

# IMPACT OF NON-AQUEOUS PHASE LIQUIDS (NAPLs) ON GROUNDWATER REMEDIATION

*Charles J. Newell,<sup>1</sup> Richard L. Bowers,<sup>1</sup> and Hanadi S. Rifai,<sup>2</sup>*

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## **ABSTRACT**

Nonaqueous Phase Liquids (NAPLs) are immiscible (undissolved) hydrocarbons in the subsurface that exhibit different behavior and properties than dissolved contaminant plumes. NAPLs have a tremendous impact on the remediation of contaminated aquifers, as it is very difficult or impossible to remove all of the NAPL from a hazardous waste site once released to the subsurface. Although many NAPL removal technologies are currently being tested, to date there have been few field demonstrations where sufficient NAPL has been successfully removed from the subsurface to restore an aquifer to drinking water quality (EPA, 1992a). The residual NAPL that remains trapped in the soil/aquifer matrix acts as a continuing source of dissolved contaminants to ground water, and effectively prevents the restoration of NAPL-affected aquifers for tens or hundreds of years.

This is particularly true for groundwater pump-and-treat systems, the most common remediation technology for addressing contaminated aquifers. This technology pumps groundwater out of contaminated zones to remove dissolved contaminants and, if present, to slowly dissolve any trapped NAPLs. The pumped water is then treated on the surface to remove or destroy the dissolved contaminants.

To help designers of pump-and-treat systems evaluate the impact of NAPLs on groundwater remediation, a simple design model has been developed that provides the user with the number of recovery/injection wells and time required to reach cleanup standards. The method uses 1) dissolution data from a simplified dissolution model based on the work of

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<sup>1</sup> *Groundwater Services, Inc., 5252 Westchester, Suite 270, Houston, Texas 77005*

<sup>2</sup> *Energy and Environmental Systems Institute, Rice University, P.O. Box 1892, Houston, Texas 77251*

Powers et al. (1994) or field data from dissolution pilot tests, 2) an assumed well configuration typical for pump-and-treat systems, and 3) relationships of concentration vs. pore volumes of clean water flushed. In addition, design charts for zones with only dissolved-phase groundwater contamination are also presented. These design tools are being incorporated into a large computerized Decision Support System now being developed by one of the authors (Rifai et al., 1994) for evaluating U.S. Air Force groundwater pump-and-treat systems.

The design models were used in an example application to evaluate remediation alternatives for a hypothetical NAPL-contaminated site. This example serves to demonstrate the simple use of the models for the rapid estimation of pump-and-treat system design requirements.

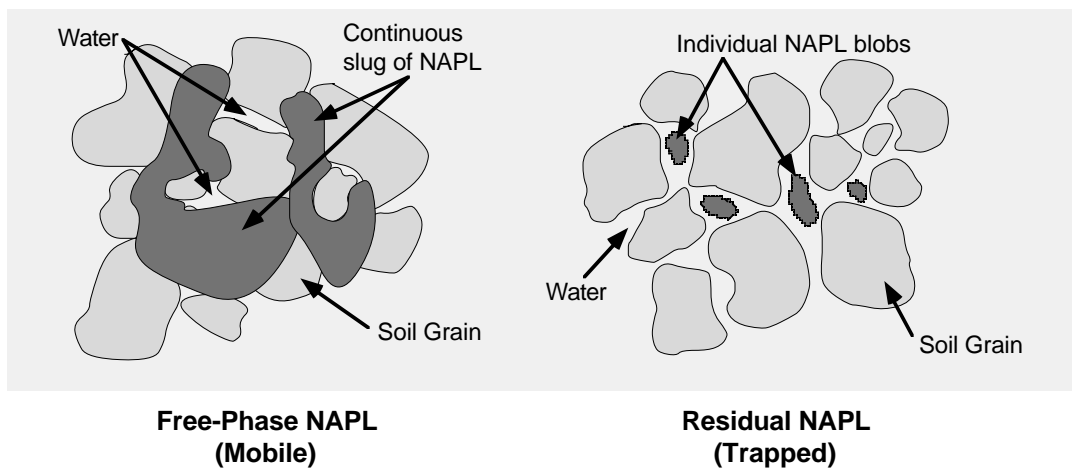


Figure 1. Free-Phase vs. Residual Phase NAPLs

## INTRODUCTION

Nonaqueous Phase Liquids (NAPLs) are immiscible (undissolved) hydrocarbons in the subsurface that exhibit different behavior and properties than dissolved contaminant plumes. While dissolved plumes are invisible to the naked eye and travel with the flow of groundwater, NAPLs form a visible, separate oily phase in the subsurface whose migration is governed by gravity, buoyancy, and capillary forces (Bedient, et al., 1994). When released at the surface, *free-phase* or *mobile* NAPL is forced into the pores of the soil/aquifer matrix by the hydrostatic

