CHAPTER 2

PRINCIPLES AND THEORIES

2.1 VOCs Contamination

Nonaqueous Phase Liquids (or NAPLs) are water-immiscible liquids that are commonly found contaminants in both vadose zone and groundwater aquifers. They may have densities that are greater than water (dense nonaqueous phase liquids, or DNAPLs) or densities that are less than water (light nonaqueous phase liquids, or LNAPLs). They are partially soluble in water, so that both dissolved as well as nonaqueous phases may be present. Two-phase flow may occur below the water table with the presence of water and a DNAPL. Three-phase flow may occur in the vadose zone with the presence of air, water, and NAPL. In the vadose zone, the NAPL may partition into the air as a vapor phase. There may be multiple compounds in the nonaqueous phase, each with different physicochemical properties. NAPL flow is dependent upon the densities, viscosities, and interfacial tensions of the liquids. In addition to dispersion and diffusion, compounds can undergo adsorption and chemical and biological degradation (Fetter, 1999).

A NAPL that is lighter than water (LNAPL) will float on the water table or the top of the capillary fringe. If a sufficient depth of LNAPL collects on top of the capillary fringe, it can flow into a shallow monitoring well. The thickness of LNAPL measured in a monitoring well is normally greater than the thickness of the free LNAPL in the subsurface. Common LNAPLs include gasoline and diesel fuel.

DNAPLs may have greater mobility than water due to their greater density/viscosity ratio. A DNAPL will sink in the vadose zone, although it can spread laterally on the top of strata with small apertures. DNAPL trapped in fractures may diffuse into the groundwater in the pores of the rock or clay matrix. Pools of mobile DNAPL may form at the bottom of an aquifer. They will spread in the direction that the underlying aquitard is sloping. A monitoring well screened at the bottom of an aquifer may be used to detect the presence of a DNAPL. DNAPL compounds include chlorinated hydrocarbons, such as tetrachloroethylene, trichloroethylene, and 1,1,1-trichlorethane, as well as coal tar and creosote.

The U.S. Environmental Protection Agency (U.S. EPA) defines the term Volatile Organic Compounds (VOCs) as any compounds of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions (EPA, 2009). VOCs such as monoaromatic hydrocarbons and chlorinated solvents can escape to the atmosphere when they come into contact with a gas phase in the unsaturated zone of an aquifer or during sampling and analysis. Common VOCs are, for examples, methane, ethane, benzene, tetrachloroethylene, trichloroethylene, 1,2-dichloroethane, and vinyl chloride monomer. VOCs are not normally found in surface waters (Nikolaou et al., 2002) because of their high volatility, but they are the most common contaminants found in groundwater (Golfinopoulos et al., 2001).

Most volatile organic compounds, even at low concentrations, are probably carcinogens (Baudoin et al., 2002). VOCs can be absorbed by skin and brought to the skin cancers. Furthermore, there is evidence that benzene can cause leukemia (e.g. Glass et al., 2003; Roma-Torres et al., 2006). Moreover, they are accumulated in fatty tissues in relation to their chemical properties causing chronic diseases especially in industrial workers (Alkan et al., 2004; Burstyn et al., 2003). VOCs can enter the environment in several different pathways. Because they are extremely mobile, having enough vapor pressure under atmospheric pressure to vaporize significantly, they enter the atmosphere, soils, and groundwaters. In fact, rain can wash VOCs out of the air and sediments and transport them to aquatic environments (Johnson et al., 2003; Edil, 2003).

2.2 Principles and Theories of Groundwater Flow

The movement of groundwater in the natural conditions is governed by established hydraulic principles: the conservation of mass and the Darcy's law (Freeze and Cherry, 1979; Todd, 1980; Fetter, 1988). Henry Darcy, a French hydraulic engineer, investigated the flow of water through porous media (shown in Figure 2.1). He established the Darcy's law which states that rate of fluid flow (Q) through a cylinder packed with sand is directly proportional to the cross-sectional area of the flow (A) and the loss of the hydraulic head between two points of measurements (Δh), and it is inversely proportional to the distance between two piezometers (L). Hydraulic conductivity (K) is a proportional constant that serves a measure of the permeability of porous medium and has unit of velocity,

$$Q = KA\frac{\Delta h}{L} \tag{2.1}$$

or

$$Q = -KA\frac{dh}{dl}, \tag{2.2}$$

where dh/dl is the hydraulic gradient. The negative sign indicates flow in the direction of decreasing hydraulic head.

The above equations can be rewritten in terms of volumetric flux or flow per unit area, which is called specific discharge or Darcy velocity (v):

$$v = \frac{Q}{A} = -K\frac{dh}{dl}, \qquad (2.3)$$

where v is the groundwater velocity [L/T].

