

Modeling contaminant transport through subsurface systems*

R.J. Charbeneau^a and J.W. Weaver^b

^a*Center for Research in Water Resources, Balcones Research Center #119, University of Texas, Austin, TX 78712 (USA)*

^b*Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, P.O. Box 1198, Ada, OK 74820 (USA)*

Abstract

Modeling of contaminant transport through soil to groundwater to a receptor requires that consideration be given to the many processes which control the transport and fate of chemical constituents in the subsurface environment. These processes include volatilization, degradation, sorption and multiphase partitioning, leaching, advection and dispersion. Mathematical models for simulation of these processes may require significant data inputs. This paper reviews the important factors involved in modeling of subsurface transport as well as the data requirements and uncertainties. An application of a hydrocarbon spill screening model is presented.

Introduction

An understanding of the factors that affect the fate and transport of contaminants in the unsaturated soil and in groundwater, and the ability to develop and apply mathematical models which include these factors, is important for many applications. This understanding is necessary for determining the assimilative capacity of a soil and whether chemicals are likely to accumulate within the soil profile or leach to contaminate groundwater. An understanding of these factors will help identify suitable remediation methods and proper land disposal sites. The factors determine what happens to chemicals under closure conditions and how to avoid groundwater contamination. The models may be used to determine the type and quantity of air emissions that may occur, the necessity and immediacy of remedial action, and potential exposure concentrations at receptor points. The factors and processes that are important include those that affect losses, retardation, solubility, and transport. For

*Paper presented at the GCHSRC Fourth Annual Symposium on Ground Water — The Problem and Some Solutions, Lamar University, Beaumont, TX, U.S.A., April 2-3, 1992.

Correspondence to: R.J. Charbeneau, Center for Research in Water Resources, Balcones Research Center #119, University of Texas, Austin, TX 78712 (USA).

protection of public health and the environment, particularly groundwater, it is desirable to enhance losses and retardation.

The objective of this manuscript is to review the important factors involved in modeling of contaminant transport through soil to groundwater to a receptor. The important processes are discussed, as are the uncertainties and the data that one needs to know or have. In addition, the application of models, and their value and limitations are discussed with reference to a screening model for hydrocarbon spills.

Factors and processes that affect transport

Figure 1 shows a schematic view of the processes that affect the subsurface fate and transport of chemical constituents. The figure shows a near-surface source of contamination such as a spill, landfill, or storage tank. Some of the chemical may be immobilized within the source zone. The remainder is free for transport through one of the mobile phases. Multiphase partitioning determines how much of the chemical constituent will reside in each phase. From the vapor phase the chemical is lost to the atmosphere by the process of volatilization. The soluble components may be leached from the source zone by infiltrating water. The rate of movement of the chemicals during leaching may be significantly less than the rate of water movement if the chemicals are significantly sorbed on the soil, or partitioned into an immobile hydrocarbon phase which may be present. In the source zone and during transport, some of the chemical may be lost due to degradation, either of biotic or abiotic origin. If the losses and retardation are not sufficient, then some of the chemical will reach the water table and be transported with groundwater flow to potential points of exposure. The goals of modeling subsurface transport include prediction of exposure concentrations and evaluation of the relative importance of the various processes and parameters which control this subsurface transport and fate.

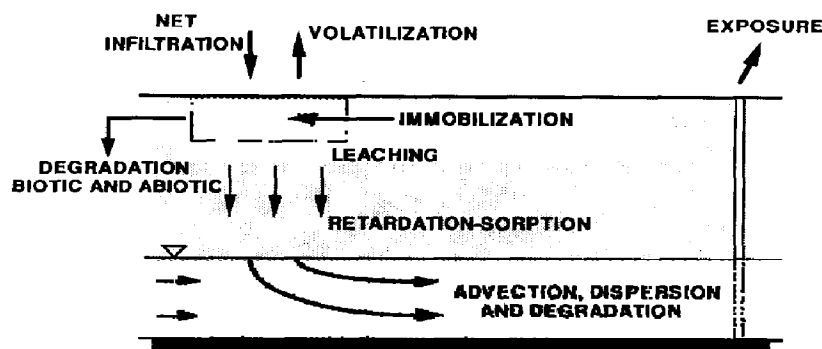


Fig. 1. Processes which influence the subsurface fate and transport of chemicals.