pressure on the continuous body of NAPL. Because the NAPL is under pressure, it can enter even very small pores and fractures in the subsurface as long as the original NAPL entry point, such as a waste pond or leaking underground storage tank, is active. When the supply of new NAPL is exhausted, however, the pressure on the free-phase NAPL is removed and small blobs (or "ganglia") of NAPL "snap-off" or "bypass" the once continuous NAPL body and become trapped in individual pores or small groups of pores by capillary forces (see Figure 1).

The *residual saturation*, defined as the fraction of total pore volume occupied by residual NAPL under ambient groundwater flow conditions, is an important parameter in groundwater remediation problems because it indicates the amount of NAPL that is trapped in the subsurface. The actual residual saturation value at a particular location site is determined by the type of chemicals that comprise the NAPL, whether the NAPL is in the saturated zone or vadose zone, and most importantly, the structure and hydrogeologic characteristics of the soil/aquifer matrix.

### Defined Areas at a NAPL Site

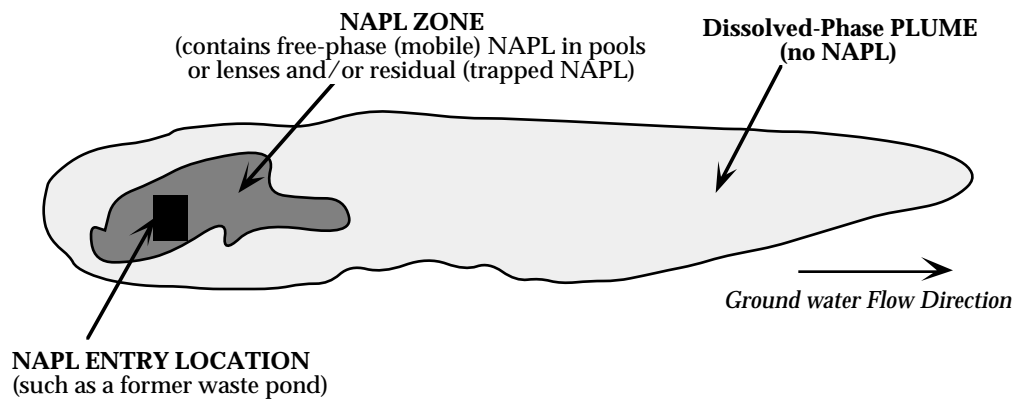


Figure 2. Groundwater Contamination at Hazardous Waste Sites Can Be Divided Into a NAPL Zone and Dissolved-Phase Plume Zone

### Effect of NAPLs on Groundwater Remediation

In recent years, extensive scientific research has been conducted to identify those characteristics of hazardous waste or Superfund sites which particularly impede the ability of

groundwater remediation systems to achieve targeted cleanup levels. In particular, the presence of NAPLs has been shown to be a significant limiting factor in site remediation (U.S. EPA, 1992d, 1992b, 1992c, 1992a). Following removal of the mobile fraction of the NAPL, the residual NAPL can act as a continuing source of dissolved contaminant release to groundwater, preventing the restoration of the affected aquifer zone to applicable water quality standards (U.S. EPA, 1992a). Figure 2 shows a hazardous waste site divided into two zones: one containing NAPLs and one containing dissolved-phase contaminants only.

The EPA has acknowledged that groundwater contamination is one of the most prevalent and challenging problems at hazardous waste sites (U.S. EPA, 1989). In order to address perceived problems with groundwater extraction systems, the EPA assembled information from 19 operating pump-and-treat systems to show: 1) how such systems were being used at hazardous waste sites, 2) how their performance compared with expectations, and 3) what factors were limiting their success. The data indicated that while groundwater extraction systems were generally effective for preventing contaminant plumes from migrating and for removing some contaminant mass, complete aquifer restoration generally proceeded more slowly than expected at most sites (U.S. EPA, 1989). The main factors impeding the ability to achieve cleanup goals were:

- Hydrogeologic factors, such as numerous low permeability layers,
- System design factors, such as poorly designed or improperly located extraction wells,
- Contaminant factors, such as continued leaching from NAPLs in the subsurface.

