

Transport and Fate of Chlorinated Hydrocarbons in the Vadose Zone — A Literature Review with Discussions on Regulatory Implications

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ABSTRACT: Chlorinated hydrocarbons (CHCs) are one of the pollutant groups most commonly found in hazardous waste sites. Understanding the transport and fate of these compounds in the vadose zone is crucial to identifying pollution sources, assessing the threat to groundwater, and evaluating the need and adequacy of cleanup. CHCs exist in various physical phases in the subsurface, linked by interphasal processes. These, combined with unsaturated water flow in the vadose zone, which is complicated by the multifluid (air and water) situation, geologic heterogeneity, and a highly site-specific preferential flow pattern, create a possibly four-fluid flow condition, with interactions among different phases of CHCs and between chemicals and geologic materials. Superimposed on these are various biotic and abiotic transformations. Integration of these processes is being attempted by mathematical modeling; however, natural heterogeneity and site-specific factors render these efforts partially successful at best. Regulators are faced with considerable uncertainties and cannot expect simple solutions with the current level of understanding of subsurface processes.

KEY WORDS: chlorinated solvents, solute transport, subsurface transport, unsaturated zone, contaminant migration, non-aqueous phase liquid (NAPL), multiphase transport, subsurface environment.

I. INTRODUCTION

The vadose zone usually consists of a heterogeneous geologic medium that provides crucial pollution protection to the groundwater through various physical, chemical, and biological processes. Vadose zone investigation provides valuable information regarding the source, extent, and strength of subsurface contamination, its (potential) impact on groundwater, and implications for remediation, such as evaluating the need and adequacy of certain remedial actions. Findings from vadose zone investigations also have important regulatory ramifications for identifying sources of groundwater contamination.

Due to the importance of groundwater as a natural resource, a large number of studies on subsurface contamination were performed in the last decade. It became clear that there are significant uncertainties in the study of subsurface contaminations, especially those by toxic organic chemicals such as chlorinated solvents. These studies also highlighted the multidisciplinary nature of this particular environmental problem.

There are a number of recent reviews on this topic, each with different emphases (e.g., Jury and Flühler, 1992; Nielsen *et al.*, 1986; Schwille, 1984; USEPA, 1989, 1990, 1991). The present review contains a progressive discussion of important components and processes in the vadose zone environment for common one- and two-carbon chlorinated hydrocarbons (CHCs), such as tetrachloroethene (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (TCA), carbon tetrachloride (CT), and their precursors and/or degradation derivatives. These compounds are widely used as industrial solvents and are found in many contaminated aquifers. Because of the potential health effects of these toxic chemicals, their subsurface transport and fate processes elicit considerable regulatory interest.

II. MULTIPHASE DISTRIBUTION

Once introduced into the vadose zone, organic contaminants, including CHCs, gradually partition into different phases based on their physicochemical properties. Figure 1 illustrates a four-phase system in the vadose zone, consisting of soil solids, soil water, interstitial air, and nonaqueous phase liquid.

A. Nonaqueous-Phase Liquid

Nonaqueous-phase liquid (NAPL) refers to organic contaminants immiscible with water and that therefore exist in a purely organic phase in the subsurface environment. NAPL is usually further divided into “light” (INAPL) and “dense” (dNAPL), based on the specific gravity. All of the CHCs selected for this study fall into the category of “dense” NAPL.

In most of the leaking underground tanks, pipes, and surface spills, NAPL is the primary phase of contaminant being introduced to the subsurface. The presence of NAPL in the subsurface has several important consequences:

1. NAPL may migrate under the influence of gravity. The transport is affected by the multiphase interactions among NAPL, soil water and air, and the porous medium. Given time, NAPL may penetrate the vadose zone (or even saturated zone in the case of dNAPL) and reach the groundwater, where it serves as a continuous source of contamination, or the migration may cease before the NAPL front reaches the water table.

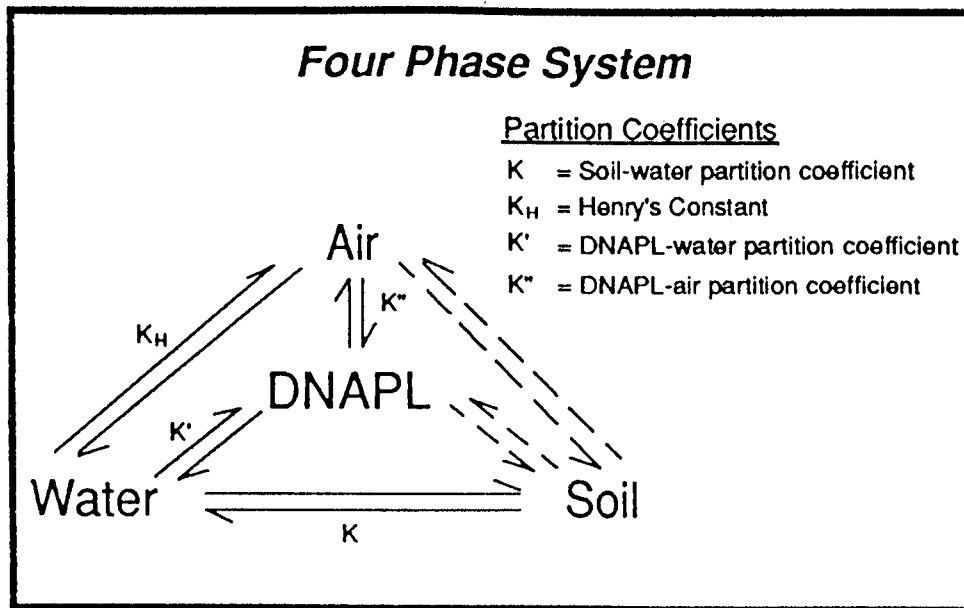


FIGURE 1. Distribution of chlorinated hydrocarbons in four phases in the Vadose Zone.

2. In the trail of NAPL migration, “blobs” or “ganglions” of NAPL are left in the vadose zone; these are called “residual saturation”. Schwille (1988) demonstrated the formation of NAPL blobs in an idealized situation using spherical glass beads. Hunt *et al.* (1988), on the other hand, discussed the immobilization of NAPL in the vadose zone through the counteraction of gravity and capillary forces, and presented a method for estimating NAPL ganglion dimensions. In a recent work, Conrad *et al.* (1992) focused on the visualization of residual organic liquid trapped in aquifers by fixing and isolating the chemically transformed NAPL blobs for physical observations. These residual saturations of NAPL act as a continuous source for vapor and dissolved-phase contaminant migration (Schwille, 1984, 1988).
3. The residual saturation of NAPL may occupy a relatively small volume in the vadose zone, but contains a disproportional mass of contaminants compared to other phases. These concentrated blobs and ganglions, which are heterogeneously distributed in the subsurface, represent a special problem to the detection, characterization, and remediation of soil contamination. A recent study by Poulsen and Kueper (1992) indicated that the heterogeneity of a pure PCE distribution in a sandy soil is dependent on source strength and the intrinsic properties of the porous medium; and the sample size required to obtain a true measurement of the distribution of residual satura-

tion is on the order of the scale of permeability variation, which, in their study, is millimeters.