This equation is valid only for laminar conditions. Moreover, the velocity, which is calculated from total water flow through a whole section area of porous medium, is not a true velocity.

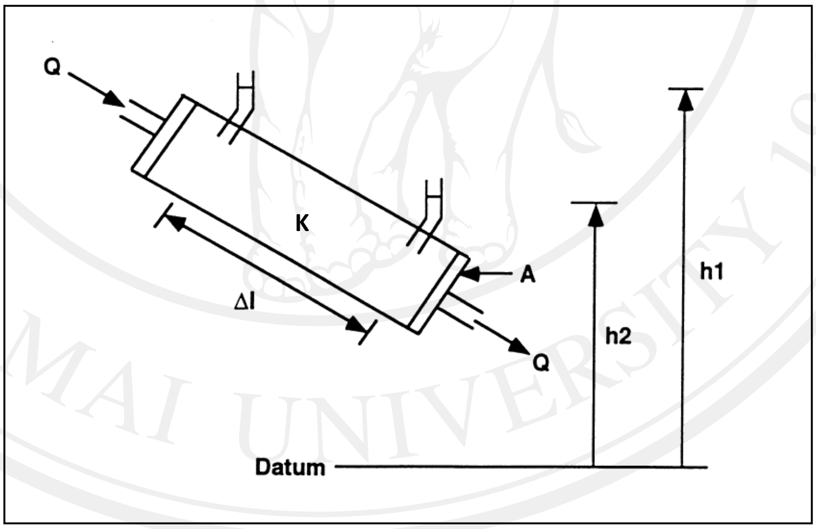

Figure 2.1 The porous media model to elaborate Darcy's law.

The true velocity which water is actually moving, the specific discharge is divided by the effective porosity to represent the velocity in the pores of the medium:

$$\bar{v} = \frac{Q}{n_e A} = -\frac{K}{n_e}\frac{dh}{dl}, \qquad (2.4)$$

where $\bar{v}$ is the average linear velocity [L/T], and

n_e is the effective porosity.

The mass conservation states that fluid involved in a change of volume or in a change in the mass stored in the fluid, or both, cannot result in a net change in the mass. Any change in mass flowing into the small volume of the aquifer must be balanced by a corresponding small volume change or both (Freeze and Cherry, 1979). The conservation of fluid mass statement is:

$$\text{Inflow rate} - \text{Outflow rate} = \text{change in storage with time.} \tag{2.5}$$

In confined aquifer, the water-saturated layer is trapped by impermeable layer. Groundwater can be released from the aquifer by changing its pressure (measured in terms of head, *h*). Although the potentiometric surface may decline and the water pressure may decrease, the aquifer remains saturated. Groundwater in confined aquifer can be released from a unit volume of an aquifer when the groundwater head decline by a unit amount is described as an aquifer's specific storage (S_s) which has a dimension of inverse of length [L^{-1}].

In unconfined aquifer, water table and water pressure decline as a result of pumping. Groundwater is released from voids and causes a decrease in the saturated thickness. The aquifer's storage can be described using specific yield (S_y) which is dimensionless. The specific yield can be defined as the volume of water that is released from a unit volume of an aquifer through gravity drainage when the head is reduced a unit amount.

The storage coefficient (S) is the term for the above processes. For an aquifer, which has a thickness (b), the storage coefficient can be determined as

Confined aquifer: $$S = S_s b,\tag{2.6}$$

Unconfined aquifer: $$S = S_y + S_s b.\tag{2.7}$$

The numerical value of S_y are commonly much higher than S_s. Therefore, for most of unconfined aquifers the S values will be close to the S_y values.

2.3 Principles and Theories of Solute Transport

Solute or mass transport in groundwater aquifer refers to a process where a dissolved species moves from an area of greater concentration toward an area where it is less concentrated. This process is known as molecular diffusion, or diffusion (Fetter, 1999). Diffusion will occur as long as a concentration gradient exists, even if the fluid is not moving. The mass of fluid diffusion is proportional to the concentration gradient, which can be expressed as Fick's first law:

$$F = -D_d\left(\frac{dC}{dx}\right),\tag{2.8}$$

where F is mass flux of solute per unit area per unit time [M/L^2/T],

D_d is diffusion coefficient [L^2/T]

C is solute concentration [M/L^3]

$\frac{dC}{dx}$ is concentration gradient [M/L^3/L].

For systems that the concentrations are changing with time, Fick's second law applies. In one dimension this is

$$\frac{\partial C}{\partial t} = D_d\frac{\partial^2 C}{\partial x^2},\tag{2.9}$$

where $\frac{\partial C}{\partial t}$ is change in concentration with time [M/L^3/T].