In late 1990, EPA initiated a second phase of the groundwater extraction evaluation project, this time focusing on the role of NAPLs in particular (U.S. EPA, 1992c). After reviewing updated information from the original 19 case studies and obtaining data from five new ones, the EPA concluded that NAPLs were "a key factor in the longer-than-anticipated time frames for aquifer restoration." NAPLs were recognized as a continuing source of contaminants to the groundwater, sources that typically take "a very long time" to deplete solely by groundwater extraction.

### *Decision Support Systems*

Decision support systems are a class of software that incorporates a number of tools to approach problems that are broadly defined or where conventional programming may be difficult or impractical to apply (Newell et al., 1990). A "toolbox" approach lends flexibility for solving a variety of types of problems and makes the solving of many problems accessible to nonexperts. Unlike expert systems, however, where the problem solving process is generally controlled by the software, a decision support system supports rather than replaces the decision making of the user. The user must decide how to apply the available tools towards the solution to a particular problem.

A decision support system can include a number of different software tools with varying degrees of complexity. The OASIS groundwater modeling system, for example, integrates text references, hydrogeologic databases, chemical databases, a simple expert system, and three levels of groundwater analysis tools: a Darcy's equation calculator, a simple groundwater transport model, and a complex finite-difference in-situ biodegradation model (Newell et al., 1990).

### *Objective*

The objective of this project was to provide screening-level tools that will allow groundwater managers to quickly evaluate the effects of NAPLs on groundwater remediation systems. These tools are designed to be simple to use and require a minimum of input data for quick "back-of-the envelope" estimates of either:

- the number of recovery/injection wells required to reach site clean-up standards, assuming a simple well field configuration, or
- the number of pore volumes of clean water required to reach site clean-up standards, so that a conventional groundwater flow model can be used to estimate the number of required recovery/injection wells.

These tools are designed for two applications: 1) as a system of design charts (presented in this paper) and 2) as software tools in a decision support system (currently being developed).

## BASIS FOR NAPL EVALUATION TOOLS

While the effect of NAPLs on groundwater cleanups are easy to observe, there is a lack of simple-to-use tools for quantifying these effects. Currently one can employ research NAPL dissolution models (Powers et al., 1994; Borden and Kao, 1992) or conduct pilot tests at NAPL sites. The time, data, and expense required for either of these options makes a screening-level analysis of NAPL problems a very difficult undertaking. Such problems that lack a clearly defined structure lend themselves to decision support system tools which incorporate a number of simplifying assumptions. These tools can reduce the time, cost, and effort required to develop simple conceptual designs or to evaluate broad remediation alternatives.

### *Simplified Hydrogeologic/Hydraulic Assumptions*

To use the design model, the hydrogeologic and hydraulic conditions at the site are simplified by assuming that the contaminated aquifer is a homogeneous porous medium with respect to hydraulic conductivity and porosity. The pump-and-treat system which is to be evaluated is assumed to consist of a field of extraction and injection wells that are equally distributed over a rectangular-shaped area in a "five-spot" configuration (see Figure 3). In addition, hydraulic gradients are assumed to be constant between all wells and between wells and the normal piezometric surface.

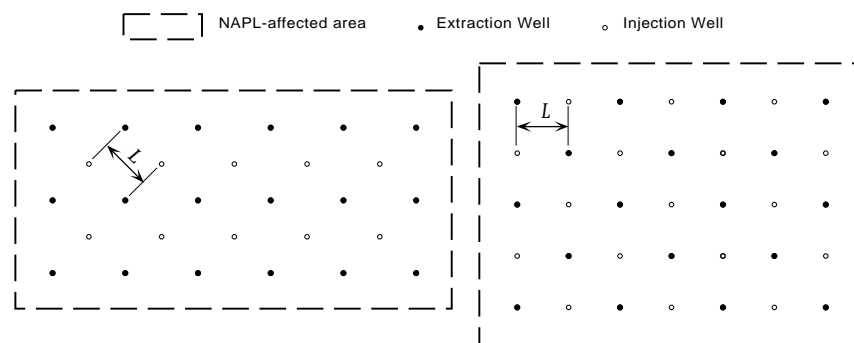


Figure 3. Assumed Configuration of Pumping/Injection Wells in Five-Spot Well Configuration