B. Dissolved Phase

Dissolved CHC may either be directly discharged to the ground through various industrial activities that generate CHC containing waste water or be a result of the dissolution of dNAPL in the vadose zone. The extent of dissolution depends on the solubility and availability of CHC. Dissolved contaminants migrate with soil water, although these dissolved chemicals, or solutes, usually do not move as fast as water because of the many interactions to be discussed later.

C. Sorbed Phase

“Sorption” is a generic term describing a range of physicochemical interactions between organic contaminants and soil particle surfaces. Chiou (1989) used the term for uptake of a solute or vapor by soil regardless of mechanism, while “adsorption” means condensation of vapor or solute on the surface or interior pores of soil particles by physical or chemical forces, and “partition” describes a model in which the sorbed material essentially dissolves into the network of an organic phase (in the case of CHC sorption in the subsurface, the organic phase is usually organic matter on soil particles). Weber *et al.* (1991) presented detailed discussions of the basic principles at work in various forms of sorption phenomena.

Sorbed contaminant molecules are in effect retained by the soil particles. There is a dynamic equilibrium between contaminants in the sorbed phase and other phases. It is commonly believed that the majority of sorbed contaminants, based on Chiou’s (1989) definition, are partitioned into organic matter on soil particle surfaces, while a minor portion is adsorbed to inorganic or mineral surface features on soil particles (e.g., Bouchard *et al.*, 1989; Lee *et al.*, 1989; Piwoni and Banerjee, 1989).

On the whole, sorbed-phase contaminant may comprise a significant part of the total contaminant mass, depending on the organic carbon content of the soil and the physicochemical property of the CHC. Interactions between contaminants sorbed on the immobile soil matrix and those in the mobile phases significantly affect the transport rate of the contaminant in the subsurface.

D. Vapor Phase

Due to the high vapor pressure of the CHCs in question, a considerable portion of the contaminants may exist as vapor in the subsurface. The relative concentration of the vapor phase depends on the physicochemical properties of the compound.

Organic vapor is a highly mobile phase. It is able to spread laterally, mainly through diffusion, much more efficiently than NAPL or the dissolved phase. It can also migrate toward groundwater when NAPL or dissolved-phase migration has stopped. Because the vapor phase can be responsible for significant spreading of the contaminants, it must be incorporated into vadose zone transport analyses. Vapor-phase transport may also serve as a sink for subsurface contaminant molecules through emission to the atmosphere.

E. Other Phases

Other than NAPL, dissolved, sorbed, and vapor phases, some organic contaminant molecules may be present under conditions that do not allow easy classification. McCarthy and Zachara (1989) described various types of colloids (particles with diameters less than 10 μm) that may affect the transport of organic contaminants in the subsurface. These colloids may include macromolecular components of “dissolved” organic carbon, such as humic substances, microorganisms, microemulsions of NAPL, mineral precipitates, and rock and mineral fragments. Depending on the properties of the colloids, CHC and other organic contaminants may be sorbed onto colloids; nonetheless, in contrast to molecules sorbed to the solid matrix, these “sorbed” contaminants travel with the highly mobile colloids, therefore increasing the apparent rate of contaminant transport (Bouchard *et al.*, 1989; McCarthy and Zachara, 1989).

Although McCarthy and Zachara (1989) focused mainly on the effects of colloids in contaminant transport in groundwater, similar effects are expected in the vadose zone. Due to difficulties in sampling and lack of basic information about colloids, the precise effect of colloids on subsurface contaminant transport remains to be determined. In the following discussion, colloids are not considered.

III. INTERPHASE PROCESSES

CHC molecules in various phases are in a dynamic equilibrium condition, although this theoretical equilibrium state may never be attained in the real world because the vadose zone is never a real closed system, and there are large differences in the kinetics of various processes. These interphase processes are affected by geologic properties of the vadose zone, the physicochemical properties of CHC, and environmental factors such as temperature.

A. Multimedia Partitioning

Figure 2 is a diagrammatic presentation of the six interactions among the four phases existing in the vadose zone. However, only four of the six are studied

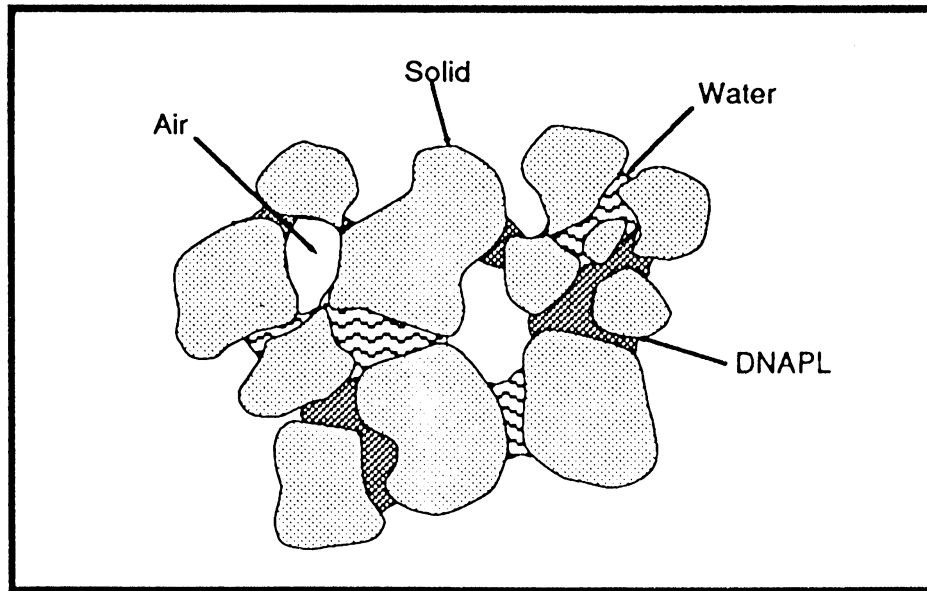


FIGURE 2. Interactions among chlorinated hydrocarbons in four phases in the Vadose Zone.

intensively, mainly because of the widely accepted assumption that soil particles are always surrounded by a layer of water, which is usually true except in the topsoil of arid or semiarid regions; therefore, all interactions with soil particles must first go through soil water.

B. NAPL-Water

The distribution of CHC between NAPL and water depends on the solubility of the compound. Most of the one- to two-carbon CHCs have relatively low water solubility compared to other organic compounds. Another way to express the interaction between these two phases is a NAPL-water partition coefficient. This is almost always a net one-way process from NAPL (pure CHC) to dissolved CHC because the reverse direction is thermodynamically unfavorable. Powers *et al.* (1991) reported that nonequilibrium dissolution of NAPL may have a significant effect on subsurface contaminant transport.

