th percentile from the normal distribution and equals 2.33.

(3) Once M has been determined in Step 2, find n+1-M and take as the confidence limits the order statistics, X(M) and X(n+1-M).

(4) Compare the confidence limits found in Step 3 to the clean-up standard. If the lower limit, X(M) exceeds the compliance limit, there is statistically significant evidence of contamination. Otherwise, ground water is within the clean-up standard.

Both the nonparametric and parametric tests for short-term analyses described provide comparison between the mean of the site data and the site clean-up standard. Other comparisons can be made against the median, percentiles or proportions of concentration data for both parametric and nonparametric analyses (see USEPA, 1992c; Helsel and Hirsch, 1992; and Gilbert, 1987).

4.3 TREATMENT TERMINATION: LONG-TERM ANALYSES

Analyses of long-term concentration trends provide models that can be used in P&T system termination decisions (Stage 3) and to determine if the goals of the remediation are feasible. Several statistical methods of evaluating long-term concentration trends exist. These methods include regression analyses (trend analyses) and time-series analyses.

It is important to note that changes in system stress (e.g., pumping rate changes or an external influence, such as seasonal fluctuations in recharge), can result in changes in concentration variation, and correlation. These "fluctuations" can make regression analyses difficult. However, certain trends can be removed from the data prior to regression analyses. To determine if the data are serially correlated, the Durbin-Watson test can be applied. Methods for correcting for serial correlation are described in USEPA (1992c, Section 6.2.4).

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4.3.1 Parametric Trend Analyses

A regression or trend analysis of ground-water contaminant levels provides information on concentration level trends over time and predicted concentration levels in the future. Regression analysis techniques fit a theoretical curve or model to a set of sample data. Actual time-concentration data is replaced by a model that can be used to predict concentrations within a specified confidence or prediction interval. By applying confidence intervals to a regression line fit, the following assumptions are made:

- The assumed model or fitted-curve form is correct.

- The data used to fit the model are representative of the data of interest.

- The variance of the residuals is constant with time. A residual is the difference between the observed concentration measurement and the corresponding concentration value predicted by the regression model.

- Residuals are independent, and, therefore, free from serial correlation. Serial correlation is the interdependence of residuals in a time sequence.

- Residuals are normally distributed.

Sources of variability that can cause the data collected not to be normally distributed include (API, 1991):

- Seasonal or short-term natural fluctuations.

- Spatial heterogeneity in the contaminant distribution in the aquifer so that water volumes containing variable amounts of contaminants flow past a fixed sampling point.

- Sampling errors such as the collection of non-representative samples, or not using the sampling technique consistently over time.

- Sample handling or preservation problems so samples contain different amounts of contaminant at the time of analysis than were present at the time of collection.

- Analytical variability caused by (a) differences in analytical technique and instrumentation among different laboratories or within a given laboratory over the long term, and (b) intrinsic imprecision in analytical measurements.

Formal tests for normality include the Shapiro-Wilk test, the Shapiro-Francia test and the Kolomogorov-Smirnov test (USEPA, 1989). A relatively simple way for checking the normality of residuals is to plot the residuals ordered by size against their expected values under a normal distribution (USEPA, 1992c). Under normality, the residuals against their expected values should plot as a straight line.

Both straight-line and curvilinear regression models can be used. The initial choice of regression model can be made by observing a plot of the sample data over time (USEPA, 1992c). Straight-line regressions are appropriate if a plot of concentration versus time forms a straight line. For most P&T systems, long-term concentration declines will be curvilinear; i.e., concentration versus time does not form a straight line when plotted. Under certain circumstances, however, the concentrations versus time relationship can be modeled as a straight line by transforming either the dependent or independent variable (USEPA, 1992c) (i.e., log linear).

Regardless of the model of regression analysis, an assessment of the fit of the theoretical curve or regression model to existing data is required. The diagnostic statistical parameters that test the fit of the theoretical curve include:

- SSE = Sum of Squares Due to Error is a measure of how well the model fits the data. If the SSE is small, the fit is good; if it is large, the fit is poor.

- MSE = Mean Square Error provides an estimate of the variance about the regression. The lower the MSE the better the fit.

- R^2 = Coefficient of Determination represents the proportion of the total variance in the observed value that is accounted for by the regression model. A value of R^2 close to 1 represents a good fit of the data to the regression line. Low values of R^2 can indicate either a relatively poor fit of the model or no relationship between the concentration levels and time (USEPA, 1992c). The fit of the model should not be judged based solely on the corresponding R^2 value.

A full description of the development and application of these parameters for both straight and curvilinear regression is provided in the USEPA (1992c) guidance document entitled "Methods For Evaluating the Attainment of Cleanup Standards, Volume 2: Ground Water."

Once the fit of the regression line has been assessed, predictions and conclusions about trends and future concentration values can be made. These determinations can be compared to clean-up standards to decide whether or not remediation can be terminated.

One termination analysis method that can be applied is the zero-slope method (USEPA, 1989). This method requires the demonstration that contaminants have stabilized at a level below the clean-up standard and will remain at that level with time (zero slope). Typically, ground-water concentrations in a P&T system "level off" with time and trend toward an asymptotic limit (with a slope of zero). An example of the application of the zero-slope method to concentrations trends in Box 4-2 uses data in Table 4-2. In this example, the slope calculated for the best fit regression line is compared to zero by determining the standard error of the estimated slope of the regression line. By knowing the standard error, the degree of confidence in the estimated regression line slope can be determined to quantify the degree of potential error of the slope estimate. To statistically test if the "steady-state" concentration level reached at the zero slope point is below the clean-up standard, confidence intervals about the regression line can be determined. By applying confidence intervals to any conclusion derived from the regression line, the fitted curve residuals are assumed to be normally distributed as described above. The concentration trends presented in Table 4-2, the corresponding best fit regression line, and the corresponding upper 95 percent confidence interval line are depicted in Figure 4-3.

A computer program, REGRESS, has been developed through funding by the American Petroleum Institute (API, 1992) to assess asymptotic conditions with first order and polynomial (exponential) regression techniques. This program performs sequential linear regression analyses (e.g.,

Box 4-2. Analysis of Zero-Slope Trending Data

The estimated regression line for the last six data points in Table 4-2 and Figure 4-3 has the following linear equation based on least squares estimates:

$$C = -0.00022x + 1.93053$$

where C is the concentration in ppb at a given time and x is the time in months.

A confidence interval about the slope -0.00022 can be used to determine if a downward trend exists. The confidence interval about the slope is given by:

$$b_1 \pm t_{1-\frac{\alpha}{2};N-2} s(b_1)$$

where b_1 is the estimated slope of the regression line,

$$t_{1-\frac{\alpha}{2};N-2}$$

is the student t statistic for N-2 degrees of freedom with an significance level, and s(b_1) is the Standard Error of the estimated slope.

The Standard Error of the estimated slope can be determined by

$$s(b_1) = \sqrt{\frac{MSE}{S_{xx}}}$$

where

$$MSE = \sum_{i=1}^{N} \frac{(C_i - \hat{C}_i)^2}{N-2}$$

C_i = the actual concentration at time i; †$_i$ = the estimated concentration based on the estimated regression line at an equivalent time as C_i ; N = the total number of samples taken; N-2 = the degrees of freedom; i = the sample time;

$$S_{xx} = \sum_{i=1}^{N} x_i^2 - \frac{S_x^2}{N},$$

$$S_x = \sum_{i=1}^{N} x_i.$$

For the data presented in Table 4-2 s(b_1) = 0.008815. For a 95 percent confidence level, α = 0.05. The student t statistic $t_{1-\alpha/2;N-2}$ for an a of 0.05 is 2.776 (see Appendix A of USEPA, 1992c).

The confidence interval about the slope is -0.00022 ± 2.776 (0.008815), and the slope will range from 0.02425 to -0.02469 within a 95 percent confidence level. The upper confidence value of the slope is greater than zero and the lower confidence value is less than zero. This signifies that the slope is not significantly different from zero (i.e., no positive or negative trend exists).

The data presented in Table 4-2 suggest that the clean-up standard (10 ppb) was reached at time 104 days. Based on this information and the fact that there is a zero slope in concentration, the treatment system can be terminated, and post-termination monitoring can proceed.

TABLE 4-2. CONCENTRATION VERSUS TIME DATA SHOWING AN ASYMPTOTIC ZERO SLOPE (REGRESSION ONLY PERFORMED ON LAST SIX SAMPLES).

Time, i (days)	*Actual Concentration, Ci (ppb)*	*Estimated Regressed Concentration, † in ppb*	*Upper 95% Confidence Concentration in ppb*
1	150.0		
8	41.0		
16	41.0		
21	24.0		
37	15.0		
48	51.0		
62	7.0		
104	10.0		
134	3.0	1.90	6.18
161	0.3	1.89	5.92
189	3.0	1.89	5.76
217	0.5	1.88	5.71
272	2.0	1.87	5.96
302	2.3	1.86	6.27

subsets consisting of the last five data points, the last six data points, etc.) until the final data set regressed includes all the data. The subset of the regression curve assigned as having approximately a zero slope is defined to be the asymptote of the concentration values.

Hirsch et al. (1982) showed that if the seasonal cycles are present, and/or the data are not normally distributed, and/or the data are serially correlated, the true slope as calculated by confidence intervals may not be correct, in fact, a zero slope may actually occur and not be detected by the regression analysis.

If asymptotic concentration levels exceed the clean-up standard, then a reassessment should be made of the P&T methods and goals. P&T operation may need to be modified by increasing pumping rates, adding new recovery wells, etc. Note, however, that, in some cases, the clean-up standards may be unobtainable,using the best available technology. For this case, if the standards cannot be relaxed based on institutional controls or a reevaluation of risk, then the remedial goal should be reevaluated and may be modified to long-term hydraulic containment. Additional guidance is provided in USEPA, 1993.

In a similar application to Box 4-2, it can be statistically determined if concentration levels will follow a downward trend after reaching the clean-up standard. If this condition occurs, the P&T system may be terminated. An example of this method, as applied to the concentrations in Table 4-3, is presented in Box 4-3, and Figure 4-4.