### *Simplified Dissolution Relationship for NAPLs*

The dissolution of residual nonaqueous phase liquids (NAPLs) by moving groundwater is a complex process, and the amount of clean water required to reach certain clean-up levels in the NAPL zone is an active area of research (Powers et al., 1994, 1992, 1991; Borden and Kao, 1992; Miller et al., 1990; Imhoff et al., 1994; Anderson et al., 1992; Geller and Hunt, 1993 ).

Powers, et al. (1994) developed a NAPL dissolution model that quite closely reproduces observed NAPL dissolution in laboratory columns. This model, unlike earlier dissolution relationships, had the ability to represent a range of porous media properties as well as chemical properties into the determination of NAPL dissolution rates. As with most research dissolution models, dispersion is also incorporated in the model, requiring significant computational effort to solve the resulting partial differential equation. The work by Powers et al. (1994) relied on a Galerkin finite element model to predict the rate of dissolution.

As part of this project, the Powers model was modified to yield a simple design model. In most scenarios involving NAPL dissolution cases, dispersion is relatively minor term and can be ignored with little loss in accuracy (see Figure 4). By using this approach, the dissolution relationship can be reduced to a simple form that can be solved in a computer spreadsheet format as opposed to a FORTRAN finite difference or finite element model. This spreadsheet model was then used to generate a simplified design model (described below) for evaluating groundwater pump-and-treat systems in NAPL zones.

### *1-D Advection Dispersion Model for Dissolved-Phase Zone*

A companion tool for the dissolved-phase only zone was also developed to augment the NAPL dissolution tool. As with the NAPL model, the goal was to estimate the pore volumes of clean water that were required through an aquifer with dissolved-phase contaminants only (no NAPLs) in order to reach a desired cleanup standard. The 1-dimension advection dispersion equation was modified and several simplifying assumptions were made to yield a simple design model for the dissolved-phase zone.

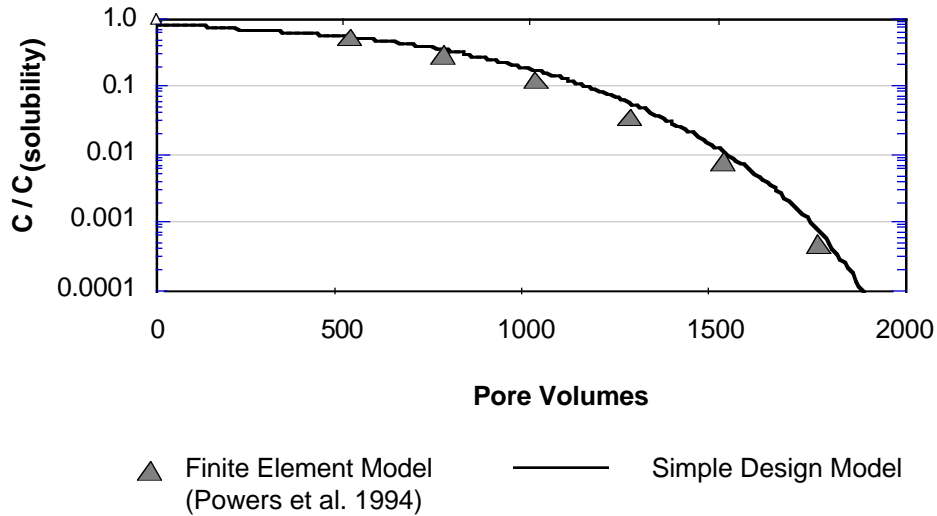


Figure 4. Comparison of Powers et al. (1994) Finite-Element Model to Simple Design Model for Simulating Dissolution of Pure Styrene NAPL in Ottawa Sand

## DESCRIPTION OF MODEL WORKSHEETS

Both the simple design model for NAPL zones and dissolved-phase zones were converted to a generalized worksheet format (see Worksheets 1 and 2). The worksheets are intended to be a screening-level or "back-of-the-envelope" tool for evaluating design alternatives and for estimating the feasibility of restoring NAPL-contaminated aquifers using pump-and-treat technology. The worksheet consists of several "fill-in-the-blank" equations for approximating the number of wells or time required to reach various cleanup goals for either dissolved contaminants or NAPLs. These equations are supplemented with descriptive text, tables, and charts provided as guidelines for input parameter selection or estimation.