Multiphase partitioning

Investigations of fate and transport of chemicals in the unsaturated zone must inherently deal with a multiphase system consisting of water, air, and soil. In addition, for certain applications such as spills, leaking tanks, or land treatment of petroleum hydrocarbons, there also is a separate non-aqueous phase present. The pore space must be filled by the sum of the fluids present so

$$n = \theta_w + \theta_a + \theta_o \quad (1)$$

where n is the porosity, θ_i is the i th phase volumetric content, and the subscripts refer to water, air, and non-aqueous phase liquid (NAPL) or "oil". Individual chemical constituents will partition themselves amongst the various phases according to thermodynamic equilibrium principles (same activity in each phase) and kinetic factors. The majority of the models in use are based on the assumption of local equilibrium and/or solubility controls. The concentrations of a constituent in the three fluid phases are designated c_w , c_a , and c_o , all on a mass per unit volume basis. The soil phase concentration is specified as mass sorbed per mass of soil and is designated c_s . The bulk concentration, m , which is the mass of constituent per bulk volume is then given by

$$m = \theta_w c_w + \theta_a c_a + \theta_o c_o + \rho_b c_s \quad (2)$$

where ρ_b is the soil bulk density. Equation (2) is perfectly general. When considering the transport of the constituent within the multiphase system, a fundamental question concerns how the concentrations within the various phases relate to each other. The simplest and most common approach assumes that the rate of mass transport within a phase is slow compared with the rate of mass transfer between phases in contact locally. If this is the case, then the concentrations remain in thermodynamic equilibrium, and the assumption that such conditions hold is called the local equilibrium assumption. The local equilibrium assumption appears to be valid for many situations of practical interest. There are exceptions, however, where mass transfer kinetics is important and equilibrium assumptions do not apply. Examples include cases where intra-particle diffusion or dissolution of droplets is important. Nevertheless, in the vast majority of applications, equilibrium partitioning is assumed. To reiterate, the local equilibrium assumption says that the concentration in any phase can be related to that in any other through the thermodynamic partition coefficient. This is shown schematically in Fig. 2.

For the analysis of solute transport in a multiphase system in local equilibrium, it is convenient to refer all concentrations to the water concentration; while for analysis of volatilization the air phase concentration is more appropriate. This allows one to express the bulk concentration in terms of the concentration in a particular phase alone. The linear partitioning relationships are also shown in Fig. 2. In these equations, K_H is the Henry's Law constant

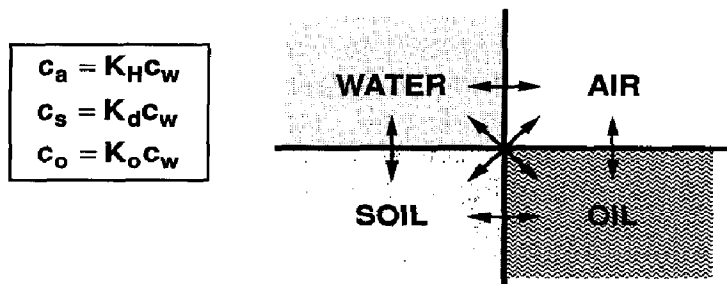


Fig. 2. Partitioning in a multiphase system.

while K_o and K_d are the oil-water and soil-water partition coefficients, respectively. Both K_H and K_o are dimensionless, while K_d has units of volume per mass. Substituting these equilibrium relations in eq. (2) gives

$$m = (\theta_w + \theta_a K_H + \theta_o K_o + \rho_b K_d) c_w = B_w c_w \quad (3)$$

B_w is called the bulk water partition coefficient. Equation (3) shows the relation between the bulk concentration and the aqueous concentration. If one determines the bulk concentration of a soil by chemical extraction, then this equation may be used to estimate the aqueous concentration. Similar relations may be written for each of the other phase concentrations, and one may introduce bulk air, soil, and oil partition coefficients. The important parameters include the volumetric fluid contents and the partition coefficients.