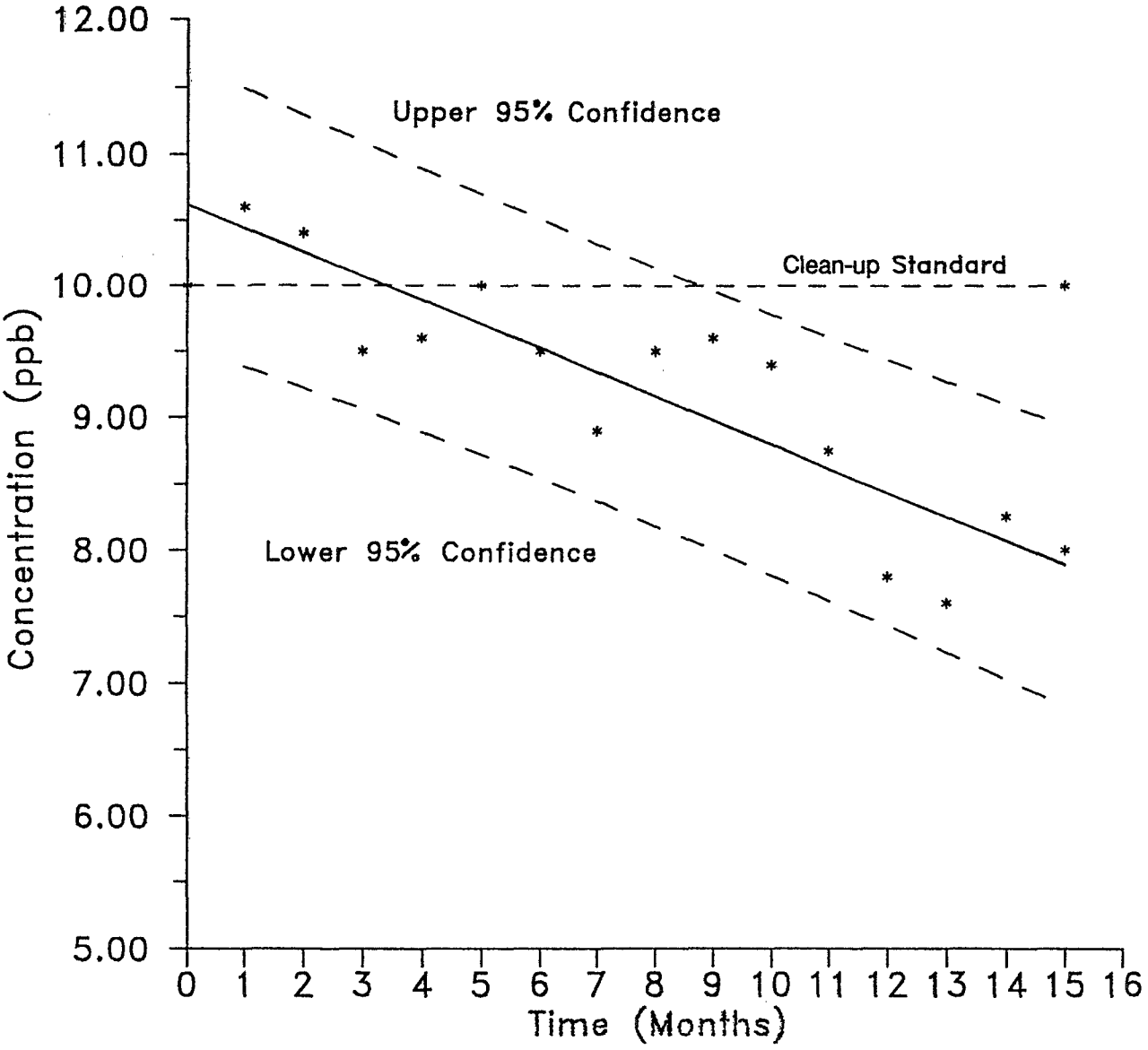

Figure 4-3. Best-fit regression line and 95% confidence interval for the concentration trend of data given in Table 4-2.

TABLE 4-3. CONCENTRATION VERSUS TIME DATA SHOWING A DOWNWARD TREND.

Time, i (months)	*Actual Concentration, Ci (ppb)*	*Estimated Regressed Concentration, † in ppb*	*Upper 95% Confidence Concentration in ppb*	*Lower 95% Confidence Concentration in ppb*
1	10.6	10.44	11.49	9.38
2	10.4	10.26	11.29	9.22
3	9.5	10.07	11.09	9.06
4	9.6	9.89	10.89	8.89
5	10.0	9.71	10.70	8.72
6	9.5	9.53	10.51	8.54
7	8.9	9.34	10.32	8.37
8	9.5	9.16	10.14	8.18
9	9.6	8.98	9.96	8.00
10	9.4	8.80	9.78	7.81
11	8.75	8.61	9.61	7.62
12	7.8	8.43	9.44	7.43
13	7.6	8.25	9.27	7.23
14	8.25	8.07	9.10	7.03
15	8.0	7.89	8.94	6.83

4.3.2 Nonparametric Trend Analyses

When the residuals from a regression analysis are not normally distributed, or of an unknown distribution, then nonparametric trend analyses are recommended. Examples of nonparametric trend analyses include the Mann-Kendall trend test, Sen's nonparametric procedure, and a curve smoothing procedure, LOWESS (Locally Weighted Scatterplot Smoothing). Each of these methods can be used to calculate a model for concentration trends over time. Sen's nonparametric procedure can be used to estimate the magnitude of the trend. When seasonal variation is present in the data, then the seasonal Kendall test and seasonal Kendall slope estimator may be used to adjust for seasonal effects (Carosone-Link et al., 1993). Several references which describe nonparamtric trend analyses, as applied to water studies, include Gilbert (1987), Helsel and Hirsch (1992), and USEPA (1992c).

4.3.3 Time Series Analysis

Time series analysis is very similar in use to regression, except that time series makes predictions based on serial correlation with trends removed, whereas regression tries to eliminate these correlations and analyze trends. Three time-series techniques, the general linear model (GLM), auto-regressive moving average (ARMA), and auto-regressive integrated moving average (ARIMA), may provide some additional information about the direction in which the mean is trending, and its stability (USEPA, 1989). These methods are usually computer intensive; their use requires a familiarity with time-series analysis.

Box 4-3. 4nalysis of Downward Trending Data

The estimated regression line for the data in Table 4-3 and Figure 4-4 has the following linear equation based on least squares estimates:

$$C = -0.1832x + 10.62$$

where C is the concentration in ppb at a given time, x is the time in months.

A confident interval about the slope -0.1832 can be used to determine if a downward trend exists. The confidence interval about the slope is given by:

$$b_1 \pm t_{1-\frac{\alpha}{2};N-2} s(b_1)$$

where b_1 is the estimated slope of the regression line;

$$t_{1-\frac{\alpha}{2};N-2}$$

is the student t statistic for N-2 degrees of freedom with an a significance, and $s(b_1)$ is the Standard Error of the estimated slope.

The Standard Error of the estimated slope can be determined by

$$s(b_1) = \sqrt{\frac{MSE}{S_{xx}}}$$

where

$$MSE = \sum_{i=1}^{N} \frac{(C_i - \hat{C}_i)^2}{N-2}$$

C_i = the actual concentration at time i; †$_i$ = the estimated concentration based on the estimated regression line at an equivalent time as C_i; N = the total number of samples taken; N-2 = the degrees of freedom; i = the sample time;

$$S_{xx} = \sum_{i=1}^{N} x_i^2 - \frac{2}{i} - \frac{S_x^2}{N};$$

$$S_x = \sum_{i=1}^{N} x_i.$$

For the data presented in Table 4-3. $s(b_1) = 0.026173$

For a 95 percent confidence level, $\alpha = 0.05$. The student t statistic $t_{1-\alpha/2;N-2}$ for an of 0.05 is 2.160 (see Appendix A of USEPA, 1992c). The confidence interval about the slope is -0.1823 ± 2.160 (0.026173) and the slope will range from -0.1258 to -0.2388 within a 95 percent confidence level. The negative slope within the confidence interval strongly suggests that concentrations are on a downward trend.

The upper confidence interval line (Figure 4-4) suggests that the clean-up standard (10 ppb) was reached at time 8.9 months. Based strictly on this information and the fact that there is a downward slope in concentration, the treatment system can be terminated, and post-termination monitoring can proceed.

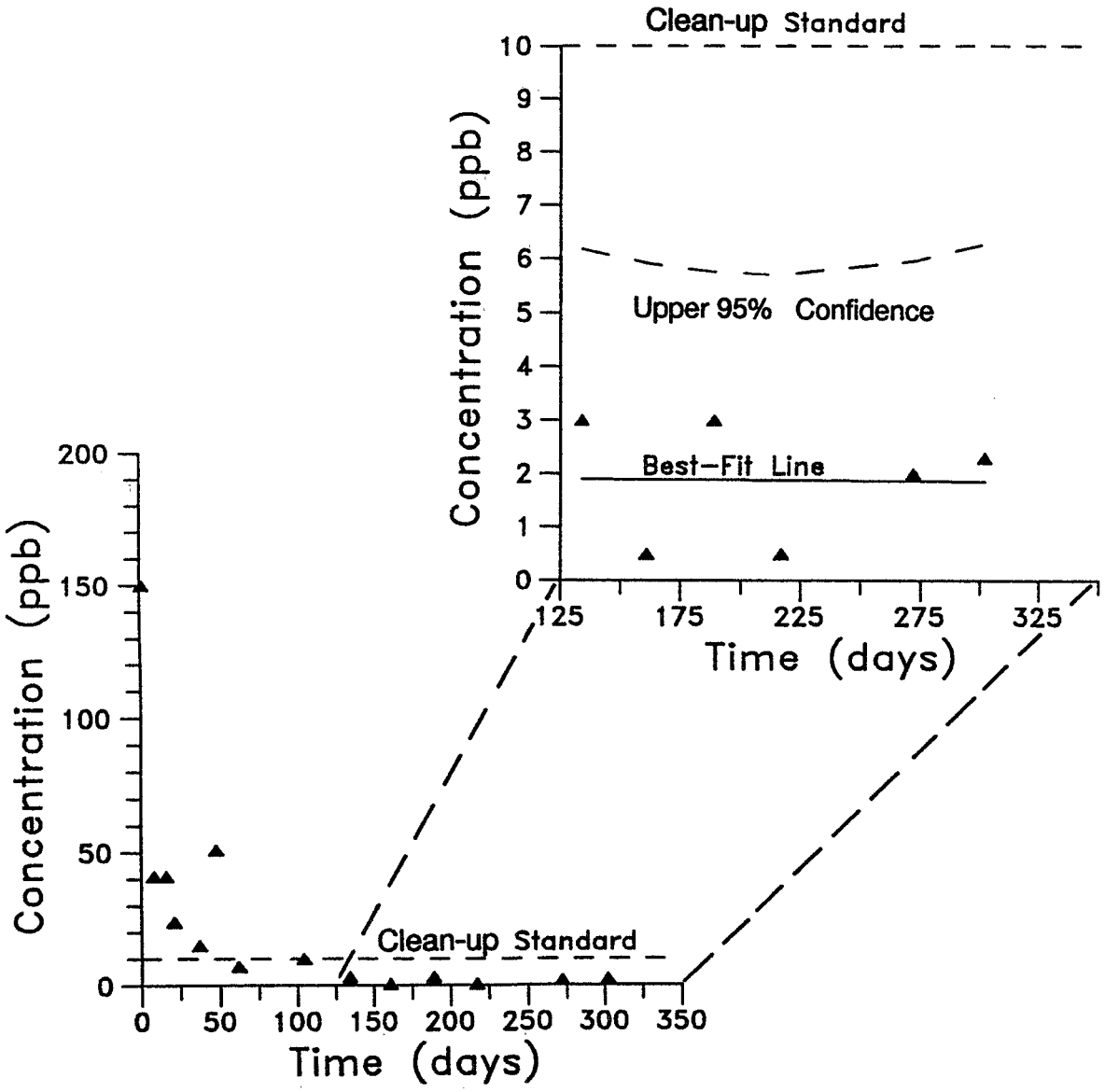

Figure 4-4. Best-fit regression line and 95% confidence interval for the concentration trend in Table 4-3.