### *Input Requirements*

Input requirements for the worksheets include: 1) the area of the contaminated zone; 2) aquifer porosity and hydraulic conductivity; 3) typical drawdown in extraction wells or head difference between extraction and injection wells; 4) representative groundwater concentrations and retardation factors for dissolved constituents or residual saturation, density, and solubility for

NAPLs, and 5) the target contaminant concentration for recovered groundwater. For a given number of wells or cleanup time, the remaining unknown may be solved.

The basic equation employed by the worksheet is derived from the spacing between wells determined by Darcy's law and the definition of a pore volume. For wells equally distributed over a rectangular-shaped area, this becomes:

$$N \cdot t = \frac{(Z \cdot A) \cdot \eta \cdot PV}{K \cdot \Delta H_{\max}}$$

where  $N$  is the total number of wells (extraction and injection) in the pump-and-treat system and  $t$  is the cleanup time in years.  $Z$  is a unit conversion factor provided on the worksheet,  $A$  is the area of the contaminated zone (acres, ft<sup>2</sup>, or m<sup>2</sup>),  $h$  is porosity (unitless),  $K$  is hydraulic conductivity (cm/sec), and  $\Delta H_{\max}$  (ft) is the maximum head change attainable between production wells and the normal piezometric surface (drawdown) between production and injection wells.  $PV$  is the number of pore volumes required to be flushed through the aquifer to reach the desired level of cleanup. Its value is estimated with the worksheet as described below.

$PV$  corresponds to the number of times the groundwater in a given volume of aquifer must be replaced by fresh water to achieve the target cleanup level. Determination of this value depends on whether residual NAPL is present in the contaminated zone. For a dissolved contaminant plume with no NAPL,  $PV$  is estimated by  $PV = R \cdot PV_{R=1}$ .  $R$  is the retardation factor of the contaminant in the aquifer and may be estimated for selected chemicals with the table included in the worksheet or calculated using the provided equation if more specific porous media and chemical parameters are known.  $PV_{R=1}$  is the pore volumes required for the case where  $R = 1$  (no retardation). A graph on the worksheet relates  $PV_{R=1}$  to  $C/C_o$  based on one-dimensional advection-dispersion, where  $C$  and  $C_o$  are the target and initial contaminant concentrations in the groundwater, respectively.

Where residual NAPL is present,  $PV$  is determined by

$$PV = \frac{\rho}{\alpha \cdot C_s} \cdot S_{ors}$$

where  $r$  and  $C_s$  are the density and water solubility of the NAPL in equivalent units and  $S_{ors}$  is its residual saturation in the aquifer. Values of  $r$  and  $C_s$  are tabulated on the worksheet for selected NAPLs.  $a$  is a coefficient which scales the solubility to an average effluent concentration of dissolved NAPL over the time required to reach the target concentration. This value also corresponds to an average NAPL dissolution rate over time. A graph based on the Powers (1994) NAPL dissolution model is provided on the worksheet to relate  $a$  to  $C/C_s$  for three values of hydraulic conductivity and for uniform and well-graded porous media.

### EXAMPLE APPLICATION OF SIMPLE DESIGN MODEL

To demonstrate the use of the worksheets, a simple example is provided based on remediation of a hypothetical NAPL-contaminated site. The hypothetical scenario to be considered consists of a 100 ft x 100 ft former waste pit (10,000 ft<sup>2</sup>) where the dense chlorinated solvent trichloroethene (TCE) is known to contaminate a shallow unconfined sandy aquifer. Nonaqueous phase TCE has been discovered in the saturated zone directly beneath the pit at a residual saturation of approximately 25 percent, and groundwater testing further indicates a 2.5 acre plume of dissolved TCE extending from the pit at an average concentration of 10 ppm (see Figure 5). Hydrogeologic properties of the aquifer have been estimated as: average saturated thickness, 24 feet; hydraulic conductivity, 0.001 cm/sec; and porosity, 0.30. The fraction of organic matter in the sand is assumed to be very low. The cleanup level set forth by the state is a dissolved concentration of 0.005 ppm TCE in the groundwater.