In porous media, diffusion cannot proceed as fast as it can in water because the ions must follow longer pathways. To account for this, an effective diffusion coefficient (D^*) must be used,

$$D^* = wD_d \,, \tag{2.10}$$

where w is a coefficient that related to the tortuosity. Tortuosity is a measure of the effect of the shape of the flow path followed by water molecules in a porous media.

Dissolved solids are carried along with the flowing groundwater. This process is called advective transport, or convection. For one-dimensional flow normal to a unit cross-sectional area of the porous media, the quantity of water flowing is equal to the average linear velocity ($\bar{v}$) times the effective porosity (n_e).

The one-dimensional mass flux (F_x) due to the quantity of water flowing times the concentration of dissolved solids (C) and is given by equation:

$$F_x = \bar{v} n_e C \,. \tag{2.11}$$

Solute-containing water is not all travelling at the same velocity that mixing occurs along the flowpath. This mixing is call mechanical dispersion which results in a dilution of the solute at the advancing edge of flow. The mixing that occurs along the direction of the flowpath is called longitudinal dispersion. And the advancing solute front will also tend to spread in the normal direction of flow because at the pore scale the flowpaths can diverge. The result of this is mixing in normal flow directions called transverse dispersion.

The process of molecular diffusion cannot be separated from mechanical dispersion in flowing groundwater. The two are combined to define a parameter called the hydrodynamic dispersion coefficient (D). That is represented by the following formulas (Fetter, 1999):

$$D_L = a_L v_i + D^*, \tag{2.12}$$

and

$$D_T = a_T v_i + D^*, \tag{2.13}$$

where D_L is hydrodynamic dispersion coefficient parallel to the principal direction of flow (longitudinal)

D_T is hydrodynamic dispersion coefficient perpendicular to the principal direction of flow (transverse)

a_L is longitudinal dynamic dispersivity

a_T is transverse dynamic dispersivity

The dispersion coeffient tensor (D_{ij}) was calculated from coordinate transformation. For example, if the principal groundwater flow direction is in the x-direction (i.e., aligned with the model coordinate and $\bar{v}_x \neq 0$ and $\bar{v}_y = \bar{v}_z = 0$), the dispersion coefficient tensor is defined as follows.

$$D_{ij} = \begin{bmatrix} D_L & 0 & 0 \\ 0 & D_{T,h} & 0 \\ 0 & 0 & D_{T,v} \end{bmatrix}, \tag{2.14}$$

where the diagonal terns of the tensor in x-,y- and z-directions are $D_L = a_L |\bar{v}_x|$, $D_{T,h} = a_{T,h} |\bar{v}_x|$, and $D_{T,v} = a_{T,v} |\bar{v}_x|$, respectively. Note that the parameters a are normally obtained from field tracer test or literature.

In the case where the principal groundwater flow direction does not perfectly aligh with the x-direction (i.e., $\bar{v}_x,\ \bar{v}_y,\ \bar{v}_z \neq 0$), a coordinate transformation is required to transform dispersion coefficient tensor shown in equation (2.14) to full tensor as shown in equation (2.15)

$$D_{ij} = \begin{bmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{bmatrix}, \tag{2.15}$$

where the diagonal terms of the tensor (in the principal direction) are $D_L = \alpha_L \| \bar{v}_x \|$, $D_{T,h} = \alpha_{T,h} \| \bar{v}_i \|$, and $D_{T,v} = \alpha_{T,v} \| \bar{v}_i \|$, respectively.

2.4 Numerical Model

2.4.1 Groundwater Flow Model

Only Darcy's law is not enough to describe the groundwater flow in the natural conditions. General flow equation is formulated by combining the law of mass conservation with a controlled volume of an aquifer. The governing equation for groundwater flow through a three-dimensional porous media that can show in the steady state form (Freeze and Cherry, 1979):

$$\frac{\partial}{\partial x}\left(K_x \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial h}{\partial z}\right) \pm W = 0, \tag{2.16}$$

where K_x , K_y , K_z are values of hydraulic conductivity in the x-, y-, and z-directions [L/T]

h is the hydraulic head [L]

W is a volumetric per unit volume and it represents sources/sinks

In the transient condition, the groundwater flow equation can show as

$$\frac{\partial}{\partial x}\left(K_x \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial h}{\partial z}\right) \pm W = S_s \frac{\partial h}{\partial t}. \qquad (2.17)$$