4.4 POST-TERMINATION MONITORING

After terminating P&T operation, a period of time must pass to ensure that any transient effects of treatment on the ground-water system no longer exist (stage 4 in Figure 4-2). This period allows ground water to reequilibrate hydraulically and chemically with the new flow field. Ground water can only be judged to attain the clean-up standard if both present and future contaminant concentrations are acceptable.

Changes in ground-water flow velocities and flow paths are induced when a P&T system is initiated. These changes redistribute contaminant pathways and affect the rate at which ground water will travel. Any change to the P&T system (e.g., increased pumping rates) will change ground-water flow velocities and contaminant pathways. Following system termination, ground-water sampling may continue, but only data collected after steady-state conditions have been reached (attainment sampling) may be representative of long-term conditions.

Steady-state conditions occur when ground-water concentrations and elevations no longer are influenced by the effects of the P&T system. When sampling to determine whether the ground-water system is at steady-state, three decisions are possible (USEPA, 1992c):

- Steady-state conditions exist and sampling for assessment attainment can begin;
- The current contaminant concentrations indicate that the clean-up standard is unlikely to be reached, and further treatment must be considered; or
- More time and sampling must occur before it can be confidently assumed that the ground water has reached steady state.

To determine if post-remediation steady-state conditions have occurred, it is useful to have a knowledge of steady-state conditions prior to initiation of the remediation. Ground-water elevations may not, however, return to preremediation conditions if the remediation includes permanent features such as slurry walls.

The frequency of data collection will depend on the correlation among consecutively obtained values (USEPA, 1992c). If serial correlation seems to be high, the time interval between data collection efforts should be lengthened. With little or no information about seasonal patterns or serial correlations in the data, at least six observations per year are recommended (USEPA, 1992c).

Underlying trends in ground-water chemistry and elevation data will suggest whether steady-state conditions exist. All data should be plotted over time for visualization of potential trends. Statistical methods for determining trends include parametric trend analyses and nonparametric trend analyses, and were discussed previously. Other formal procedures for testing for trends also exist, including the Seasonal Kendall Test, Sen's Test for Trend, and a Test for Global Trends. All three of these tests require the assumption of independent observations. If this assumption is violated, these tests tend to indicate that there is a trend when one does not actually exist (USEPA, 1992c).

4.5 MONITORING FOR ATTAINMENT

After ground-water conditions have reached a new equilibrium or steady-state, long-term cleanup attainment can be assessed (stages 5 and 6 in Figure 4-2). Long-term post-remediation monitoring is critical in ensuring no future impact from contaminants gradually leaching out of the remediated matrix. Post-operational monitoring may be required for a period of two to five years or more after termination, depending on site conditions. As discussed in Chapter 1, contaminant concentrations can rebound significantly after terminating a P&T operation (e.g., Robertson, 1992).

Two potential measures of long-term site cleanup consist of comparisons between clean-up standards and mean concentration, or comparisons between clean-up standards and a selected percentile of all samples. The procedures used to make these comparisons depend on whether a fixed number of samples is to be analyzed (e.g., 20 samples over a two-year period), or samples are to be taken sequentially at set intervals without specifying a total number of samples. Methods for determining if clean-up standards have been maintained are similar to those methods for short-term comparisons. Additional considerations include corrections for seasonal effects, determination of appropriate sample sizes, determination of appropriate sampling frequency and, for sequential analysis, determining an appropriate rate of data analysis. Guidance for statistical analysis of fixed and sequential sampling is provided by USEPA (1992c).

4.6 CONCLUSIONS

General descriptions of the statistical techniques used to determine the time of remediation termination have been presented in this chapter. For further guidance on the application of statistical methods to assessing environmental data, refer to USEPA (1989 and 1992c), Helsel and Hirsh (1992), and Gilbert (1987).

5. CHEM-DYNE SITE CASE STUDY

It is important to note that selected data from the Chem-Dyne site in Hamilton, Ohio, are used only to illustrate some of the monitoring methods described within this document. Much of the data was obtained a number of years ago. Issues, such as the potential presence and sources of NAPLs, the effects of near-site pumping, and changes in the remediation system since its initiation, are not considered for this purpose. Extraction wells placed along and within the contaminant plume at the site are designed to hydraulically contain and remove contaminated ground water for treatment. An overview of the P&T design, monitoring, and results are provided in this chapter. Other P&T case studies are provided by CH_2M Hill (1992).

5.1 BACKGROUND

The Chem-Dyne site occupies approximately 20 acres along the Great Miami River within Hamilton. Hazardous waste, accepted for solvent reprocessing from 1974 to 1980, resulted in contamination of soil and ground water. The hydrogeologic environment at the site consists predominantly of glaciofluvial sand and gravel, lacks extensive clay layers, and receives induced infiltration from the Great Miami River. Generally, two hydrostratigraphic units exist: (1) a lower unit consisting of medium gravel or sand and gravel, and (2) a shallow unit comprised of silts, clayey silts, and silty and fine sands.

A Remedial Action Plan implemented in 1985 included: (1) excavation and disposal of contaminated surficial soils; (2) installation of a low-permeability cap; and (3) development of a P&T system to hydraulically contain and remove contaminated ground water within the 0.1 ppm total Priority Pollutant volatile organic compounds (VOCs) isopleth (Figure 5-1). Priority Pollutant VOCs account for approximately 96% of the contaminant mass detected mostly in the shallow depth wells open to the upper five to ten feet of the aquifer (Papadopulos & Assoc., 1985). Sampling and analysis of intermediate depth wells screened between a depth of approximately 55 to 65 ft also detected concentrations greater than 0.1 ppm total VOCs. The P&T design utilizes extraction wells within the zone of contamination and along the plume boundary to hydraulically contain and remove the contaminated ground water. A portion of the treated ground water is reinjected upgradient of the extraction wells to increase the pore volume flushing rate. The system was originally designed to pump an average 2.6 pore volumes per year through the contaminated zone. A ten year clean-up time was projected to reduce total dissolved Priority Pollutant VOCs to below 0.1 ppm throughout the aquifer.

Limited operations of the ground-water P&T system began in February 1987. Data were collected to assess the initial mechanical and operational performance of the system. Beginning January 1988, the Chem-Dyne site P&T system was fully operational. Five full years (1988 to 1992) of operational and monitoring data have been collected and can be utilized to evaluate the effectiveness of P&T remediation at Chem-Dyne.

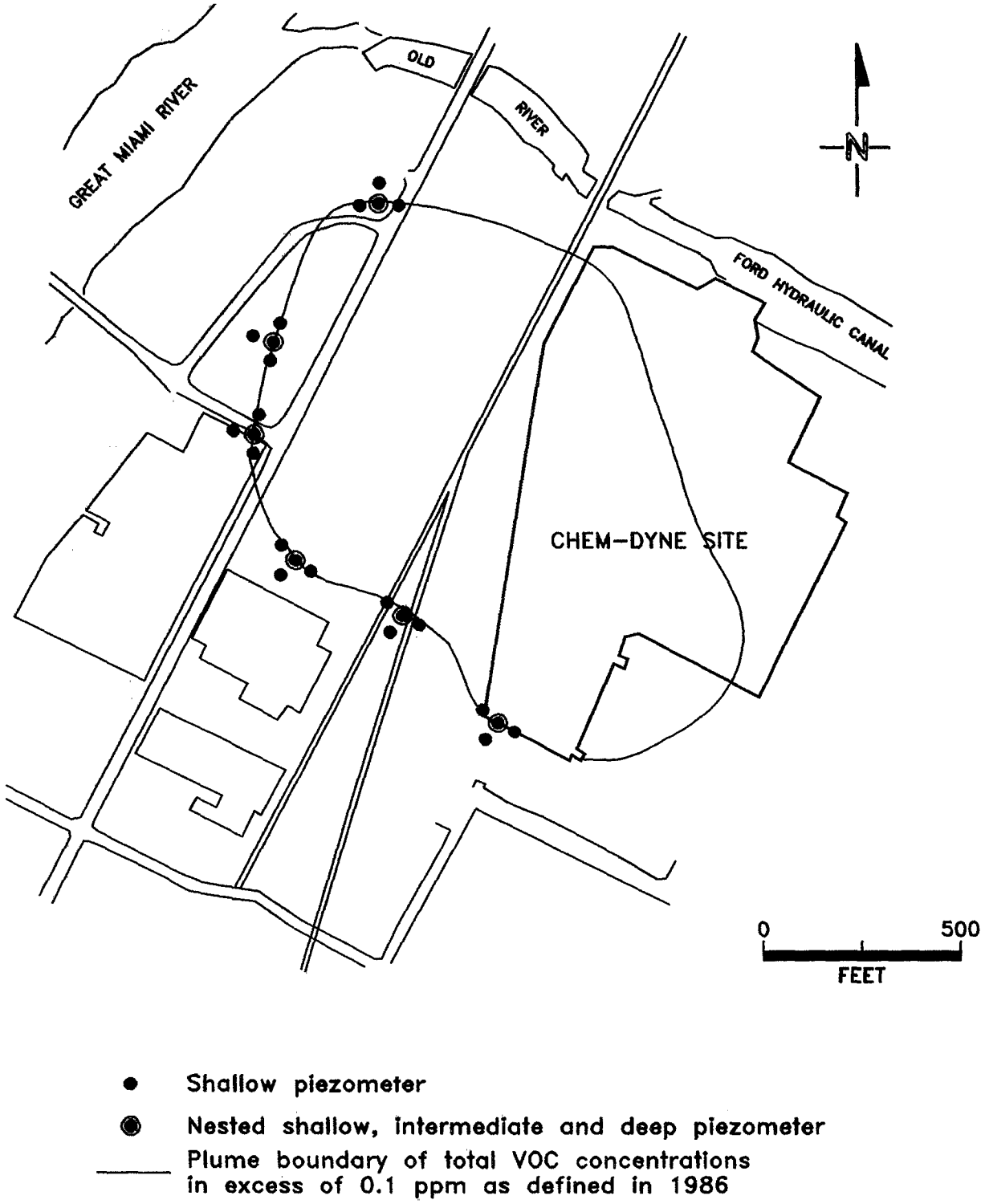

Figure 5-1. Boundary of 0.1 ppm total VOC plume and location of nested piezometers at the Chem-Dyne site (from Papadopulos & Assoc., 1993).