The Henry's Law constant, K_H , is dimensionless. This constant may also be written as the ratio of the vapor density (ρ_{vp}) to the solubility (S), where the vapor density is related to the vapor pressure through the ideal gas law, $\rho_{vp} = P_{vp}/RT$, where R is the gas constant and T is the temperature in degrees Kelvin. The vapor pressure, solubility, and Henry's law constant for many chemicals have been tabulated. See, for example, Mercer et al. [14].

Non-polar organic compounds in the subsurface are found to be sorbed by the medium on existing solid organic matter present in the porous medium [2]. This sorption is due primarily to hydrophobic interactions resulting in weak, non-specific sorption forces. When the organic compounds are present in trace concentrations, linear sorption isotherms are often observed. The distribution coefficient (K_d) is found to be a function of the hydrophobic character of the organic compound and the amount of organic matter present, and may be written [3-5]

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

where K_{oc} is the organic carbon partition coefficient and f_{oc} is the fraction of organic carbon within the soil matrix. Sorption partition coefficients, indexed to organic carbon (K_{oc}) are relatively invariant for natural sorbents, and K_{oc} 's

can be estimated from other physical properties of pollutants such as aqueous solubility or octanol–water partition coefficients (K_{ow}). Equation (4) is valid only for $f_{oc} > 0.001$. Otherwise, sorption of organic compounds on nonorganic solids (clays and mineral surfaces) can become significant. Also, the linear isotherm model is valid only if the solute concentration remains below one-half of the solubility limit of the compound. Use of the hydrophobic theory to estimate the distribution coefficient in equations for modeling subsurface pollutant transport assumes that the sorbed concentration is in equilibrium with the concentration in solution.

Very little is known in detail about the magnitude of K_o , except that it is not a constant but rather depends on the composition of the “oil” phase. Since this composition changes with time as the pollutant ages, one may anticipate that K_o will change with time also. Compositional models are required for estimating how K_o evolves over time. For the partitioning between the water and oil phases Corapcioglu and Baehr [6] apply Raoult’s Law which states that the aqueous phase concentration is equal to the aqueous phase solubility of the constituent in equilibrium with the pure constituent phase multiplied by the mole fraction of the constituent in the oil phase. The resulting compositional model leads to

$$K_o = \frac{\omega_k \sum_{j=1} c_{oj} / \omega_j}{S_k \gamma_k} \quad (5)$$

Equation (5) is written for a species k which is one out of N species which make up the oil phase. ω_j is the molecular weight of the j th constituent (g/mol), c_{oj} is the concentration of the j th constituent in the oil phase (g/L), S_k is the solubility of species k in water (g/L), and γ_k is the activity coefficient of the k th species (which equals 1 for ideal solutions). Equation (5) makes it apparent that K_o changes as the composition of the oil phase changes (because of dissolution, volatilization, and degradation of constituents). Ultimately, one might expect that the value of K_o will approach that of K_{oc} for the constituent.

Volatilization

Volatilization from the soil is a process which involves mass transfer from the soil, aqueous, and air phases that are present in the porous medium to the atmosphere, which serves as the ultimate sink. Since the mass must enter the atmosphere within the air phase, it is often assumed that gaseous transfer must dominate the mass transfer process. However, if the mass transfer between phases is sufficiently fast so that local equilibrium conditions are achieved, the concentration gradient in the air phase follows that in the other phases. This means that one can model the volatile flux in terms either the air concentration, the bulk concentration, the water concentration, etc., whichever is most convenient. In any case, the mass transfer in all phases may be important.