2.4.2 Solute Transport Model

The fate and transport of dissolved contaminants in groundwater can be described by the advection-dispersion-reaction equation:

$$\frac{\partial c}{\partial t} = \frac{\partial}{x_i}\left(D_{ij} \frac{\partial h}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(v_i c\right) + \sum R_n , \qquad (2.18)$$

where D_{ij} is dispersion coefficient tensor

R_n is a reaction term

v_i is the pore velocity

Advection represents the movement of a contaminant with the flowing groundwater. Hydrodynamic dispersion on the other hand, involves both molecular diffusion and mechanical mixing. The latter is a result of local variations in velocity around some mean velocity of the flow as a result of soil heterogeneity. Laboratory investigations indicate that at the macroscopic scale, dispersion is a function of pore velocity and a factor called dispersivity. The dispersion of solutes in groundwater can occur not only in the direction of groundwater flow, but also lateral to the direction of flow. The last term in equation (2.18) represents the total mass loss or generation due to other physical, chemical and biological processes such as adsorption, biodegradation, and self-decays (e.g. radionuclides).

2.5 Stochastic Theory

The flow and transport parameters that appeared in the equations governing equations (2.4), (2.16), and (2.18), are generally measured or determined at only a few locations despite the fact that they are highly variable in space at all length scales (macroscopic to regional). A combination of sparsity of observations and measurement errors lead to uncertainty in the values of the formation properties and thus uncertainty of predictions using simulation models that solve the governing equations. The stochastic theory provides a method for evaluating these uncertainties using probability or related quantities such as statistical moments (Zhang, 2002). Material properties that define field heterogeneity are not completely random, but assumed to exhibit some correlation structure resulting from natural depositional processes that created the formation. This spatial correlation structure is defined using random space functions that are quantified using joint probability distributions or joint statistical moments.

A commonly used geostatistical approach used in stochastic formulations is to characterize the heterogeneity (in terms of permeability) of the aquifer by the first and second moments of a probability distribution function (pdf) which are referred to as mean, and variance/covariance, respectively. In modeling flow and transport, the hydraulic conductivity (K) introduces the greatest uncertainty as its value varies over a very wide range in aquifer materials. The uncertainty is not only associated with the measurement at a point but also with the uncertainty of the value at locations where it is not measured. The general approach used in developing the technique assumes that the log of K is normally distributed:

$$y = \log K \, . \tag{2.19}$$

If n points in the aquifer are sampled, the estimate of the population mean is obtained from

$$\overline{y} = \frac{1}{n}\sum_{i=1}^{n} y_i \, , \tag{2.20}$$

and the estimate of the variance is given by,

$$S_y^2 = \frac{1}{n}\sum_{i=1}^{n}(y_i - \overline{y})^2 \, . \tag{2.21}$$

The pdf of the $\ln K$ distribution is defined by the mean and the variance. The variance measures the degree of heterogeneity of the aquifer. If the y_i is measured at a fixed set of points, and if it is necessary to estimate the value of y at other locations where measurements are not made, the mean and the standard deviation (square root of variance) can be used to provide the most likely estimate of the un-measured value. That is, the estimated value is the mean with an uncertainty that is normally distributed with a standard deviation equal to the standard deviation of the measurements.

A stochastic random process is a collection of random variables that vary continuously in space (or time). The stochastic process $K_{(x)}$ can be thought of as a collection (or ensemble) of realizations with the same statistical properties. A realization is single observation of the spatial variation of the process. If the pdf of a spatially random process is invariant under shifts of the spatial origin, then it is considered to be second-order stationary and commonly referred to as stationary. The importance of stationarity is the suggestion of underlying repetitive structure of the parameter. A physical description of the stationarity is captured in the covariance function that is given as,

$$\operatorname{cov}[y_1 - y_2] = E[\{y_1 - \mu_1\}\{y_2 - \mu_2\}], \tag{2.22}$$

whose estimator is

$$R_y(r) = \frac{1}{N - r}\sum_{i=1}^{n}(y_{i+r} - \bar{y})(y_i - \bar{y}), \tag{2.23}$$

where $N - r$ term is the number of pairs separated by a distance r. The covariance is independent of the origin but depends on the distance between observations. The heterogeneous aquifers can be represented as a spatially correlated random field. The descriptive statistics of the random field include the mean and variance of $\ln K$ and correlation length. Spatial correlation increases the probability that a given point will have permeability similar to that of a neighboring point. K values at points that are separated by a short distance are more likely to be similar and as the separation becomes larger they are less likely to be similar. The correlation scale is a characteristic length of the average spatial persistence of $\ln K$. A geoststistical tool for the quantification of spatial structure is the experimental semivariogram (referred to as variogram). Variograms are useful in identifying the underlying spatial structure and identifying trends. The classical experimental semivaraigram estimator $\gamma(h)$, for Gaussian data is calculated as,