5.2 PERFORMANCE CRITERIA

The P&T system was designed based on the following performance goals and criteria which were specified in a Consent Decree.

(1) After defining the 0.1 ppm total Priority Pollutant VOC plume limits, the outermost downgradienit extraction wells shall be placed at or beyond the contaminant plume boundary.

(2) The extraction/injection system shall establish and maintain an inward hydraulic gradient, both vertically and horizontally, to ensure that the contaminants within the 0.1 ppm total VOC plume boundary are contained for removal and treatment.

(3) The P&T system shall be operated for a minimum of ten years and shall be capable of reducing the total Priority Pollutant VOC concentration within the plume boundary to 0.1 ppm.

(4) Ground-water quality shall not exceed water quality criteria for the protection of human health (based on 10^{-6} risk or background, whichever is higher using best analytical techniques) at compliance points outside of the zone of hydraulic control.

The responsible parties can terminate the P&T system after ten years of operation if the total Priority Pollutant VOCs in all monitor and extraction wells within the 0.1 ppm plume have been reduced below 0.1 ppm. If the total Priority Pollutant VOC concentrations are not maintained effectively constant below 0.1 ppm after the cessation of pumping, additional corrective actions may be required. If the concentration reduction goals are not met after 20 years of operation, then the regulatory and responsible parties will determine whether further P&T operation or modification would produce significant improvement.

5.3 PERFORMANCE MONITORING

Detailed P&T monitoring requirements were specified in the Consent Decree. The performance monitoring at the Chem-Dyne site provides an example of the locations, frequency, and type of data to be collected for measuring containment and restoration performance. The Chem-Dyne monitoring program is designed to provide data to (Papadopulos & Assoc., 1985):

(1) Evaluate the performance of the extraction/injection system with respect to its design criteria and to facilitate timely adjustments;

(2) Determine whether the system will be terminated after the initial ten year period, or at what time thereafter;

(3) Assess whether performance goals have been met at compliance points and within the defined plume boundary after termination; and

(4) Develop a reliable predictive model that can be used to assess the effects of system adjustments and the impacts of residual contamination, and of noncompliance, if any, on potential receptors.

Water-level and water-quality data are collected to achieve these objectives.

5.3.1 Hydraulic Head Monitoring

Water-level data are measured regularly in approximately 130 wells. Locations for monitoring include 25 extraction wells both within the plume and along the plume boundary, 31 inside-plume monitor wells, 12 outside plume monitor wells, 18 compliance monitor wells, 6 water-supply wells, and 9 injection wells. Piezometer networks were installed at six locations along the containment area perimeter to determine whether or not inward and upward hydraulic gradients are being maintained. Each piezometer has a maximum screen length of five feet. Shallow, intermediate, and deep piezometers are completed 10 to 15, 35 to 40, and 70 to 75 ft below the mean annual water table, respectively. As shown in Figure 5-1, there are three shallow piezometers arranged in a triangle and three vertically nested piezometers within each of the plume boundary piezometer networks.

5.3.2 Water-Quality Monitoring

Water-quality data are obtained from monitor wells, extraction wells, compliance wells, and five nearby production wells. Concentrations detected during the remediation are compared to the "baseline" conditions represented by the contaminant plume boundary and concentrations in compliance and production wells in 1986. Baseline ground-water quality conditions were determined for offsite production wells and three compliance points through three consecutive monthly sampling events and in accordance with 40 CFR § 264.97. In addition, three consecutive, monthly ground-water quality sampling events at six new (1985) and existing monitor wells were completed to redefine the contaminant plume boundary. These sampling events resulted in a revised conceptualization of both the shallow and intermediate depth VOC plumes. The greater lateral extent of the redefined VOC plumes required modification of the remedial design. This example demonstrates the importance of ongoing characterization during the remedial design stages and changes that can occur in the contaminant distribution between initial characterization and remediation implementation.

Because treated ground water is injected into the aquifer and discharged to surface water (Ford Hydraulic Canal), effluent water quality sampling is performed. VOC loading to the Ford Hydraulic Canal is determined to fulfill NPDES permit requirements. Similarly, influent water quality analysis is performed to determine the chemical loading to the treatment plant and the mass of contaminants removed from the aquifer. Flow rates and water quality are used to determine these loadings. For the extraction and injection wells, flow rates are measured at individual wells. At the ground-water treatment facility, flow rates and ground-water quality are determined for the influent and effluent to the system.

5.3.3 Monitoring Schedule

The monitoring schedule for hydrodynamic and chemical data collection provides an example of performance monitoring for the containment objective and the restoration objective. Contingencies for modification of the sampling events are also included to facilitate changing concentrations during the operational and post-termination periods. The following monitoring schedule has been implemented at the Chem-Dyne site.

For the first year of operation, water-levels were measured with water-level probes semi-monthly at wells and piezometers and recorded hourly by pressure transducers/data loggers at the six piezometer clusters at the boundary of the plume. Since 1989, water-levels have been measured by hand monthly and water-levels from the central shallow piezometer from each of the six piezometer clusters have been recorded hourly by dataloggers. Semi-monthly water levels are measured for three months (within a 250 ft radius of the affected point) if any significant modification to the extraction/injection system or if unstable water levels in the monitoring network have occurred. Daily extraction and injection rates are measured at individual wells with flow meters. A remote recording system also provides a continuous registry at the treatment facility of the volumes of ground water extracted/injected from individual wells. Water flow rates are continuously measured for the treatment facility influent and treated effluent discharged to the Ford Hydraulic Canal.

During the P&T remediation, water quality sampling is performed semi-annually for Priority Pollutant VOCs and annually for all other Priority Pollutants at compliance point monitor wells as well as annually for VOCs at monitor wells within the initial plume boundary. This sampling interval will continue for five years after system termimation. To facilitate determination of system termination after ten years of operation, all monitor wells and extraction wells at and within the plume boundary will be sampled quarterly for Priority Pollutant VOCs for the last three years of the ten year period. Upon termination of the system, ground-water quality sampling will continue at these wells for five years: quarterly for the first two years and semi-annually for the next three years. For wells beyond the defined 0.1 ppm total Priority Pollutant VOC isopleth, VOC sampling will be performed annually during system operation and for five years after system termination.

The Chem-Dyne ground-water quality sampling plan also incorporates contingencies for the monitoring program. For example, if the concentrations of VOCs at compliance point monitor wells exceed compliance standards during operation or post-termination monitoring, sampling frequency will be increased to quarterly for a minimum of six months. Also, if concentrations of total VOCs exceed 0.1 ppm at monitor wells outside the plume boundary during operation or post-termination monitoring, the sampling frequency will be increased to quarterly for a minimum of six months. Further, if this exceedance occurs during two consecutive sampling events, the significance of the occurrence will be determined.

Water quality analysis of the effluent of the ground-water treatment facility is currently performed monthly for Priority Pollutant volatile organics (EPA Methods 601 and 602), quarterly for Priority Pollutant organics (EPA Methods 624, 625, and 608), and semi-annually for Priority Pollutant heavy metals.

5.4 DATA EVALUATION AND EFFECTIVENESS

Several methods are utilized to demonstrate the effectiveness of the P&T system in attaining containment and progressing toward restoration. To verify containment, water-level data are evaluated to assess whether hydraulic control of the plume is maintained laterally and vertically. To evaluate restoration, water quality of influent, effluent, monitor wells, and extraction wells is monitored.

5.4.1 Containment

Hydrographs of the monitored piezometer clusters (located at the original plume boundary) are prepared using the hourly data from the shallow piezometer and the time-weighted averages of monitor well water levels. The monthly and semi-monthly water-level measurements are also plotted on each hydrograph. Average ground-water levels of the monthly data are utilized at the Chem-Dyne site to reduce the effects of short-term disturbances and represent the conditions that are commensurate with the rates of ground-water migration and indicative of significant patterns of flow (Papadopulos & Assoc., 1993). The averages are time-weighted to reflect the relative duration of water-level conditions associated with measurements made at different days of the months.

The vertical capture of the plume is assessed by evaluating the relative hydraulic head values at the different screened depths within the piezometer clusters. Figure 5-2 illustrates an example of a piezometer nest hydrograph for 1992. Vertical containment is inferred by the upward net vertical hydraulic gradient between the deep and intermediate and between the intermediate and shallow horizons of the aquifer.

Lateral containment is verified by preparing potentiometric surface maps of the shallow, intermediate, and deep horizons of the aquifer using average ground-water levels from the monthly water-level data. Figures 5-3 and 5-4 present the average water-level conditions and the direction of groundwater flow for the shallow and intermediate zones during 1992, respectively. Figure 5-3 demonstrates that the extraction system has created a cone of depression in the shallow horizon at the leading edge of the plume boundary. The heavy dashed line illustrates the approximate limit of the shallow horizon capture zone indicating that water from within the plume boundary is captured by the extraction system. Figure 5-4 demonstrates that the intermediate interval plume is also contained by the extraction wells. The potentiometric surface contours during low and high ground-water conditions in the shallow and intermediate intervals demonstrate that containment is maintained under low and high ground-water conditions.

5.4.2 Restoration

The rate of VOC removal, the total mass of contaminants removed trom the aquifer, and contaminant concentrations in extraction and monitor wells are measured to evaluate restoration progress. Table 5-1 illustrates the rate of VOC removal for the previous five years. Yearly mass removal rates have decreased from 7500 to 1435 lbs/year as the total volume of water treated has increased since the initiation of the P&T system. However, the mass removal rates have not stabilized. Stabilization of