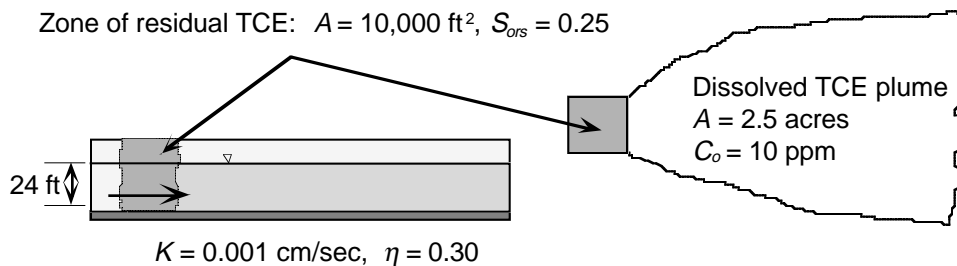


Figure 5. Configuration and Assumptions of Hypothetical Hazardous Waste Site

The pump-and-treat worksheet is used to determine a first approximation of the number of wells and time that will be required to meet the cleanup standard for both the zone of residual NAPL and the dissolved plume. While the worksheet addresses the two cases separately, the results are easily combined for a review of overall system requirements. The product of the number of wells and time required for each case is determined by a simple calculation using the equation on **Worksheet 1**. The porosity and hydraulic conductivity of the aquifer are input directly into this equation in the specified units, and the maximum head change is estimated as half of the saturated thickness as suggested on the worksheet. The only differences in the main equation between the dissolved and NAPL cases are the area (including selection of the appropriate conversion factor) and the pore volumes required to achieve the cleanup standard.

$$\frac{(Z \cdot A) \cdot \eta \cdot PV}{K \cdot \Delta H_{\max}} = N \cdot t = \frac{(Z \cdot A) \cdot 0.30 \cdot PV}{10^{-3} \cdot 12}$$

Pore volume requirements are determined with **Worksheet 2**. For the TCE dissolved-phase plume,  $C/C_o$  is first determined with the cleanup goal and TCE concentration as:

$$\frac{C}{C_o} = \frac{0.005}{10} = 5 \times 10^{-4}$$

whereby a value of  $PV_{R=1} = 3.9$  is read from the graph. Using the provided table, the retardation factor for TCE in an aquifer with low organic carbon is taken as 1.8. This gives  $PV = R \cdot PV_{R=1} = 7.0$ . Inserting this value, the area of the plume, and the conversion factor for acres in the main equation on **Worksheet 1** yields the product of  $N$  (the number of wells) and  $t$  (the time required for cleanup in years):

$$\frac{(Z \cdot A) \cdot \eta \cdot PV}{K \cdot \Delta H_{\max}} = N \cdot t = \frac{(4.21 \times 10^{-2} \cdot 2.5) \cdot 0.30 \cdot 7.0}{10^{-3} \cdot 12} = 18$$

In other words, one could remediate this portion of the site in one year with 18 wells, or with one well (if the hydraulic capture zone is large enough) in 18 years.

For the zone affected by TCE in the residual NAPL form, the lower half of **Worksheet 2** is used to figure

$$\frac{C}{C_s} = \frac{0.005}{1100} = 4.5 \times 10^{-6}$$

for TCE. Since no information is known about the particle-size distribution of the aquifer medium, a conservative value of  $a = 0.125$  is read from the graph using the  $K=10^{-3}$  cm/sec curve for a well-graded soil. Using this value, the chemical data provided for TCE, and the residual NAPL saturation,

$$PV = \frac{\rho}{\alpha \cdot C_s} \cdot S_{ors} = \frac{1.46 \times 10^6}{0.125 \cdot 1100} \cdot 0.25 = 2655$$

Going back to **Worksheet 1** one can calculate  $N \cdot t$  for the NAPL zone:

$$\frac{(Z \cdot A) \cdot \eta \cdot PV}{K \cdot \Delta H_{\max}} = N \cdot t = \frac{(9.67 \times 10^{-7} \cdot 10,000) \cdot 0.30 \cdot 2655}{10^{-3} \cdot 12} = 642$$

These results are easily combined to review the approximate well and time requirements for an overall pump-and-treat system.