C. NAPL-Air

CHC molecules volatilize from NAPL to the vapor phase based on the vapor pressure of the particular compound. The relationship can also be expressed with

a NAPL-air partition coefficient. Again, this is a mostly net one-way process from NAPL to volatilized CHC dictated by thermodynamics.

D. Water-Solid

This is probably the most researched interphase interaction because the water-solid interaction (sorption) determines the retardation of organic contaminant migration relative to water, which is a very important factor to be considered in subsurface transport studies, including computer simulations (Priddle and Jackson, 1991).

CHCs distribute themselves between the dissolved and sorbed phases according to a sorption coefficient (sometimes called partition coefficient), which is the ratio of the CHC concentration sorbed to solid to the concentration dissolved in water. Contrary to the above two interactions, because this one does not involve pure CHC, the process is usually two way, i.e., a net CHC transfer to either water or the solid phase is possible as long as the concentration ratio in the two phases is favorable to the transfer direction.

Numerous studies were performed on this process to resolve uncertainties such as:

1. Microscopically, the basic mechanisms of sorption are complicated and not well known (Chiou, 1989; Mokrauer and Kosson, 1989; Mingelgrin and Prost, 1989; Weber *et al.*, 1991; Zielke *et al.*, 1989). Weber *et al.* (1992) even devised a composite model just to simulate the sorption behavior. As mentioned earlier, the current assumption is that most of the sorption is due to organic matter on the soil particle surface, while the contribution of the mineral surface is minor. However, other mechanisms have been proposed, and some experimental results apparently contradict the prevalent assumption, especially in soil with very little organic matter (Pavlostathis and Jaglal, 1991).
2. Macroscopically, the sorption phenomena are complicated in the sense that they are nonlinear and nonequilibrium, and the kinetics are also complicated (Bouchard *et al.*, 1988; Piwoni and Banerjee, 1989; Voice and Weber, 1985).
3. Sorption and desorption may not follow the same kinetics (Pavlostathis and Jaglal, 1991; Pavlostathis and Mathavan, 1992; Szecsody and Bales, 1989).
4. Sorption is compound specific. Although there have been attempts to formulate prediction methods for the sorption coefficient, many uncertainties remain (Bahnick and Doucette, 1988; Woodburn *et al.*, 1986).
5. The presence of more than one organic contaminant results in cosolvent effects that are usually hard to predict from the sorption behavior of individual compounds (Rao *et al.*, 1990; Brusseau *et al.*, 1991).

6. The water-solid interaction involves the soil matrix, which is heterogeneous and site specific (Ball and Roberts, 1991a, b). Besides, the exposure history of the soil matrix to other organic compounds may significantly change the sorption phenomenon (Boyd and Sun, 1990; Lee *et al.*, 1989).

E. Water-Air

The coefficient that describes the concentration ratio in air and water is called Henry's law constant. This process is usually two way. Compared with the water-solid interaction, the mechanism behind the water-air process is relatively simple. Although Henry's law constants are also compound specific and are subject to cosolvent effects, they are more predictable than the sorption coefficients.

F. Other Interactions

The two interphase processes not covered in the above discussions are soil-air and soil-NAPL. Some research has been done on the soil-air interactions for soil in arid or semiarid conditions (Ong and Lion, 1991a, b; Peterson *et al.*, 1988). Strong direct sorption of CHC to soil matrix has been demonstrated; however, slight increases in soil moisture drastically reduce CHC sorption, possibly because of competition for binding sites on soil particles (Chiou and Shoup, 1985; Ong and Lion, 1991a; Smith *et al.*, 1990). This limits the relevancy of the information because, except for very dry soils, e.g., exposed topsoil in arid areas, these direct soil-air interactions may be overshadowed by indirect processes through soil water. There are very few studies on soil-NAPL interactions except for residual saturation retention in soil, as discussed earlier.

IV. TRANSPORT PROCESSES

This section superimposes transport processes onto the interactive multimedia (soil matrix, water, and air) and multiphase (NAPL, dissolved, sorbed, and vapor) scenario.

A. Fluid Flow In a Porous Medium

The flow of water in the vadose zone is dominated by gravity. Nonturbulent water flow in a porous medium is described by Darcy's equation, which describes the flow velocity through a porous medium as proportional to the difference in hydraulic head across a unit distance. The proportionality constant in Darcy's equation

(hydraulic conductivity) is a function of the porous medium characteristics and the fluid properties. The equation is based on the assumption of a homogeneous, isotropic (uniform properties in all directions from a given point), porous medium with an infinite horizontal boundary.

B. Unsaturated Flow

The unsaturated condition in the vadose zone complicates the flow problem by introducing the air phase. Air occupies a portion of the pore space in the vadose zone; therefore, not all the pore space is available for water flow. Most of the early attempts at solving the unsaturated flow problem treated the air phase as a part of the immobile porous medium. However, since air is also a fluid, it can flow simultaneously, and many times countercurrently, with water and should be considered in the unsaturated flow system (Vauclin, 1989). Unsaturated flow should be viewed as a multiphase flow with two fluid components.

The most important properties that determine unsaturated flow are the water content and hydraulic conductivity of the porous medium (Nielsen *et al.*, 1986; Rawls and Brakensiek, 1989). The hydraulic conductivity in the vadose zone is a function of the water content, which is the portion of void space occupied by water, and thus available for water flow. Even in a relatively homogeneous geologic medium, the water content and hydraulic conductivity are actually never constant, but vary spatially with the microscopic heterogeneity of soil, and temporally. Therefore, unsaturated flow is almost impossible to describe exactly on a microscopic scale, although average values of those two parameters may be estimated for a specific site and used to simulate the flow behavior macroscopically.

C. Unsaturated Flow with Geologic Heterogeneity

In addition to the problem of unsaturated flow, the real vadose zone is never homogeneous. The heterogeneity of the vadose zone is very site specific and adds a stochastic factor to the unsaturated flow in the vadose zone (Jury *et al.*, 1987a, b; Russo, 1991).

The heterogeneity not only arises from variations in soil grain and pore sizes, but also from the presence of macropores due to soil structure (soil aggregation) and plant and animal activities. These macropores create conduits for fluid migration. Water essentially passes freely through these macropores. Many studies were performed to describe and investigate this phenomenon (e.g., Edwards *et al.*, 1988; Richard and Steenhuis, 1988; Simpson and Cunningham, 1982).

Even in relatively homogeneous soils, “fingers” of rapid flow paths are formed once water is introduced at the surface (Glass *et al.*, 1988; Richard and Steenhuis, 1988). This “fingering” phenomenon is initiated by the liquid wetting-front in-

stability and is chaotic and unpredictable. Once formed, these fingers provide pathways that are already “wetted”, and thus are less resistant to water flow. This usually shortens the time for water to penetrate a certain soil layer based on prediction of normal unsaturated flow. Fingering was even observed in carefully packed homogeneous sand in sand box experiments (Schwille, 1988). The macropores and fingering phenomena are usually referred to as preferential flow in the vadose zone.