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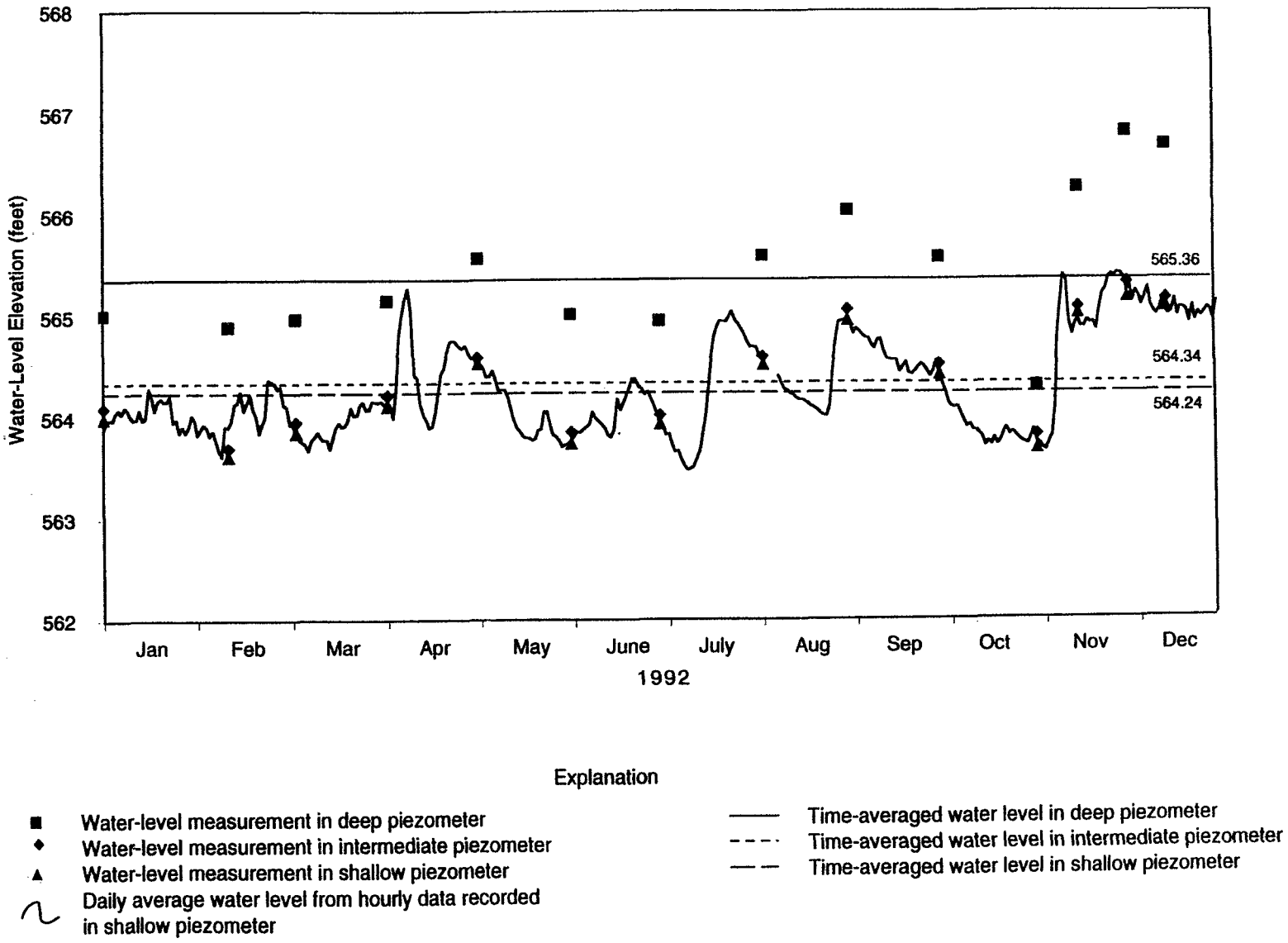

Figure 5-2. Nested piezometer hydrograph for 1992 at the Chem-Dyne site (from Papadopulos & Assoc., 1993).

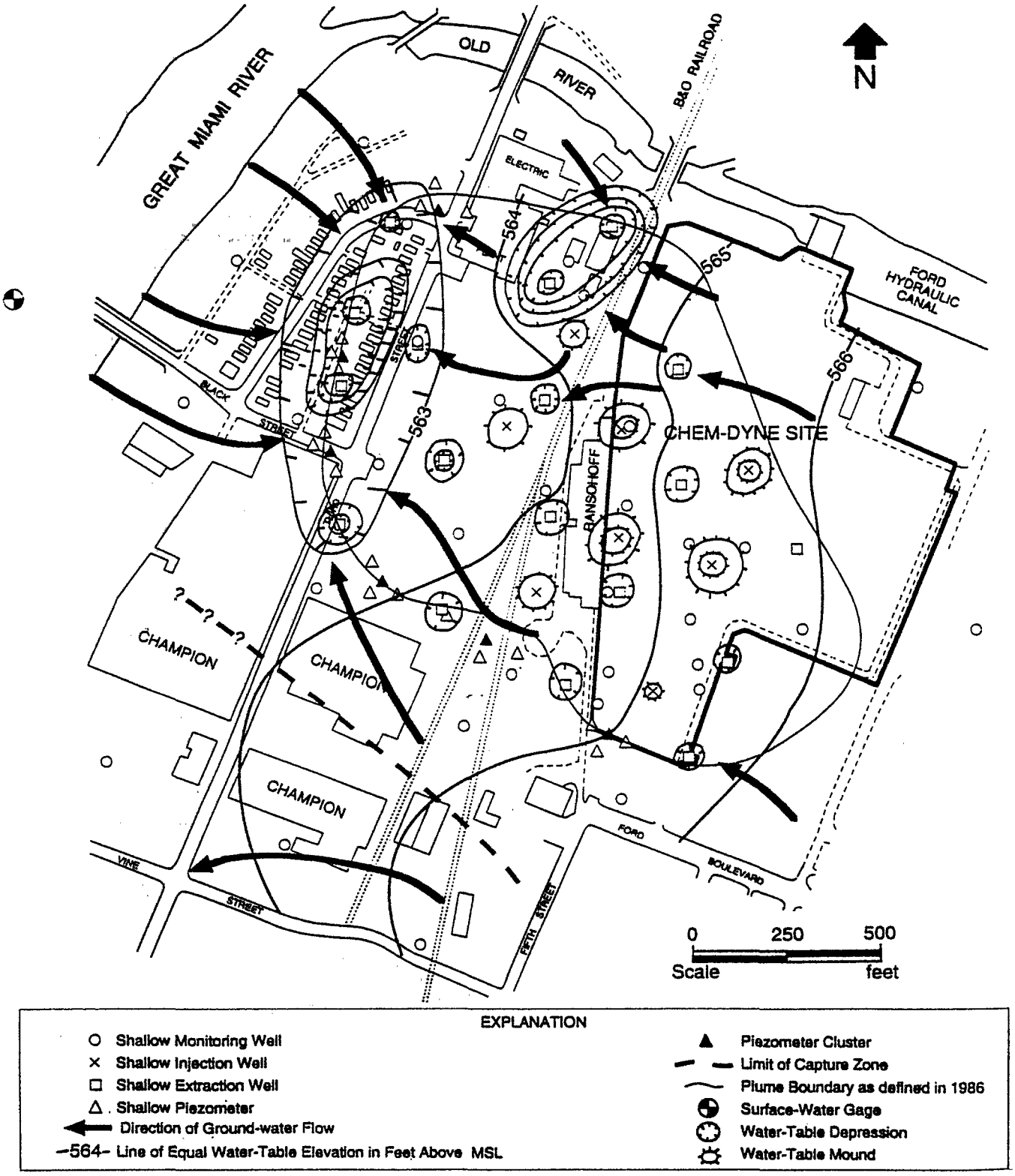

Figure 5-3. Average water table and direction of ground-water flow in the shallow interval in 1992 at the Chem-Dyne site (form Papadopulos & Assoc., 1993)

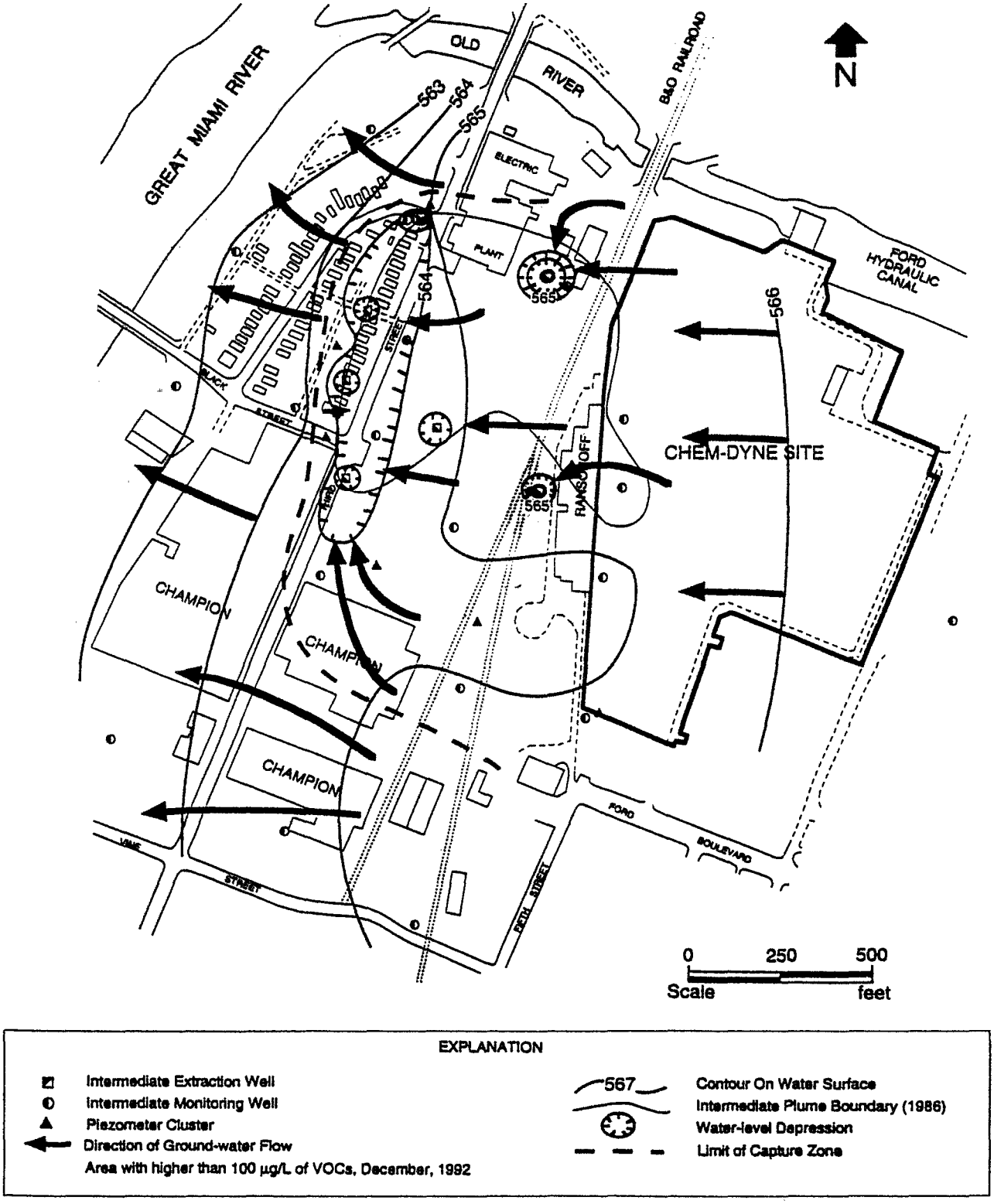

Figure 5-4. Average potentiometric surface and direction of ground-water flow in the intermediate interval in 1992 at the Chem-Dyne site (from Papadopulos & Assoc., 1993).

TABLE 5-1. ANNUAL MASS OF VOCs AND VOLUME OF GROUND WATER EXTRACTED FROM THE CHEM-DYNE SITE (PAPADOPULOS & ASSOC., 1988 AND 1993).