$t$ (years)	$N$ (Dissolved-Phase Zone)	$N$ (NAPL Zone)	<b>Total No. of Wells (Both Zones)</b>
2 Years	9	321	<b>330 Wells</b>
10 Years	2	64	<b>66 Wells</b>

As one can see, the simple design model indicates that it may be feasible to use pump-and-treat system to remediate the dissolved-phase zone (no NAPL) as long as other constraints such as adsorption, preferential pathways, or low permeability zones are not a major factor. In the NAPL zone, however, the design model indicates that it would be infeasible to dissolve away the NAPL using a pump-and-treat system as the required number of wells would be excessive (335 total wells in a 100 ft by 100 ft area, corresponding to an average spacing 5.5 ft apart). In this case, site managers might prescribe a pump-and-treat system for the dissolved-phase plume only, and utilize some type of long-term containment approach (i.e. hydraulic containment with a

few pumping wells or physical barriers with low-level pumping) to prevent migration of hazardous constituents from the NAPL zone to potential receptors.

Note that the simple design model is only an approximation of actual dissolution rates in the field. A case study performed by Newell et al. (1991) showed that measured dissolution rates in the field were only one-half of the rate predictions from a finite difference model developed by Borden and Kao (1989). As with dissolved-phase remediation problems, low-permeability zones and hydrophobic adsorption can greatly reduce the rate of aquifer cleanups. In addition, contaminant concentration "bounceback" has been observed in several groundwater remediation projects where contaminant concentrations have increased after a pump-and-treat system was shut down. Therefore the results from the simple design model should be considered to be best-case scenarios, and appropriate safety factors should be included to ensure a successful design.

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# Worksheet 1

**A** is the area of contamination in one of the units given below. **Z** is a corresponding units-conversion factor.

Area in:	Z
acres	$4.21 \times 10^2$
ft <sup>2</sup>	$9.67 \times 10^7$
m <sup>2</sup>	$1.04 \times 10^5$

$\eta$  is the porosity of the aquifer. If unknown, may be estimated by a value of 0.3.

**PV** is the number of pore volumes to be flushed through the aquifer to reach a desired cleanup level. This corresponds to the number of times the groundwater in a given volume of aquifer is replaced by fresh water. It may be determined with a method provided on the following page depending on whether the contaminant is dissolved in the groundwater or exists as a separate nonaqueous phase liquid (NAPL).

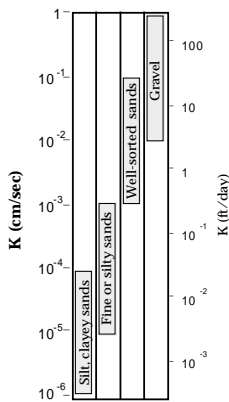
$$\frac{Z \cdot A \cdot \eta \cdot PV}{K \cdot \Delta H_{\max}} = N \cdot t$$

**t** is the remediation time in years.

**N** is the total number of wells.

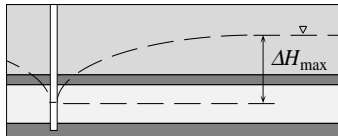
**K** is the hydraulic conductivity of the aquifer in cm/sec. It may be estimated with this chart.

(1 ft/day =  $3.53 \times 10^{-4}$  cm/sec)

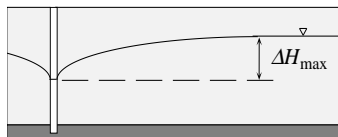


$\Delta H_{\max}$  is the maximum head change in feet attainable between production wells and the current piezometric surface or between production and injection wells.

For confined aquifers,  $\Delta H_{\max}$  is the confining head plus half of the aquifer thickness.



For unconfined aquifers,  $\Delta H_{\max}$  may be estimated as simply half of the saturated thickness.