Various groups have conducted field studies on unsaturated flow using nonreactive solutes, or tracers. These studies generated valuable field data that were used to verify various theoretical works and provide a valuable field work viewpoint (e.g., Butters and Jury 1989; Butters *et al.*, 1989; Ghodrati and Jury, 1992; Roth *et al.*, 1991). In one of the recent publications, Roth *et al.* (1991) concluded that “[a]t present time, we do not see any viable alternative to carrying out an actual tracer experiment” to crudely estimate “the velocity with which a chemical would move in a given soil”, which, in a sense, summarizes our current knowledge, or the lack of it, about unsaturated flow.

In summary, a more accurate description of vadose zone water flow must be based on multiphase flow and include the stochastic factor of natural variation of soil properties. Even then, the chaotic phenomenon of preferential flow may still evade description or prediction.

D. Basis of Contaminant Transport Phenomena

Discussions in the previous three sections dealt only with water flow in the vadose zone. Now the contaminants are introduced to the transport process. The main driving forces behind subsurface contaminant transport are diffusion and advection.

1. Molecular Brownian motion is the basis of diffusion of organic contaminants. Diffusion tends to move contaminant molecules from high-concentration regions to relatively low-concentration regions.
2. Advection is a collective term for contaminant movement originating from extramolecular forces. Gravity is the single most important origin of advective force. The prevalent direction of advection in the vadose zone is downward; gravity can also exert its effect indirectly through other physical properties of subsurface substances, such as density or pressure gradients. In the case of groundwater flow, advection appears in the form of hydraulic head, which usually had a significant horizontal component. An artificial disturbance such as pumping can generate advection totally against natural gradients.

The manifestation of these two basic transport processes in a porous medium creates another fundamental transport phenomenon —hydrodynamic dispersion.

Dispersion results from physical interactions between substances moving under the influence of advection or diffusion and the porous structure of the medium. Advection usually dominates hydrodynamic dispersion except in very low-velocity scenarios, where diffusion may be the predominant mechanism.

Dispersion basically is mechanical mixing that results in the spreading and dilution of molecules. The molecular basis of dispersion includes:

1. Differences in velocity within a single soil pore due to surface drag
2. Differences in bulk fluid velocity in soil pores with different pore size and surface features
3. Differences in travel time for molecules taking different pathways with varying lengths due to tortuosity and branching of pore space (Freeze and Cherry, 1979)

The term “solute transport” is commonly used to describe the migration of the dissolved contaminant, or the solute, in contrast to the unretarded flow of soil water. However, the general term “contaminant transport” may be more appropriate to include contaminant migration in all mobile phases.

E. Unsaturated Flow with Geologic Heterogeneity and Multiphase Fluids

Among the multiphase contaminants described earlier (i.e., NAPL, dissolved sorbed, and vapor phases), the sorbed phase is the only nonmobile one, while the other three phases are capable of their own migration:

1. NAPL can migrate by gravity as a separate liquid phase once introduced into the subsurface in a significant amount (large enough to overcome the initial capillary retention) (Schwille, 1984). Some illuminating experiments conducted by Schwille (1988) demonstrated that NAPL takes tortuous, and many times, preferential pathways through the vadose zone. NAPL “fingering” is very common. NAPL migration is usually a relatively short-term process for a one-time spill. Schwille (1988) reported vadose zone penetration by NAPL on the order of minutes to hours in experiments using a sand box about 1.6 m in height. A recent field study by Poulsen and Kueper (1992) using dyed PCE reported similar observations. NAPL flow may also be continuous if there is a continuous source of NAPL (e.g., a leaking storage tank). The behavior of NAPL flow remains an active area of research.
2. Dissolved contaminants essentially migrate with soil water. For simplicity, interactions with the immobile sorbed phase are neglected for the time

being, but are discussed in a later section. Water movement in the vadose zone is dominated by gravitational advection; diffusion is relatively minor in comparison.

3. Contaminants in the vapor phase can move with soil air as another mobile fluid, by both diffusion and advection, although the more prominent movement will probably be diffusion of the CHC vapor in various directions. In some instances, CHC vapor originating from a geographically limited discharge may be spread by the vapor phase and cause serious groundwater contamination (Baehr, 1987; Mendoza and McAlary, 1990). When the CHC vapor concentration is high, e.g., in areas near a NAPL source, the dense vapor “cloud” may move as a fluid independent of soil air in a density-driven flow because the saturation vapor density of the CHC in question is higher than average soil air. This dense vapor flow is another route for contaminants to reach groundwater (Falta *et al.*, 1989; Mendoza and Frind, 1990a, b; Schwille, 1988; Sleep and Sykes, 1989a, b).

In summary, it is possible to have a maximum of four different fluids (i.e., NAPL, soil water with dissolved CHC, soil air with volatilized CHC, and dense CHC vapor) flowing simultaneously in the vadose zone, although for a one-time spill, the situation is likely to reduce to a three-fluid flow (i.e., contaminated soil water, soil air, and possibly dense vapor, depending on the quantity of residual saturation) when the NAPL flow ceases in a relatively short period of time. For a non-NAPL source (i.e., dissolved CHC source), it is most likely to have only the contaminated soil water and soil air flow.

All these fluids are subject to similar hydraulic and geologic conditions described for soil water in previous sections, and each of these fluids simultaneously affects the flow of others by occupying pore space and excluding other fluids. Multiphase flow is a highly temporal and spatially dependent process that is difficult to describe or predict.

F. Unsaturated Flow with Geologic Heterogeneity, Multiphase Fluids, and Interactions with Soil Matrix

Finally, the interphase interactions must be added to the dynamic transport system. A large amount of research was performed in the area of contaminant sorption mainly because of its critical role in determining the transport of contaminants through soil. A “retardation factor” is usually derived from the sorption characteristics of a certain organic contaminant to estimate the retardation in movement in relation to water (e.g., Priddle and Jackson, 1991). Due to the heavy dependency of the sorption phenomena on site-specific soil properties, and the nonlinearity or nonequilibrium of some sorption phenomena (e.g., Bouchard *et al.*, 1988; Voice

and Weber, 1985), sorption of organic contaminant in the subsurface environment remains an active area of research.

There have also been some studies on the retardation of contaminants in the vapor phase. “Vapor-phase retardation factors”, which are analogous to the dissolved-phase factors, are calculated on the basis of coupled air-water/water-solid interphase processes (e.g., Falta *et al.*, 1989; Mendoza and Frind, 1990a). As for NAPL flow, there has not been much research integrating flow and interphase processes.

It is obvious that the complexity of vadose zone contaminant transport demands a tremendous amount of simultaneous process integration. However, before proceeding to process integration, the fate processes must be addressed.