Year	*Average Flow Rate[1] (GPM)*	*Total Volume Treated (million gallons)*	*Average Concentration of PPVOCs in Treatment Effluent (Fg/L)*	*Average Concentration of PPVOCs in Treatment Influent(Fg/L)*	*Mass of VOCs Removed[3] (pounds)*
1987	625[2]	240	2936 to 820[5]	11580 to 6081[5] 3565 to 1442[6]	7500
1988	--	270	25[4]	2000	4630
1989	791	362	6.5	1630	4970
1990	726	355	92.7	1660	4685
1991	796	381	131	1294	3794
1992	833	423	39	414	1435
TOTAL	--	2,031	--	--	27,014

[1] Average extraction rate based on operating hours and volume pumped to treaiment plant
[2] Average between June and December 1987
[3] Net mass removed after injection
[4] After modifying the air stripping system, the average effluent concentration decreased to 10 Fg/L
[5] Range during March and April
[6] Range during September through December

contaminant mass removal rates, contaminant mass-in-place, and ground-water concentrations might indicate that a P&T system is approaching a point of diminishing returns. This stabilization is not suggested by the performance monitoring data at the Chem-Dyne site.

Performance of the P&T remediation is also demonstrated by the total mass of contaminant removed from the saturated subsurface. A determination of the total mass removed is obtained from extracted ground-water quality and extraction rates. At the Chem-Dyne site, influent water quality combined with flow rates are used to provide time-weighted calculations of VOCs delivered to the treatment plant (Figure 5-5). Because treated ground water (containing VOCs) is returned to the aquifer by injection, the mass of VOCs delivered to the treatment plant does not represent the mass of contaminants removed from the aquifer. Water quality and flow rates of the effluent and of discharges to the Ford Hydraulic Canal are used to determine the net mass removal of VOCs from the aquifer. For example, during 1992, the mass of VOCs in plant influent, effluent, discharges to the canal, and injectate was calculated to be 1,470 ± 55, 140 ± 4, 105 ± 4, and 35 lbs, respectively (Papadopulos & Assoc., 1993). Therefore, the net mass removal for 1992 is approximately 1,435 ± 55 lbs. These calculations are

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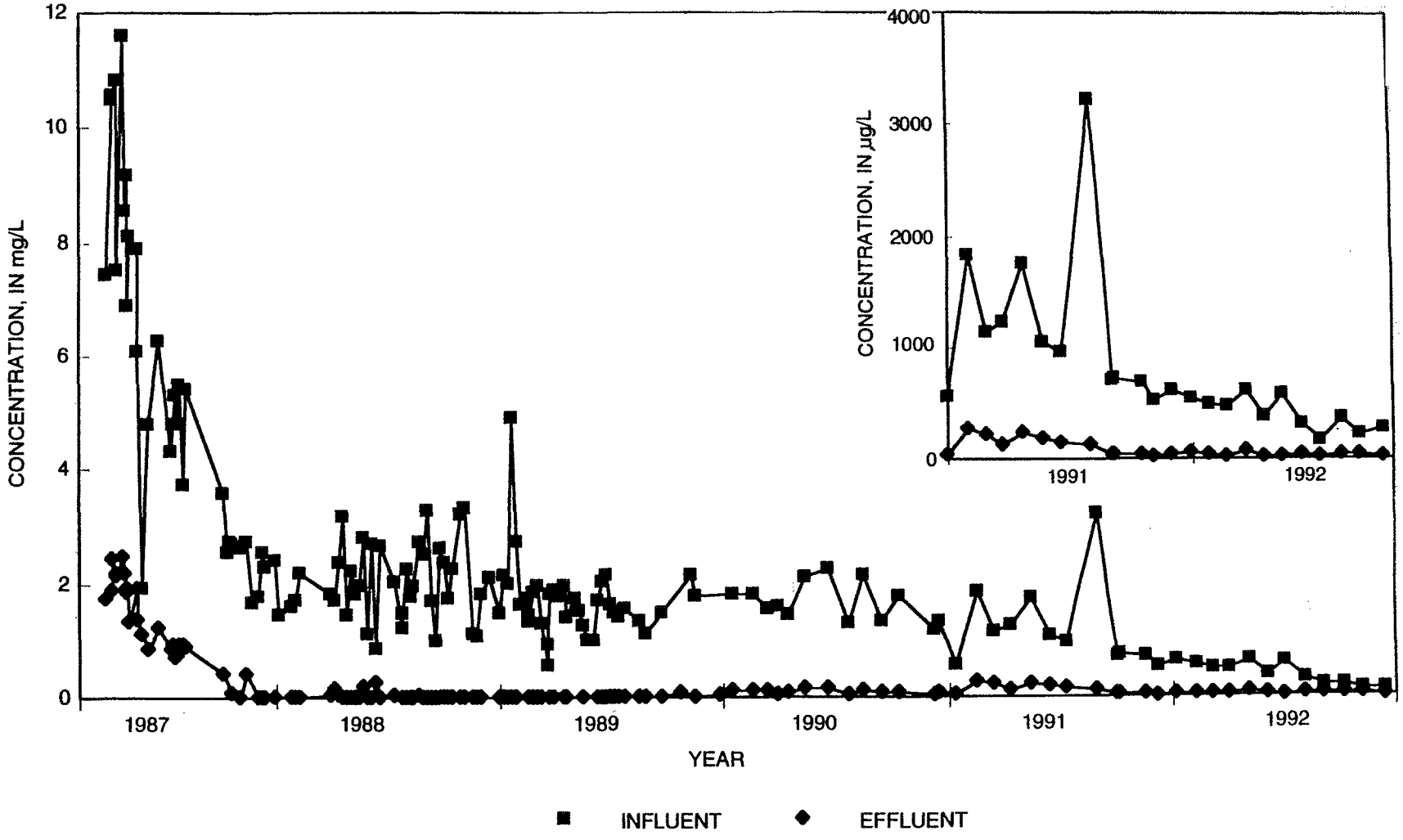

NOTES: 1. Concentrations for October, November and December 1992 are estimates;

2. Concentrations include 1,2 - cis - DCE, not a priority pollutant.

Figure 5-5. Influent and effluent VOC concentrations (mg/L) at the Chem-Dyne treatment plant from 1987 to 1992 (from Papadopulos & Assoc., 1993).

peformed monthly to monitor the cumulative mass of Priority Pollutant VOCs removed since pumping commenced in 1987 (Figure 5-6). Approximate 27,000 lbs of VOCs have been removed from the aquifer since the system became operational.

To evaluate this removal performance, the mass removed is compared to the original mass-in-place. The estimated mass of VOCs dissolved in the ground water prior to the system operation within the 0.1 ppm plume boundary was 4,500 lbs (Papadopulos, 1993). The mass of VOCs sorbed on the aquifer materials was estimated to be 36,000 lbs, therefore, the total mass of VOC contaminants in the aquifer (assuming no NAPL) prior to P&T remediation was 40,500 lbs (Papadopulos, 1993). The P&T system has removed 67% of the estimated original mass-in-place in less than half of its planned operational period. However, the dissolved contaminant mass remaining in the aquifer, discussed below, must be evaluated to confirm this apparent progress.

Performance of the restoration is also demonstrated at the Chem-Dyne site by comparing the mass of dissolved contaminants remaining in the aquifer through time. The dissolved mass-in-place provides an average of the distribution of contaminants, therefore, tracking the decrease in the dissolved mass provides a basis for evaluating the effectiveness of the restoration. The estimates of dissolved mass are based on contoured ground-water quality data, thickness of the contaminated zone, and porosity. Figures 5-7 and 5-8 present the December 1992 concentrations of Priority Pollutant VOCs in the shallow and intermediate wells in comparison to the 1986 0.1 ppm VOC plume boundary. Figures 5-9 and 5-10 present the October/November 1987 concentrations of Priority Pollutant VOCs in the shallow and intermediate wells. The reduction of contaminants in the aquifer and significant reduction of contaminants in individual wells evidences the effectiveness of the P&T system. Based on the concentrations of total VOCs detected in extraction and monitor wells within the 0.1 ppm plume boundary the mass of contaminants dissolved in ground water prior to the commencement of the P&T system was 4,500 pounds (Papadopulos, 1993). Sampling results indicate that the mass of dissolved contaminants was reduced to approximately 235 pounds in 1992 (Papadopulos & Assoc., 1993). This reduction of mass of dissolved contaminants appears promising, however, a comparison of the reduction in dissolved mass of contaminants in, the aquifer (4,265 pounds) with the amount of contaminants removed (27,000 pounds) reflects the presence of NAPL and/or sorbed contamination. Physical and chemical conditions discussed in Chapter 1 may result in future extraction with limited dissolved mass-in-place reduction.

5.4.3 Termination

Data evaluation will also be performed to determine whether the Chem-Dyne P&T system can be terminated after the 10-year operation period or at any time thereafter. This determination will be based on the attainment of the performance goals stated above. The determination of whether VOC concentrations within the plume have become effectively constant will be made for each extraction and monitor well within the plume boundary according to the following procedures (Papadopulos & Assoc., 1985).