$$\gamma(h) = \frac{1}{2n(h)}\sum_{i=1}^{n(h)}[y(x_i + h) - y(x_i)]^2, \tag{2.24}$$

where h is the separation distance between observations and $n(h)$ is the number of data pairs separated by distance h. If the $\ln K$ data are statistically homogeneous (stationary), then the variogram is dependent only on h. A theoretical exponential model can be fitted to the variogram as,

$$g(h) = s^2(1 - e^{-h/l})\,. \qquad (2.25)$$

The model parameter l is the correlation length that is a measure of the distance over which the y values are correlated. Figure 2.2 shows a plot of the theoretical and a measured semivariagram from a laboratory sand packing experiment conducted by Compos (Compos, 1998). For a small separation distance h, the correlation between sample pairs is high and $g(h)$ is small. When distance between points increases, the correlation decreases (i.e. $g(h)$ increases) and variogram will eventually reach a plateau.

In general, two approaches of stochastic formulations are used. In the first approach, uncertainty analysis is incorporated directly into the model to define the predictions in terms of their mean and covariance. The second approach uses a Monte Carlo-type analysis involving a series of realizations of the uncertain parameters (Gelhar and Axness, 1983). In our laboratory experiments and numerical studies, the second approach was used. Several realizations of hydraulic conductivity field (more correctly, $\ln K$) were generated and used for further analyses.

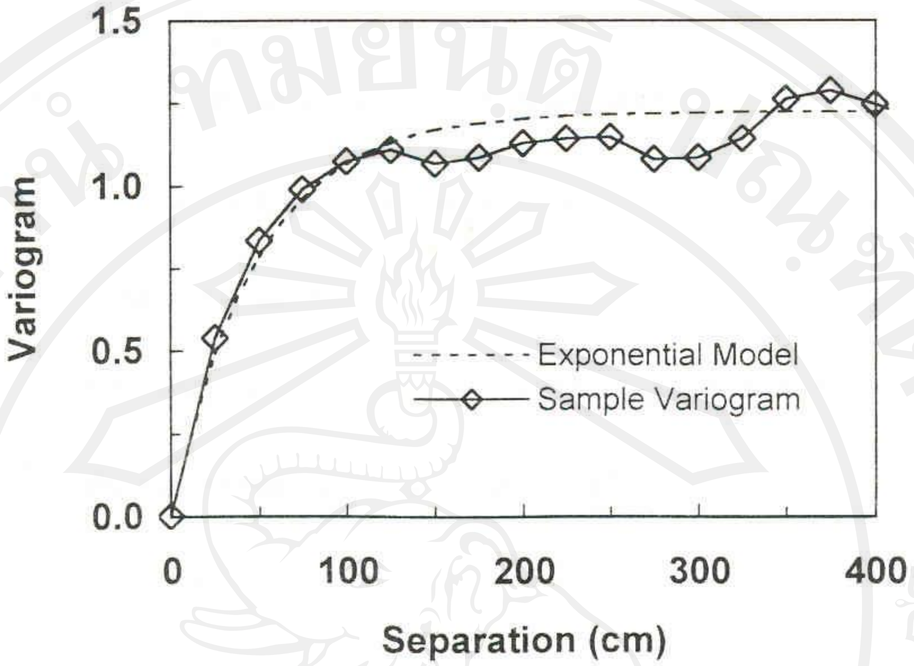

Figure 2.2 Typical semivariogram for stationary process (Compos, 1998).

2.6 Remediation Techniques

There are a number of remedial techniques that can be used to remediate both soils and groundwater that are contaminated with VOCs. These techniques are, for examples, soil vapor extraction, pump-and-treat, in-situ bioremediation, permeable reactive barrier based on in-situ chemical oxidation.

Soil Vapor Extraction (SVE)

Soil vapor extraction (SVE) is an in situ remediation technique that is used to remove VOCs from vadose zone soil. Air flow is induced through contaminated soil by applying a vacuum to vapor extraction vents and creating a pressure gradient in the soil. As the soil vapor migrates through the soil pores toward the extraction vents, VOCs are volatilized and transported out of subsurface soil. Advantages of SVE system over other remediation technologies for soil contaminated with organics are the relative simplicity of installing and operating the system and the minimal amount of equipment required (U.S. Environment Protection Agency, 1997).