V. FATE PROCESSES — BIOTRANSFORMATION

In the current study, “fate processes” mainly refer to biochemical (biotic) and chemical (abiotic) transformations, rather than changes in physical states, although evaporation is discussed later as one of the sinks for CHC in the vadose zone.

A. Current Research Approaches

Natural degradation of CHCs is relatively less understood than transport processes, probably because CHCs are rather recalcitrant to degradation. Many recent studies on CHC fate processes are driven by the potential of bioremediation of contaminated groundwater. Because of this, and considerations of experimental design, almost all of the studies reviewed below were conducted under saturated conditions.

These studies essentially fall into one of the following categories:

1. Laboratory batch experiments, where microbes are exposed to CHC in a completely controlled environments
2. Column or bench-scale degradation studies, where microbes already proven capable of degrading certain CHCs by laboratory experiments are tested in pilot systems designed to remediate contaminated groundwater
3. Field studies. These studies apply microbes to field situations for groundwater remediation. Many engineering and hydrogeologic considerations are involved. There are relatively few studies in this category because of obvious limitations of resources and regulatory considerations.

Although all of these studies were performed in the saturated zone, it is reasonable to expect similar reactions to occur in the vadose zone, provided essential

elements such as water, nutrients, pH, redox potential, and availability of proper microbes are fulfilled.

Regarding the potential of biodegradation of CHC in the vadose zone, a group of scientists actively working on CHC bioremediation stated that (McCarty *et al.*, 1991):

1. There is little field evidence of CHC biodegradation in the vadose zone.
2. There are very few studies on the abundance of microbes capable of degrading CHCs in the vadose zone.
3. It was postulated that CHC biodegradation in the vadose zone, if it occurs, would be less active than in the saturated zone, mainly because of water availability.
4. Anaerobic CHC biodegradation would be quite unlikely in the vadose zone, except possibly for some anoxic pockets.

On the other hand, research on the agricultural application of pesticides indicated that some pesticides degrade rather rapidly in soil, with environmental half-lives ranging from days to months (e.g., July *et al.*, 1987; McLean *et al.*, 1988; Rao *et al.*, 1985; Steenhuis and Naylor, 1987). Many of these pesticides are also chlorinated hydrocarbons; for example, Aldrin, Chlordane, DDT, Endrin, Heptachlor, Lindane, Toxaphene, and chlorophenoxy herbicides, such as 2,4-D and 2,4,5-T, are all chlorinated aromatic or polycyclic compounds (Manahan, 1984). Although these pesticide degradations may be a combination of abiotic and biotic processes, these studies demonstrated that fate processes of CHC in the subsurface environment must be considered.

B. Mechanisms and Microbes

It is beyond the scope of this review to go into the details of the mechanisms and kinetics of CHC biodegradation. There are a number of recent review articles covering these topics (Alexander and Scow, 1989; Baxter, 1989; Kuhn and Suflita, 1989; Vogel *et al.*, 1987; Wood *et al.*, 1985), and many of the mechanisms are still under active research.

The most critical step in biodegrading CHC is dechlorination, or, using a broader term, dehalogenation. For the one- and two-carbon CHCs, the subject of the current review, the carbon skeletons are chemically simple and pose little problem to microbial consumption. The hindrance comes from the chlorine (or other halogen) attached to the carbon atoms. Therefore, most of the biodegradation studies for CHC have focused on the process of dehalogenation; for multihalogenated compounds, the study of degradation is essentially a study of sequential dehalogenation.

Because multichlorinated CHCs are in a relatively oxidized state, they are most susceptible to reductive dehalogenation. A prominent example is the sequential

dechlorination of chlorinated ethenes by methanogenic consortia (Baek and Jaffe, 1989; Bouwer *et al.*, 1981; Freedman and Gossett, 1989, Vogel and McCarty, 1985). On the other hand, oxidative degradation is also possible; for example, oxidation of trichloroethene and other CHCs by methanotrophs is well documented (Alvarez-Cohen and McCarty, 1991 (**Au: which refs?**); Oldenhuis *et al.*, 1989; Strandberg *et al.*, 1989; Tsien *et al.*, 1989). Some of these microbes do not utilize CHCs as their primary substrate, but rather cometabolize them fortuitously due to some of their less substrate-specific enzymes (Alvarez-Cohen and McCarty, 1991a, b, c; Oldenhuis *et al.*, 1989; Zylstra *et al.*, 1989). However, exactly how much of the degradation is due to cometabolism is usually not clear (McCarty, 1988).

A whole range of microorganisms (single species and mixed cultures) are capable of degrading CHC under laboratory conditions. A brief review of articles published in one of the journals in environmental microbiology during 1989–1990 indicated quite a number of experimental reports using PCE or TCE as parent compounds. Within that time frame, at least six different bacterial species were reported to degrade TCE to different degrees (Harker and Kim, 1990; Oldenhuis *et al.*, 1989; Tsien *et al.*, 1989; Wackett *et al.*, 1989; Zylstra *et al.*, 1989). Other TCE or PCE degradation studies used mixed cultures, such as methanogenic consortia (Baek and Jaffe, 1989; Bouwer *et al.*, 1981; Freedman and Gossett, 1989; Vogel and McCarty, 1985), a sulfate-reducing enrichment culture (Bagley and Gossett, 1990), and a methanotrophic consortium (Strandberg *et al.*, 1989). Most of these experiments reported reductive dehalogenation of the chlorinated ethenes under anaerobic conditions. One notable exception is the experiment on the methanotrophic consortium, which was aerobic in nature.

Another group of studies focused on the one-carbon CHCs. Experiments demonstrated anaerobic biodegradation of CT (Criddle *et al.*, 1990a, b) and chloroform (CF) (Mikesell and Boyd, 1990).

It is well established that the following reductive dehalogenation sequences exist for the CHCs that are the subject of the present study (Baxter, 1989; Wood *et al.*, 1985; Vogel *et al.*, 1987):

Tetrachloroethene → trichloroethene → dichloroethenes
→ vinyl chloride →→ carbon dioxide

Trichloroethane → dichloroethane → chloroethane →→ carbon dioxide

Carbon tetrachloride → chloroform → methylene chloride → chloromethane
→→ carbon dioxide

C. Field Evidence of Naturally Occurring Biotransformation and Field Application of Bioremediation

There is abundant evidence that CHCs are actually degraded through biological processes in the subsurface environment. In fact, some of the laboratory degradation experiments utilized contaminated aquifer materials (e.g., Davis and Carpen-

ter, 1990; Parson and Lage, 1985; Parson *et al.*, 1984; Sewell and Gibson, 1991), soil (Kleopfer *et al.*, 1985), or ground water (Kastner, 1991) to demonstrate microbial degradation by indigenous microbial communities. Additional evidence of degradation of CHCs in the subsurface environment comes from analyses of CHC-contaminated groundwater, which usually show the contaminants and their degradation intermediates.

Results of these experiments are indirect but show convincing evidence of naturally occurring biodegradation. Although most of these data come from the saturated zone, it is reasonable to believe that similar biodegradation may also be occurring naturally in the vadose zone.