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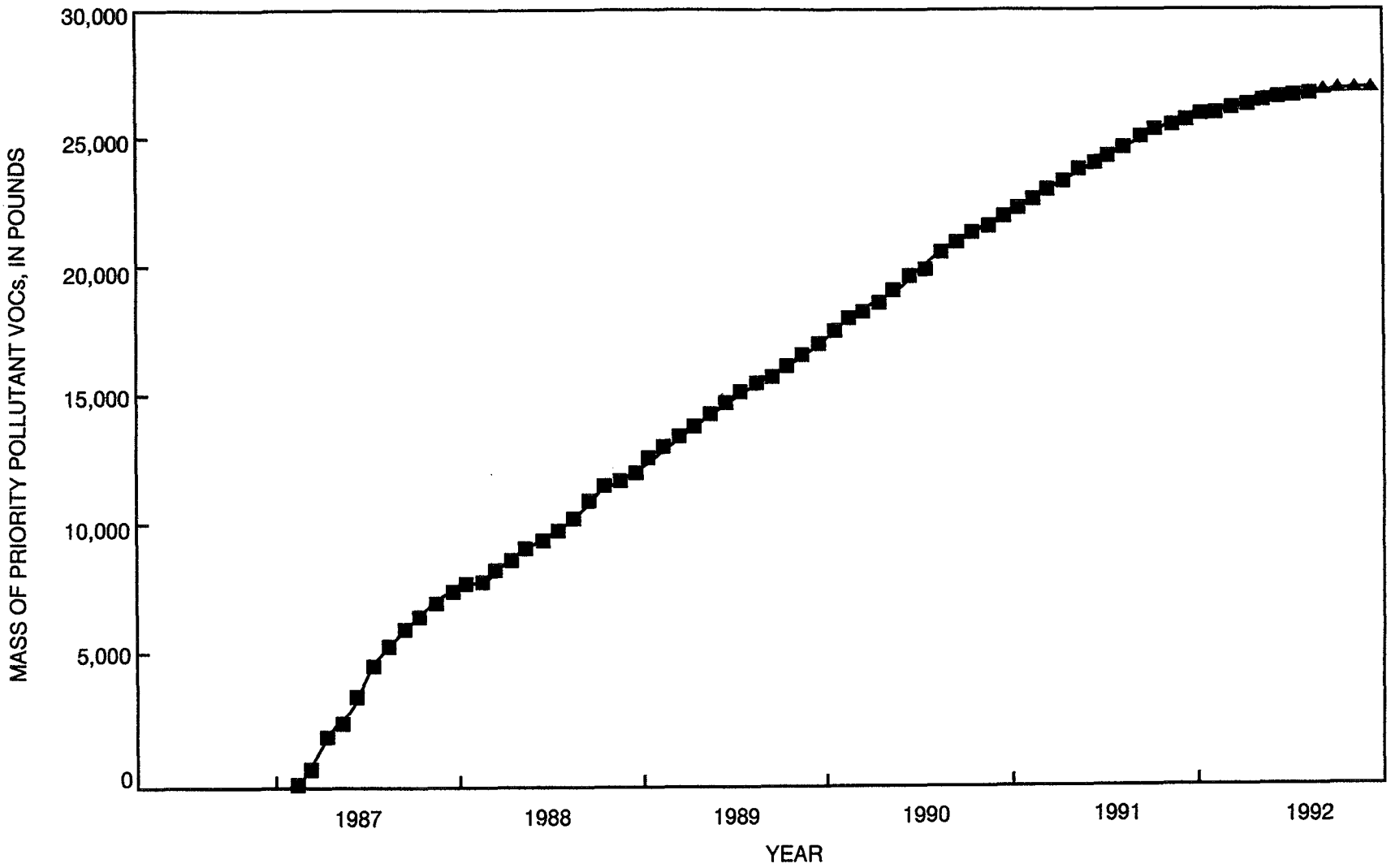

NOTES 1. September, October, November and December 1992 cumulative weights are based on estimated concentrations; potential range too small to show at this scale.

2. Mass of removed VOCs includes, 1,2-cis-DCE, not a priority pollutant.

Figure 5-6. Cumulative mass of VOCs removed from the aquifer at the Chem-Dyne site from 1987 to 1992 (from Papadopulos & Assoc., 1993).

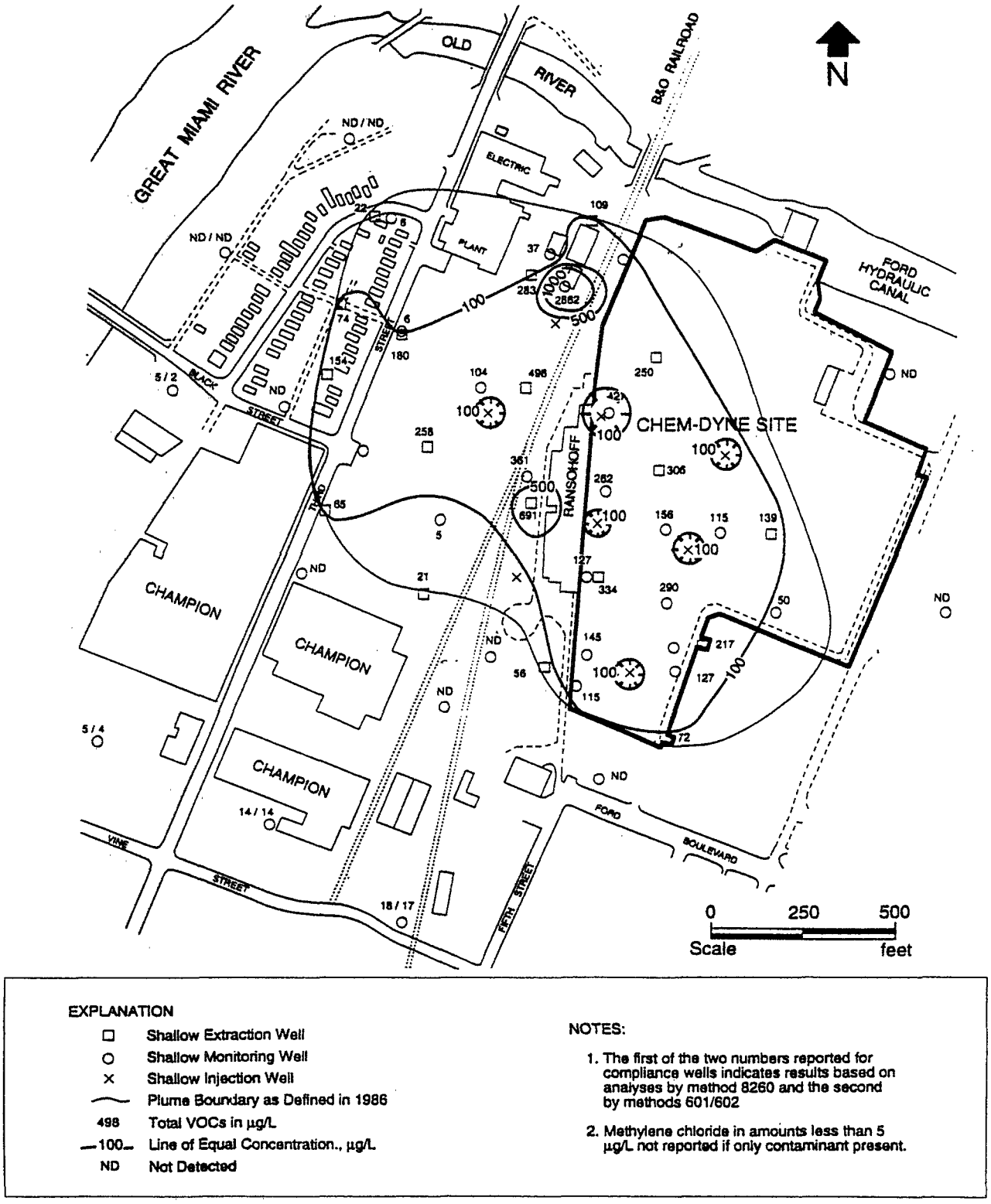

Figure 5-7. Concentrations of VOCs in the shallow interval in December 1992 at the Chem-Dyne site (from Papadopulos & Assoc., 1993).

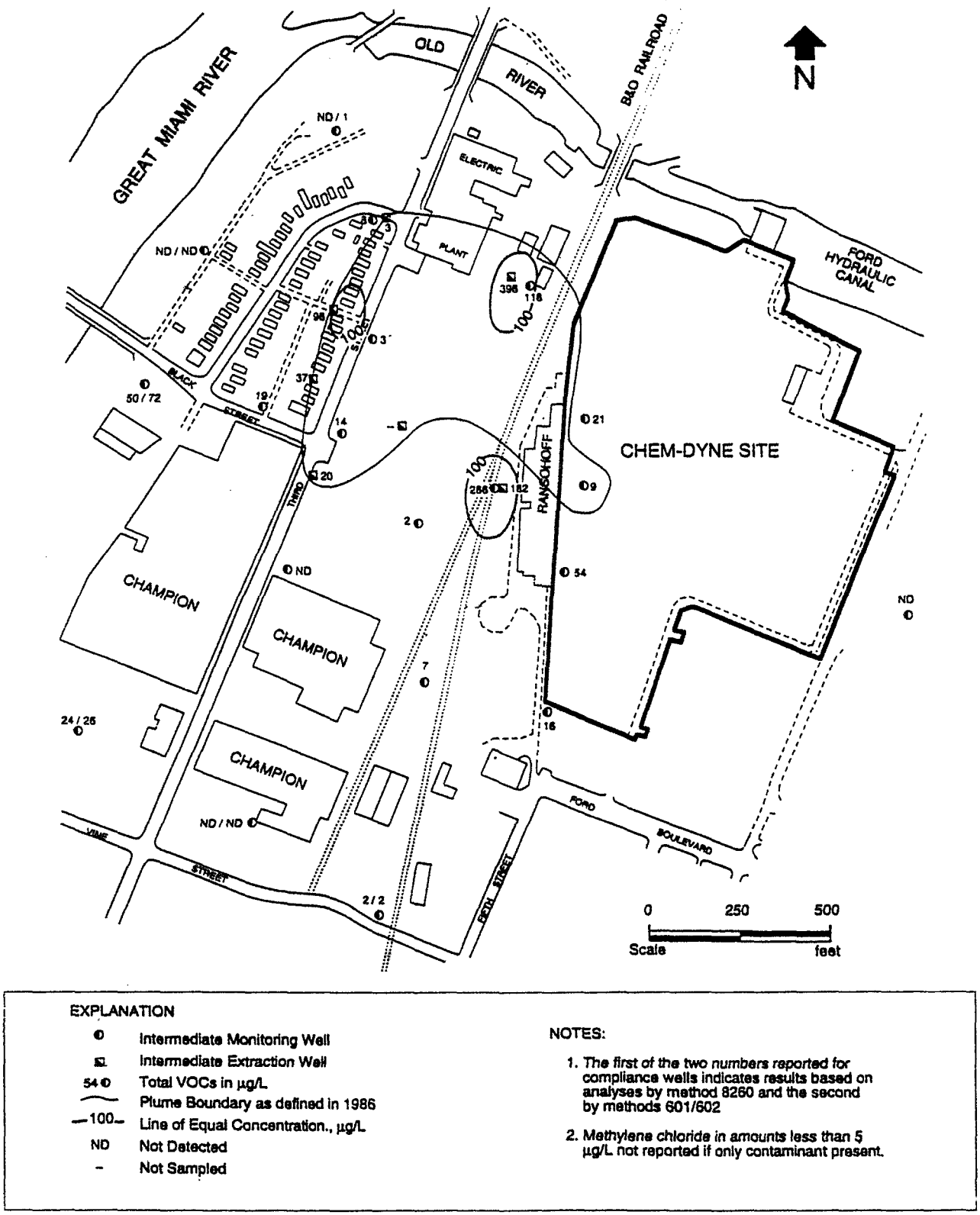

Figure 5-8. Concentrations of VOCs in the intermediate interval in December 1992 at the Chem-Dyne site (from Papadopulos & Assoc., 1993).