Pump-and-Treat (PT)

Pump-and-treat technique is used to clean up contaminated aquifers with dissolved species. The technique requires locating the groundwater contaminant plume in three dimensional space, determining aquifer and chemical properties, designing a capture system, and installing extraction wells. Monitoring wells or piezometers used to check the effectiveness of the pump-and-treat system are also integral components of the system. A pump-and- treat system may be used in combination with other remedial actions, such as low-permeability walls to limit the amount of clean water flowing to the extraction wells, thus reducing the volume of water to be treated. The objective of the pump-and-treat system is to reduce concentrations of contaminants to an acceptable level (cleanup), or to protect the subsurface from further contamination (U.S. Environment Protection Agency, 1990).

In-Situ Bioremediation (ISB)

In-situ bioremediation is the application of biological treatment to the cleanup of contaminants in groundwater. ISB uses bioaugmentation and biostimulation to create anaerobic conditions in groundwater and promote contaminant biodegradation (mainly, of chlorinated compounds) for the purposes of minimizing contaminant migration and/or accelerating contaminant mass removal. Bioaugmentation is the addition of beneficial microorganisms into groundwater to increase the rate and extent of an aerobic reductive dechlorination to ethene. Biostimulation is the addition of an organic substrate into groundwater to stimulate anaerobic reductive dechlorination. Microorganisms, such as bacteria, are discrete life forms that require a source of nutrients for their metabolism and a sustaining environment in which to live and reproduce. Under ideal conditions, bacteria can produce a new generation every 20 to 30 minutes. This exponential population growth potential gives rise to the possibility of a population explosion if sufficient food and supportive conditions prevail. Since the growth of these microbial populations can be regulated by controlling their critical nutrients or environmental conditions, they are subject to human control. These controlled, rapidly increasing bacterial populations can effectively break down contaminants and thus offer potential as a remedial technology (Interstate Technology Regulatory Council, 2005a). The technique involves an addition of nutrients, electron donors, and electron acceptors. Design configurations of in-situ bioremediation systems include direct injection, groundwater recirculation, installation of permeable reactive barriers, and bioventing (EPA, 2000).

Permeable Reactive Barriers (PRB) is defined as an in-situ permeable treatment zone designed to intercept and remediate a contaminant plume. Reactive media such as carbon sources, limestone, granular activated carbon, zeolites, and others had also been deployed in recent years to treat metals and some organic compounds. Research and deployment of bio- permeable reactive barriers (bio-PRB) systems are also growing in recent years. Bio-PRBs are often described as in-situ bioremediation deployed with the PRB design concept (i.e., a continuous, linear, flow-through zone where treatment occurs). These systems may use solid, liquid, or gaseous amendments such as wood chips, compost, lactate, molasses, etc. to create an enhanced zone of biological activity where contaminant degradation occurs. In this way, the reactive treatment zone within a bio-PRB is created indirectly through the addition of amendments (Interstate Technology Regulatory Council, 2005b). Typical studies of bio-PRB have included laboratory experiments and field studies.

Historic maintenance and repair activities over approximately fifty years of operation at Dover AFB have resulted in solvent spills and subsequent groundwater contamination. A hydraulically controlled pilot system 12-18 meters was constructed 15 meters below ground surface in an alluvial aquifer to introduce nutrients and substrate into the groundwater. TCE and *cis*-DCE concentrations in groundwater averaged 4,800 and 1,200 µg/L. Groundwater was extracted from the three downgradient wells, combined, amended, and reinjected into the three upgradient wells. Electron donors and nutrients were delivered on a 7-day pulsed feeding schedule to minimize injection well. The initial substrate feed delivered 100 mg/L as lactate. The substrate was prepared and stored as a mixture containing 94.5 L of 60% sodium lactate, 198.5 L of tap water, and 100 g of yeast extract. A nutrient mix consisting of 5 mg/L ammonia and 5.5 mg/L phosphate was then fed into the flow stream. The pilot operated for 568 days. Results by day 269 confirmed previous laboratory work showing that dechlorination did not proceed past *cis*-DCE. An ethene-forming microbial enrichment culture from the Department of Energy’s Pinellas site in Largo, FL, was injected into the pilot area. After a lag period of about 90 days, vinyl chloride and ethene began to appear in wells. The injected culture survived and was transported through the pilot area. By day 509, TCE and *cis*-DCE were fully converted to ethene (Ellis et al., 2000).