Moreover, recent field bioremediation studies demonstrated that these biodegradation processes can be utilized effectively for the remediation of groundwater contaminated by chlorinated ethenes (Semprini and McCarty, 1991, 1992; Semprini *et al.*, 1991).

D. Essential Elements and Other Considerations for Biotransformation

Many other factors must be considered before the knowledge about biodegradation can be utilized in the study of the fate and transport of CHC in the vadose zone:

1. The distribution of these microbes in the subsurface environment is heterogeneous and site specific (Federle *et al.*, 1986). Moreover, microbes may have their own subsurface transport and fate processes (Yates and Yates, 1988).
2. The availability and distribution of water, oxygen, and other nutrients, including primary substrates, can determine the microbial activity.
3. The forms and concentration of CHC available to microbes are also important. High concentrations of CHC may have toxic effects on microbes; direct microbial attack on NAPL is therefore quite unlikely. On the other hand, if the concentrations are too low, the microbes may not be able to utilize the CHC efficiently. Because most of the studies on biodegradation were performed under saturated conditions, it is unknown whether microorganisms can effectively utilize CHC in the vapor phase, although a recent study indicated significant degradation of vapor-phase petroleum fuel products in the vadose zone (Ostendorf and Kampbell, 1991).
4. The bioavailability and distribution of CHCs must be considered. Obviously, the contaminant must be accessible to the microbes before they can be degraded. This is especially important in the unsaturated zone, where contaminant distribution patterns and transport processes may not allow easy contact between microbes and CHCs.

VI. FATE PROCESSES — ABIOTIC TRANSFORMATION

Compared with biodegradation, abiotic transformation is less amenable to manipulation and therefore is less promising as a remediation alternative. This may be one of the reasons that abiotic transformation of CHC is not well understood compared with biotic processes. However, it is actually very difficult to differentiate biotic and abiotic transformations under field conditions, and there is evidence that at least some CHCs may undergo significant abiotic transformation within the time frame of subsurface migration. Unfortunately, most of the information available for abiotic transformation of CHCs pertains to saturated conditions, while the limited information for the vadose zone is mainly from pesticide fate and transport research.

A. Homogeneous Reactions — Hydrolysis

Hydrolysis in aqueous solution is probably the most prominent abiotic transformation in the subsurface environment. Wolfe *et al.* (1989) presented a review of the hydrolytic transformation of organic chemicals in the environment, and various factors that may affect the rate of reaction. They mentioned that sediments and soils are also important sites for hydrolysis; however, the reaction kinetics are different from those in a water column.

Jeffers *et al.* (1989) published homogeneous hydrolysis rate constants for 18 chlorinated methanes, ethanes, ethenes, and propanes. The calculated environmental half-lives range from days to centuries. The review by Vogel *et al.* (1987) reported similar figures for abiotic hydrolysis and dehydrohalogenation.

Barbash and Reinhard (1989) investigated the hydrolysis of 1,2-dichloroethane (1,2-DCA) and 1,2-dibromoethane and found that the presence of hydrogen sulfide facilitates the abiotic transformation rate. Roberts *et al.* (1990) reported a similar enhancement effect by sulfur (2-) species not only for hydrolysis, but also for other dehalogenation processes.

As for abiotic transformation of CHCs (in groundwater), Vogel and McCarty (1987) reported dehydrohalogenation of 1,1,1-TCA to 1,1-dichloroethene (1,1-DCE), and Cooper *et al.* (1987) reported a similar transformation of 1,1,2,2-tetrachloroethane to 1,1,2-TCE.

B. Heterogeneous Reactions — Surface Reactions on Clay Minerals

Basically all of the homogeneous abiotic transformation processes occur in the liquid phase. Although it can be assumed that the same reactions also take place in soil water retained in the vadose zone, one must also take into account the solid phase, which “introduce[s] the potential for heterogeneous reaction kinetics and thus greater complexity” (Wolfe, 1989).

An important category of abiotic transformation is surface related. Mingelgrin and Prost (1989) pointed out that some abiotic reactions occur in the interface between phases, including “heterogeneously catalyzed reactions and reactions which occur in that part of the liquid phase which is under the influence of the electric field existing near charged surfaces.”

There is very little information on CHC interaction with clay surfaces; however, due to practical necessity, some research was done for agricultural application of pesticides. Pesticides are applied to soil intentionally and need to persist in soil for a period of time to provide prolonged protection to crops, but not so long as to threaten groundwater quality. Their biotic or abiotic transformation in soil is of concern to agricultural scientists. Three recent reviews (Saltzman and Mingelgrin, 1984; Mingelgrin and Prost, 1989; Zielke *et al.*, 1989) summarized various aspects of mineral surface chemistry that may affect the fate of organic chemicals in the subsurface environment. The two most important types of interactions are sorption-desorption and surface-enhanced transformations. Thus, an uncertain area that cannot be neglected is the contribution of clay mineral surfaces to abiotic transformation of CHC in the vadose zone.

C. Other Abiotic Reactions and Evaporation at Ground Surface

In addition to hydrolysis and possibly other surface-related abiotic transformations in the vadose zone, certain photochemical reactions occur at the interface of atmosphere and soil. Although volatilization is a transport rather than a fate process, CHC volatilization at the soil-atmosphere interface is also discussed here because it can be considered a sink for CHCs at the soil surface.

In a recent review, Miller *et al.* (1989) discussed the importance of considering photolysis at the atmosphere-soil interface, which includes:

1. Photooxidation through free radicals including oxygen radical formation and subsequent reactions; in particular, organic matter and minerals in the soil photocatalyzed the production of singlet oxygen which may then react with other compounds.
2. Photoreduction, including photodechlorination was also reported for dioxin compounds.

Miller *et al.* (1989) also mentioned that, in general, solar radiation has a direct effect on soil surface temperature and moisture, which can in turn exert indirect effects on other degradation processes. However, the exact results of these are not well understood.

Miller *et al.* (1989) proposed that the effects of photolysis reactions may only affect a very thin layer of soil (e.g., <1 mm for the experiment cited in the article). Nonetheless, for surface application or spill, the atmosphere-soil interface is usu-

ally where the highest concentrations of organic contaminants are found; therefore the role of photolysis may be important.

On the other hand, volatilization has been studied by agricultural scientists as the major pathway of volatile or semivolatile pesticide loss after surface application (Jury *et al.*, 1983, 1984a, b, c, 1987, 1990; Spencer *et al.*, 1988). The importance of volatilization as a migration pathway for organic contaminants in the vadose zone relies on the vapor pressure of the compound, and the ground surface features. In the case of semivolatile pesticides with moderate volatility, volatilization is enhanced by the evaporation of water in bare fields, which brings the pesticides along and accumulates the compounds near the soil surface. This increase in shallow concentration eventually results in a significant release of the compound into the atmosphere.