## Worksheet 2

For dissolved contaminants, PV may be estimated by

$$PV = R \cdot PV_{R=1}$$

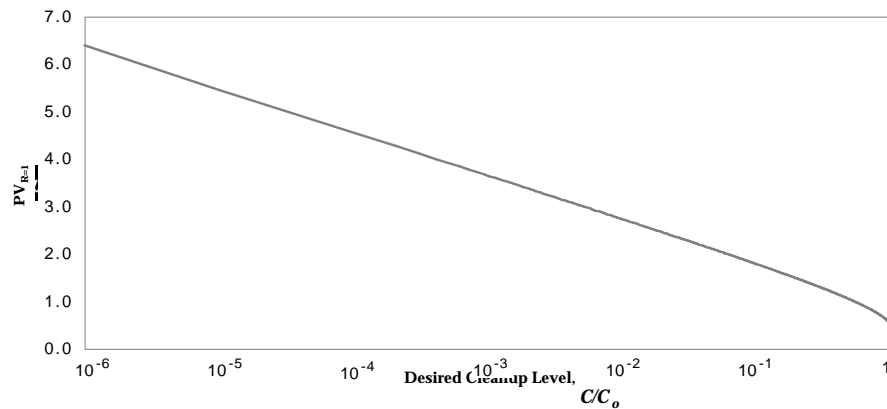
R is the retardation factor for the dissolved contaminant in the aquifer and may be estimated by

$$R = 1 + \frac{\rho_b}{\eta} \cdot f_{oc} \cdot K_{oc}$$

$\rho_b$ ,  $\eta$ , and  $f_{oc}$  are the bulk density, porosity, fraction of organic carbon of the aquifer medium, respectively, and  $K_{oc}$  is the organic carbon partitioning coefficient of the contaminant. The table to the right presents values of  $K_{oc}$  and calculated retardation factors for selected chemicals assuming  $\rho_b \eta = 6.0 \text{ kg/L}$ .

	$K_{oc}$ (L/kg)	R		
		$f_{oc} = 10\%$	$f_{oc} = 1\%$	$f_{oc} = 0.1\%$
Benzene	83	5.1E+01	6.0E+00	1.5E+00
1,1-Dichloroethane	30	1.9E+01	2.8E+00	1.2E+00
1,2-Dichloroethane	14	9.4E+00	1.8E+00	1.1E+00
1,1-Dichloroethene	65	4.0E+01	4.9E+00	1.4E+00
1,2-Dichloroethene	59	3.6E+01	4.5E+00	1.4E+00
Ethyl benzene	1100	6.6E+02	6.7E+01	7.6E+00
Tetrachloroethene	364	2.2E+02	2.3E+01	3.2E+00
Toluene	300	1.8E+02	1.9E+01	2.8E+00
Trichloroethene	126	7.7E+01	8.6E+00	1.8E+00
o-Xylene	830	5.0E+02	5.1E+01	6.0E+00

$PV_{=1}$  is the number of pore volumes required for the case where  $R = 1$  (no retardation) and may be estimated using this chart. C and  $C_o$  are the target and initial contaminant concentrations in the groundwater, respectively. (e.g. for 99.99% reduction in contaminant concentration,  $C/C_o = 10^{-4}$ ).



For NAPLs at residual saturation, PV may be estimated by

$$PV = \frac{\rho}{\alpha \cdot C_s} \cdot S_{ors}$$

$\rho$  and  $C_s$  are the density and mass solubility of the NAPL in equivalent units. The table to the right presents these parameters for selected NAPLs.  $S_{ors}$  is the residual saturation of NAPL in the aquifer.

	$\rho$ (mg/L)	$C_s$
Benzene	8.78E+05	1.75E+03
1,1-Dichloroethane	1.18E+06	5.50E+03
1,2-Dichloroethane	1.18E+06	8.52E+03
1,1-Dichloroethene	1.27E+06	2.25E+03
1,2-Dichloroethene	1.27E+06	6.30E+03
Ethyl benzene	8.68E+05	1.52E+02
Tetrachloroethene	1.62E+06	1.50E+02
Toluene	8.68E+05	5.35E+02
Trichloroethene	1.46E+06	1.10E+03
o-Xylene	8.78E+05	1.75E+02

$\alpha$  is a solubility scaling coefficient to account for decreasing NAPL solubility as water is flushed through the aquifer. (Powers, 1994) This value depends on porous media properties. The upper three curves correspond to a soil with a uniform particle-size distribution while the lower curves correspond to a well-graded soil. C is the target concentration of dissolved NAPL in the groundwater.