The TCE plume at the Chico Municipal airport is about 500 m wide and 2000 m long. About 5.4 kg of a strain of methanotrophic was suspended in 1800 L of groundwater (5.4 × 109 cells/mL) and injected into an aquifer through a single well at a depth of 27 m, several meters below the water table. The injected groundwater was devoid of TCE and growth substrates but was amended with a phosphate solution (10 mM) to buffer the pH and phenol red (20 *í*m) to act as a tracer. Approximately 50% of the injected bacteria attached to the sediments, forming an in situ, fixed-bed bioreactor of unknown geometry. Contaminated groundwater was subsequently withdrawn through the biofilter region by extracting at 3.8 L/min for 30 hours and then at 2.0 L/min for the remaining 39 days of the field experiment. TCE concentrations in the extracted groundwater decreased from 425 to less than 10 ppb during the first 50 h of withdrawal, which is equivalent to a 98% reduction. TCE concentration extracted through the biofilter gradually increased to background values at 40 days when the experiment was terminated (Duba et al., 1996)

In-Situ Chemical Oxidation (ISCO)

In-situ chemical oxidation involves an injection of oxidants and potentially co-amendments directly into the source zone and downgradient plume. The oxidants react with the contaminants, producing innocuous substances. However, there may be many chemical reaction steps required to reach those end points, and some reaction intermediates, as in the case of polyaromatic hydrocarbons and organic pesticides. Fortunately, in most cases if an adequate oxidant dose is applied, the reactions proceed to completion, and the end products are reached quickly. There are two main advantages of using ISCO over other conventional treatment technologies: large volumes of waste material are not usually generated, and treatment is commonly implemented over a much shorter time frame. Both of these advantages often result in savings on material, monitoring, and maintenance. ISCO has limitations that should be recognized. There are situations in which ISCO would be ineffective at degrading the contaminants present. It is also possible that due to the total volume of oxidant required, it would not be cost-effective to use ISCO for site remediation. Site-specific information including the applicability of ISCO to the specific contaminants, the concentration range, and hydrogeologic conditions must be gathered and reviewed when evaluating the appropriateness of using ISCO for a remediation strategy (Interstate Technology Regulatory Council, 2005c).

2.7 Biodegradation of the Chlorinated Solvents

Chlorinated solvents vary from the monochlorinated vinyl chloride (VC) to the most chlorinated tetrachloroethenes (PCE). Other members include; trichloroethene (TCE), *cis*-1,2-dichloroethene (*cis*-DCE), *trans*-1,2-dichloroethene (*trans*-DCE), and 1,1-dichloroethene (1,1-DCE). Both PCE and TCE are detected with the greatest frequency and highest concentration in groundwater systems worldwide. *cis*-DCE and *trans*-DCE occur primarily as a result of in situ microbial transformations of TCE, with *cis*-DCE being the predominant daughter product and *trans*-DCE less commonly observed in groundwater (Bradley, 2000).

Chlorinated solvents are subject to a range of microbial degradation processes that include reductive dechlorination, aerobic oxidation, anaerobic oxidation, and aerobic cometabolism. Environmental conditions under which these processes occur are known; however, it is often difficult the contribution of each process based purely on field data (Waddill et. al, 2002).

2.7.1 Reductive dechlorination

Reductive dechlorination is the most critical attenuation process that has been studied extensively in both the field and laboratory. In reductive dechlorination of PCE, TCE, and daughter products (*cis*-DCE and VC) are reduced to form ethene and, in some special cases, ethane. Microbial reductive dechlorination has been observed at anaerobic chloroethene-contaminated aquifers. In this process, chloroethene serves as electron acceptors and molecular hydrogen (H_2) reacts to replace chlorine on a chlorinated ethene molecule. PCE readily undergoes reductive dechlorination of TCE to *cis*-DCE occurs under Fe(III)-reducing conditions and in more strongly reducing environments. Reductive dechlorination of *cis*-DCE to VC requires at least sulfate-reducing conditions but proceeds more readily in methanogenic environment. Reductive dechlorination of VC to ethene is often slow and significant only under highly reducing methanogenic conditions. Complete reductive dechlorination to ethene is rare due to low electron donor availability and a sparse microbial community capable of this complete transformation. The proposed pathway for the sequential reductive dechlorination by Maymo- Gatelle et al. (1997) is as shown in Figure 2.3.

When multiple electron acceptors are available, it is assumed microbes tend to utilize them in sequence, starting with the one that provides the highest Gibbs free energy. Electron acceptors are used in the following order that start with oxygen (O_2), nitrate (NO_3), manganese (Mn(IV)), ferric iron (Fe(III)), sulfate (SO_4), and carbon dioxide (CO_2).