Although the ground is usually paved and without vegetation in industrialized areas where most CHCs are used, the importance for photolysis and volatilization as a sink for CHCs may be comparable to that of pesticides in cases where spilled solvents run off the edges of pavement onto some adjacent unpaved areas. However, when the CHC spills are limited to paved areas, the situation may be quite different. Before the CHCs penetrate the pavement, the relatively impermeable layer enhances photolysis and volatilization by prolonging the exposure of CHCs to sunlight and the atmosphere; however, once a portion of the contaminants starts to permeate the pavement, it serves as a barrier to further loss to the atmosphere or photochemical reactions. The fact that most of the industrialized areas are paved and without vegetation also eliminates evapotranspiration as a driving force to bring CHC in soil to the surface.

VII. PROCESS INTEGRATION

Even such simplified discussion of the transport and fate of CHCs in the vadose zone presented in the previous sections demonstrated that an attempt to integrate these processes is a formidable task. Most of the recent efforts have concentrated on developing computer simulation models that can integrate various processes so as to describe and eventually predict the subsurface behavior of CHCs. A comprehensive discussion of vadose modeling is obviously beyond the scope of this work, but the following is an attempt to discuss the general trend of the modeling effort and, most importantly, the limitations and relevancy to real-world subsurface investigation, remediation, and regulation.

A. Modeling Approaches — Deterministic vs. Stochastic

A number of informative reviews of solute transport modeling have been published in recent years (Addiscott and Wagenet, 1985; Bonazountas, 1991; Hern and Melancon, 1986; Jury and Flühler, 1992; Jury and Ghodrati, 1989; Khondaker *et al.*, 1990;

Loague and Green, 1991; Nielsen *et al.*, 1990; Naymik, 1987; van Genuchten and Shouse, 1989).

The earlier solute transport models adopted a deterministic approach based on advection, diffusion, and dispersion equations (or convection-dispersion equation, CDE). Other modifications were later added to account for unsaturated flow characteristics. However, this approach alone was found to be inadequate to address the geologic heterogeneity and many nonequilibrium processes. Subsequently, stochastic parameters relying on a statistical distribution, instead of fixed parameters, were added to CDE models to provide a better description. Recently, stochastic models were developed in addition to deterministic CDE models. Some stochastic models lump processes that are hard to simulate numerically into transfer functions without regard to details of the processes.

Most of the contaminant interphase, physicochemical interactions discussed above can be incorporated into the modeling effort to different extents, depending on the current knowledge of the process and the purpose of the model. Biotic and abiotic transformations are usually lumped together in the form of a “first-order kinetic”-type equation. There are also separate efforts to develop multiphase flow models describing the flow of NAPL (Pinder and Abriola, 1986) and density-driven vapor migration (Mendoza and Frind, 1990a, b; Falta *et al.*, 1989; Sleep and Sykes, 1989a, b).

Most of the early contaminant transport models started off with a one-dimensional and single, conservative (nonreactive) solute. Now, some of the models are up to three-dimensional, and some can handle more than one reactive solute.

Jury and Ghodrati (1989) adopted a classification of management model, screening model, and simulation model, which represent different levels of complexity and use. Management models are essentially practical tools with many simplifying assumptions. They may be as simple as correlations among soil types, irrigation practices, and predicted depth of pesticide migration. Screening models (e.g., Jury *et al.*, 1983, 1984, a, b, c), assume an ideal scenario and compare the behavior of various contaminants and their relative potential of impacting groundwater so attention can be focused on those compounds with the highest contamination potential. All of the solute transport models discussed above are simulation models, the most complicated category, which are targeted to simulate the actual transport and fate processes by equations and numerical techniques.

The complexity of these models depends on the intended use. However, all models are basically a selectively simplified presentation of the real world, and are far from perfectly describing, *let alone* predicting, the real processes. For example, no model can simulate preferential flow, which is site-specific and virtually unpredictable.

B. Assumptions, Uncertainties, and Applicability of Models

All of the review articles cited in the previous section discussed model assumptions, some of which were oversimplified, and process uncertainties in solute

transport modeling. An understanding of these limiting factors is crucial for proper use of the models:

1. Heterogeneous porous medium. This is already addressed in various places in this paper, and there are many recent efforts to replace the homogeneous assumption in earlier models and address the heterogeneity of the natural soil.
2. Nonlinear sorption. Many of the models assumed linear sorption; however, it is known that sorption is highly temperature dependent, and there is evidence that it may also be concentration dependent (Voice and Weber, 1985).
3. Nonequilibrium sorption. The common assumption of instantaneous sorption equilibrium is inaccurate (Bouchard, 1989; Bouchard *et al.*, 1989, 1992).
4. Hysteresis of sorption-desorption. Various authors have pointed out that the sorption and desorption of CHC from soil have different kinetics (Jury and Ghodrati, 1989; Pavlostathis and Jaglal, 1991; Pavlostathis and Mathavan, 1992).
5. In the presence of NAPL, the dissolution cannot always be assumed to be in equilibrium (Powers *et al.*, 1991). In fact, very little is known about NAPL flow in general and the possible interactions in a multiphase flow situation.
6. Most of the models that include degradation terms usually did not differentiate biotic and abiotic transformations and “assumed” first-order kinetics which actually did not have any physical basis. The real kinetics of biodegradation is always much more complicated (Alexander and Scow, 1989).
7. Most of the existing models do not have the capability to deal with multiple solutes. This capability is crucial because of common mixed discharges and that transformation processes that introduce additional CHC species into the subsurface transport scenario with time.

These are a few of the more prominent problems either not or only partially addressed in current models. Some of these may turn out to be negligible in a practical model; however, for many of the problems stated above, we do not even have enough information to make that determination.

On the other hand, many of the complex models face the problem of unmeasurable parameters crucial to the operation of the model. In order to obtain these parameters, the models are “calibrated” by adjusting parameter values based on specific site conditions to achieve an acceptable simulation. However, whether the model can be “validated” by simulating a second set of field data without altering any parameter is usually doubtful.

A recent USEPA document (1989) stated the importance of “site-specific characterization of the influences of various natural [hydrogeological, chemical, and microbiological] processes by detailed field and laboratory investigations.” It also emphasized rigorous quality control for data used for model inputs and warned that lack of natural process parameters might result in qualitatively and quantitatively incorrect field applications of models.