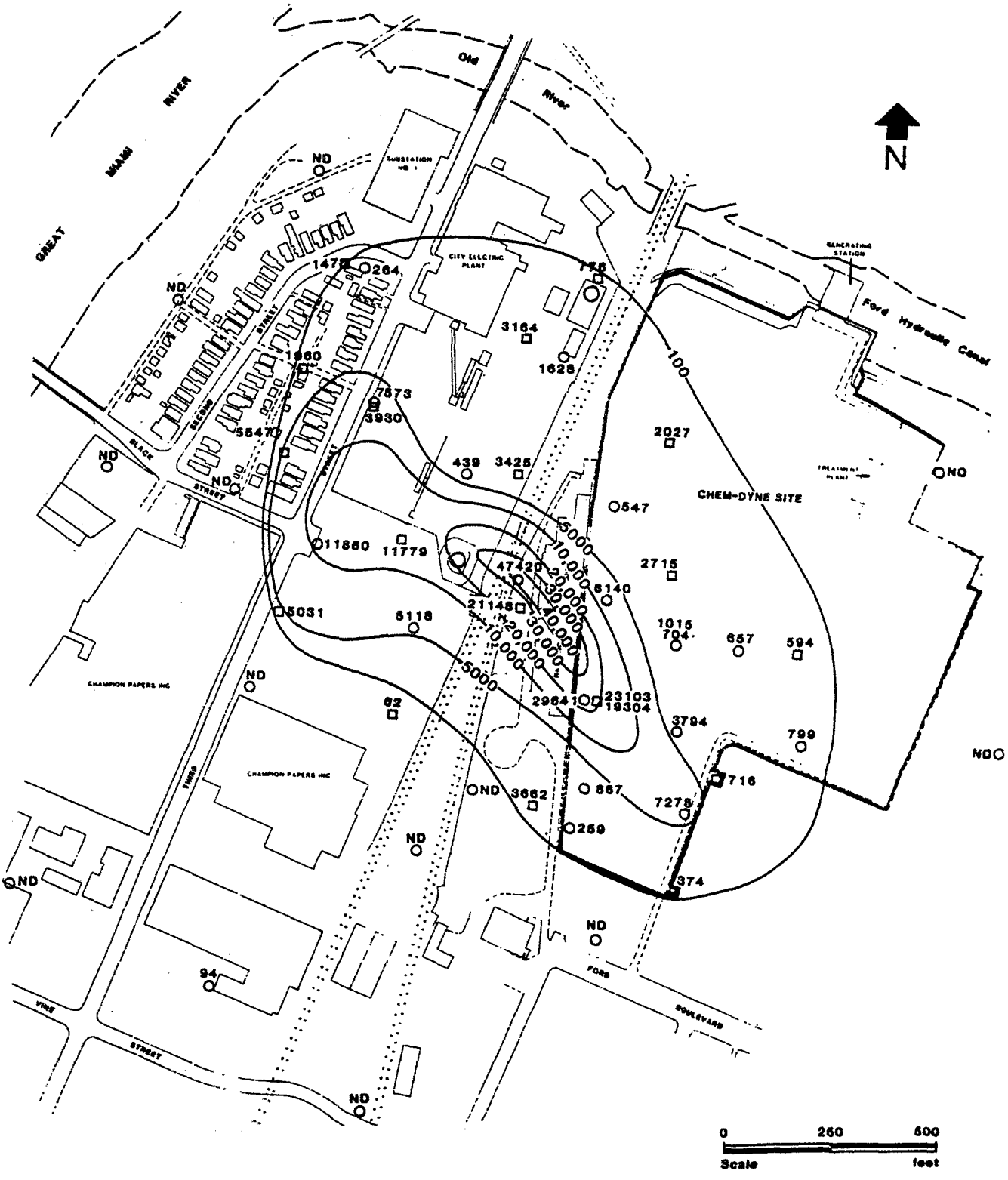

Figure 5-9. Concentrations of VOCs in Fg/L in the shallow interval during October/November 1987 (from Papadopulos & Assoc., 1988).

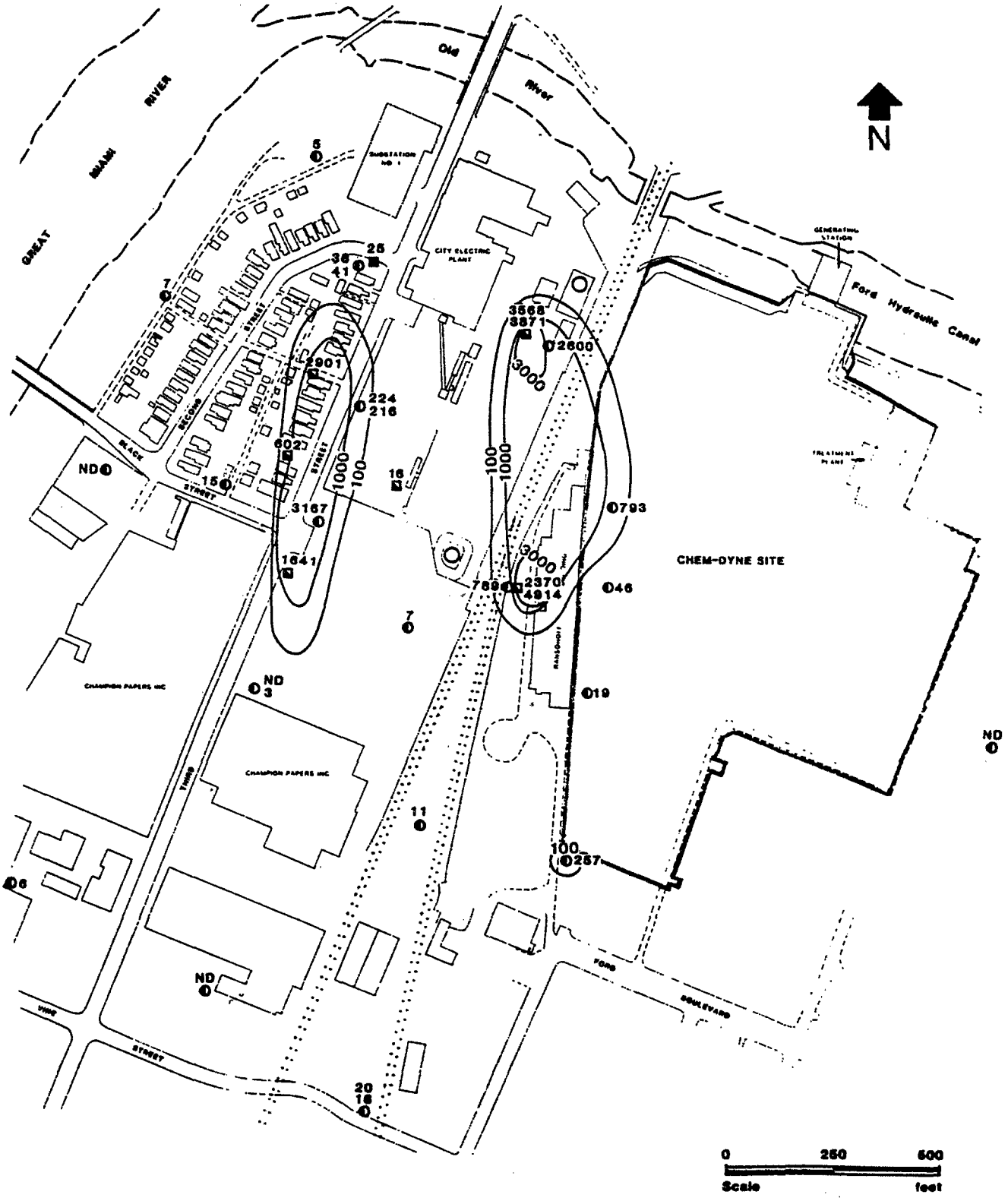

Figure 5-10. Concentrations of VOCs in Fg/L in the intermediate interval during October/November 1987(From Papdopulos & Assoc., 19880.

(1) Totals of Priority Pollutant VOCs for the 12 most recent sampling events will be plotted versus time.

(2) If the curve indicated by the concentrations is linear, a straight line will be fitted to the data using a least squares regression model. The slope of the fitted curve will be computed as the estimated slope.

(3) If the curve suggested by the data is nonlinear, then an exponential curve using a least squares regression model will be fitted to the data. The estimated slope will be the first derivative of the curve at the midpoint between the last two sample points.

(4) The estimated slope will be defined as zero if (a) the slope is #0 and $-0.02 ppm/year, and (b) the rate of change of that slope = 0 or indicates a continuously decreasing concentration.

(5) If the mean concentration in a well is #0.02 ppm and the above procedure results in a positive slope, then the 95 percent confidence interval will be calculated for the slope of the regression line; if a zero slope is within this confidence interval, then the estimated slope will be deemed to be zero.

(6) The concentrations in a well will be declared to be effectively constant if the estimated slope is defined as zero.

If the concentration of total VOCs has become effectively constant (as defined above) in each monitor and extraction well within the defined plume, but at a higher concentration than 0.1 ppm (performance goal No. 1) after ten years of operation or any time thereafter, the system will be terminated if the following two conditions are met (Papadopulos & Assoc., 1985):

(1) Substantial compliance with the performance goal of 0.1 ppm VOCs has been achieved (considering factors which may include but are not limited to variations in permeability which result in the persistence of high concentrations in certain wells, and the averaging of concentrations in wells); and

(2) Periodic evaluation of data during system operation indicates that no reasonable modification or adjustment to the system will produce significant improvement within a total operational period of 20 years.

If both performance goals are not met after the 20 years of operation, the evaluation as to whether further operation and modification would be cost-effective will be made by the parties involved.

5.4.4 Post Termination Monitoring

The Chem-Dyne site post termination monitoring plan provides an example of the verification of continued “success” of the P&T system after the operational period. Water quality analyses at onsite

monitor wells and offsite compliance points will be conducted to confirm the completion of the remediation. Monitoring will be performed for five years after termination as specified below.

The concentrations of total Priority Pollutant VOCs within and on the defined plume boundary will be monitored for five years after P&T termination to verify that concentrations do not rebound. To determine compliance with this criterion, water-quality data collected from monitor wells within the defined plume at the termination of the system will be statistically analyzed as follows (Papadopulos & Assoc., 1985):

(1) The mean value and standard deviation of total VOC concentration from all wells within and on the plume boundary at the time of P&T termination will be used as baseline conditions.

(2) The mean value and standard deviation of the total VOC concentration will be determined for each sampling event after termination.

(3) Statistical tests will be performed to determine if the variance of each sampling event is statistically equal to the variance of the baseline value and if the baseline and sampling event data are normally distributed.

(4) If the variances are equal and the data are normally distributed, a t-Test will be performed to determine whether the mean value of the sampling event is significantly different from the baseline mean at a five percent level of significance.

(5) If the variances are not statistically equal and/or the data are not normally distributed, then an appropriate statistical test will be used to determine whether the mean value of the sampling event is significantly different from the baseline mean value at a five percent level of significance.

(6) If the mean value from the sampling event is not significantly different from the baseline mean value, the concentration of total VOCs has been maintained effectively at or below the levels reached at the time of P&T termination.

(7) If a significant increase in the mean value is determined, a second round of sampling will be conducted within 30 days of receipt of the laboratory results. If this second round of sampling confirms the significant increase in the mean value, corrective action will be taken.

The concentrations of total Priority Pollutant VOCs at offsite compliance points will also be monitored for five years after P&T termination to verify that concentrations at receptors are not above the water quality criteria.

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