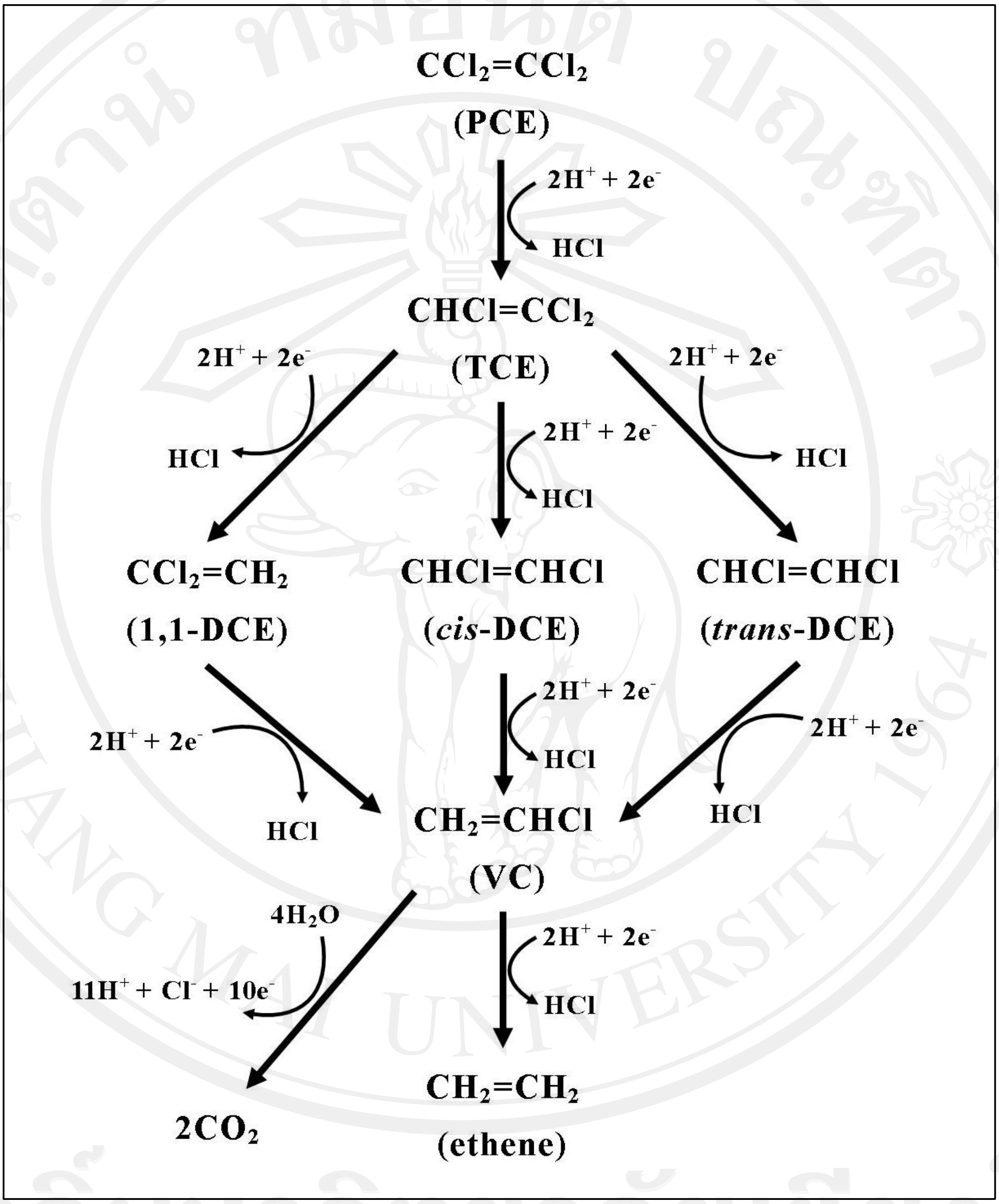

Figure 2.3 Proposed pathway for biological transformation of chlorinated ethenes (Maymo-Gatelle et al., 1997).

2.7.2 Aerobic Oxidation

Microbial degradation of VC, including mineralization, has been observed in laboratory and aquifers under aerobic condition. In the presence of oxygen, VC can serve as a sole carbon source for growth and been shown to oxidize under aerobic conditions. The oxidation of *cis*-DCE and VC will be limited at anaerobic sites where reductive dechlorination is efficient.

2.7.3 Anaerobic Oxidation

Anaerobic oxidation of *cis*-DCE and VC is a process that only been recognized recently. VC, and to a lesser extent DCE, could be oxidized to form CO_2 under Fe(III)-reducing conditions. The implications of these findings to the natural attenuation of chlorinated ethenes may be profound at sites where PCE/TCE can be readily transformed to *cis*-DCE and VC.

2.7.4 Aerobic Cometabolism

Another process that leads to microbial degradation of chlorinated ethenes is cometabolic oxidation. It is known that a wide variety of aerobic microorgaisms utilizing methane and other substrates are able to oxidize TCE, DCE, and VC to CO_2 without the accumulation of toxic intermediates. Aerobic cometabolism of chlorinated ethene requires oxygen and a primary substrate to initiate and methane do not typically co-occur in aquifers.