VIII. REGULATORY IMPLICATIONS

Important areas of regulatory implications are discussed below:

A. Site Investigation

Knowledge of vadose zone processes allows a better design and implementation of the site investigation plan. It also enhances the interpretation of site data. The following items should be considered when performing investigation at CHC-contaminated sites:

1. Site geologic heterogeneity is critical to evaluation of contaminant transport. Although it is practically impossible to collect sufficient data to accurately define fluid movement in the vadose zone, adequate sampling must be conducted to reveal major lithologic units and hopefully to indicate the presence of structures, such as macropores, that may significantly affect contaminant migration.
2. The dissolved phase may not be the only mobile form of CHC in the subsurface. In other words, water is not necessary for CHC migration. NAPL can migrate alone by gravity, and volatile CHCs can move efficiently in vapor form. Therefore, even if a hazardous waste site is capped by water-impermeable material, CHC migration will not necessarily stop. Site investigation must not neglect areas that are supposedly without water percolation as the “driving force”.
3. Measurement of vapor-phase CHC must be incorporated as an integral part of site investigation because vapor may represent a significant portion of the contaminant mass for volatile CHCs and may be responsible for rapid contaminant migration.
4. Possible degradation products must be measured in vadose zone samples. Some of the daughter products are more toxic than the parent compounds.
5. Due to site variability and practical limitations of vadose zone sampling, vadose zone data alone usually are not adequate for ensuring protection of

the groundwater underlying CHC-contaminated sites. Groundwater should always be sampled except in cases where vadose zone contamination is determined to be negligible, considering particular site conditions such as soil type, depth to groundwater, presence of preferential pathways, etc.

B. Site Remediation

Another prominent regulatory application of vadose zone transport of CHCs is remediation of hazardous waste sites, where CHC contamination threatens human health and/or natural resources, usually groundwater. Knowledge of vadose zone transport helps regulators determine whether remedial effort is required at a certain site, and if so, when it should be considered complete.

The development of simulation models definitely increases our knowledge and the power to predict subsurface contaminant transport in this respect. Models are now frequently used for justifying the choice of remedial alternatives (including “no action”) and the remediation end point. Models are also used as an aid to data reduction and interpretation, and to provide a structure for organizing and analyzing field data (USEPA, 1988). Although these modeling exercises cannot accurately predict the contaminant transport or account for site-specific heterogeneity, they can provide reasonable estimates of contaminant behavior, which are invaluable to regulatory decision-making.

In view of the uncertainties of the vadose zone transport and fate processes discussed above, it is crucial to include proper monitoring components in all such model-based remediation efforts. This usually involves monitoring groundwater quality at strategic locations to ensure that the choice of remediation alternative is appropriate and/or the remedial effort adequate. It should also include vadose zone monitoring and/or confirmatory sampling to verify modeling results. Because the goal in these cases is protection of human health and environmental quality, some uncertainties in transport and fate modeling may be acceptable as long as the ultimate goal is achieved.

C. Source Identification

Vadose zone transport modeling, on the other hand, may not satisfy the regulatory need of contaminant source identification. The focus here is on the exact transport and fate processes. Because it is generally agreed that vadose zone models cannot accurately predict, *let al.*one reconstruct, contaminant transport in the field, models may be of limited use in such cases.

A typical scenario of this nature may be two neighboring facilities in dispute about subsurface contamination liability. On a much larger scale, USEPA has been

investigating CHC contamination in two major groundwater basins in southern California that supply drinking water to more than 1.6 million people. These two basins were put on the National Priority List in the mid-1980s; i.e., they are Superfund sites (or more appropriately, Superfund areas). A main component of the USEPA investigation is identification of the responsible parties (RPs) who will be required to pay for the groundwater cleanup (CRWQCB, 1990).

This massive source identification effort has been contracted to the California Regional Water Quality Control Board (CRWQCB), Los Angeles Region. The goal is to establish a cause-and-effect relationship between potential sources and known groundwater contamination that can withstand both technical and legal scrutiny (CSWRCB, 1989).

In such a case, even a perfect vadose zone transport and fate simulation model may not be very helpful — because the “description and prediction” approach of the simulation models is based on the assumption that the source strength and history of discharge are known. However, in the real world, such basic data are rarely available from uncontrolled hazardous waste dump sites, landfills, or typical discharges in industrial operations. Unknown or undocumented discharge is the norm rather than the exception. Contaminant distribution at a particular time may be used as a “source” for the prediction of subsequent contaminant transport and fate; however, the usefulness of this type of exercise depends heavily on the completeness and accuracy of site characterization data.

Source investigation results from those two Superfund areas clearly demonstrated that vadose zone data, or modeling results, alone do not allow accurate determination of contamination liability. Ultimately, the chemical use pattern, site inspection observations, and groundwater monitoring results must be considered jointly (Yu, 1992).

D. Regulation of CHC Use

Another application of vadose transport and fate knowledge is regulating the use of CHCs, especially in agricultural applications. Understanding of the subsurface processes enables regulators to estimate, to a certain extent, the behavior of pesticides applied to the field. However, modeling may not be able to account for each particular soil type and field situation.

Jury (1991) actually questioned whether applying simulation models was a desirable approach in these cases. He proposed a screening model approach for evaluating pesticides to avoid the complications in using simulation models, but still give useful regulatory information. The screening model proposed by Jury *et al.* (1983, 1984b, c) essentially provides relative risk comparisons among chemicals to be applied in the field in idealized scenarios without considering site-specific variations. Chemicals posing high relative risks will then be selected for detailed investigations, which may include field application studies.

IX. CONCLUSIONS

It is clear that the fate and transport of chlorinated hydrocarbons in soil is another example of environmental problems that are stretching our current scientific knowledge and technical ability. This review attempts to describe current knowledge in a progressive manner, hopefully to increase our comprehension of interactions among various components of the subsurface environment. Advancement in understanding of this topic is crucial in view of the multitude of hazardous waste sites and aquifers contaminated by chlorinated hydrocarbons.

Our current level of knowledge regarding vadose zone transport and the fate of CHCs has at least the following regulatory implications:

1. Site heterogeneity, vapor phase CHCs, and degradation products must be adequately addressed in a site investigation.
2. All pertinent site information must be considered jointly with vadose zone data in view of the scientific uncertainties in vadose zone processes and resource limitations.
3. Although unequivocal description or prediction of processes in the subsurface environment is, at least for now, not possible, recent developments indicate that advanced process integration through computer modeling can provide useful guidance in certain regulatory functions, such as site characterization and remediation.
4. On the other hand, accurate simulation of subsurface processes may not be necessary for regulatory activities such as source identification or control of pesticide use.
5. Using vadose zone and groundwater monitoring, and other innovative investigation approaches, may alleviate the need of exact prediction or reconstruction of the vadose zone processes by complex computer modeling.

The complexity of the subsurface transport and fate processes implies that regulatory decisions must not be based on oversimplified assumptions or data interpretation. Most importantly, regulatory decisions must always take into account the scientific uncertainties, while evaluating the cost and benefit to the society as a whole.

Field experiments that link the results of laboratory experiments and modeling efforts to actual site conditions seem to be the most critical area for academic research in the near future. On the application side, the academia and the regulators must increase their communication and collaboration to optimize the use of limited resources in tackling subsurface contamination problems. Integrating vadose zone modeling efforts of an appropriate level of complexity with other pertinent site data appears to be a reasonable regulatory approach, consid-

ering the complexity of the problem, our current level of knowledge, and the limitations in resources.

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