Volatilization is mass transfer associated with diffusion. The rate of volatilization is affected by many factors, such as soil properties, chemical properties, and environmental conditions. Its rate is ultimately limited by the chemical vapor concentration which is maintained at the soil surface and by the rate at which this vapor is carried away from the soil surface to the atmosphere. In this regard, the mechanisms of volatilization are similar to those of evaporation of soil water, with volatilization being the 'evaporation' of a chemical constituent. The factors which control the rate of volatilization are discussed in the literature primarily in terms of their effects on evaporation of pesticides, because most previous studies of volatilization rates have concentrated on these chemicals. However, there is little that distinguishes pesticides from other organic chemicals and one may assume that the observations based on pesticides are applicable to organic chemicals in general. For reviews see [7-11].

Volatilization may be modeled using Fick's Law of diffusion. A simple model gives the cumulative volatile loss (mass per unit surface area) as

$$Q_{\text{loss}} = m_o \sqrt{\frac{4D_s t}{\pi}} \quad (6)$$

where m_o is the soil's initial bulk concentration of the volatile constituent, and the parameter D_s is the effective soil diffusion coefficient. Equation (6) is essentially the model presented by Hamaker [12] except that it accounts for partitioning and diffusive transfer in all of the phases. The effective soil diffusion coefficient may be estimated using an extension of the model presented by Millington [13]:

$$D_s = \frac{1}{n^2 B_w} (\theta_w^{10/3} D_w + \theta_a^{10/3} K_H D_a + \theta_o^{10/3} K_o D_o) \quad (7)$$

In eq. (7), D_w , D_a , and D_o are the bulk phase molecular diffusion coefficients

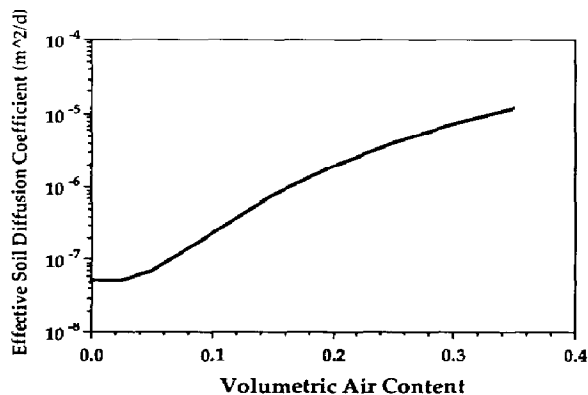


Fig. 3. Effective soil diffusion coefficient as a function of air content for a fixed volumetric oil content of 0.05.

for water, air, and oil. Typically, D_a is four orders of magnitude larger than either D_w or D_o , suggesting that the vapor phase is the major contributor to soil diffusion, except for a very wet soil where θ_a becomes small. For example, Fig. 3 shows the effective soil diffusion coefficient for xylene as a function of volumetric air content. Note that the effective diffusion coefficient increases by nearly two orders of magnitude as one goes from a fairly wet soil with $\theta_a < 0.1$ to a dry soil with $\theta_a > 0.3$.

Immobilization

Chemicals may be immobilized within the source zone due to at least two different types of mechanisms. First, individual constituents may be immobilized because of their chemical nature. This is especially true for heavy metals. The major factors affecting the immobilization of metal are the pH and redox potential of the environment, as well as the metal's solubility and speciation. Under a range of pH and E_h (redox half-wave potential), certain metals may become immobilized as precipitates. For example, uranium forms an oxide precipitate under reducing conditions. However, under oxidizing conditions, uranium forms a mobile complex with carbonates which are usually present. Different metals have different "windows" of mobility based on the pH and E_h of their environment, and especially for metals, redox kinetics may be important in designing remedial systems for contaminated sites.

There is another type of immobilization which is especially important for sites contaminated by NAPL's. An immiscible hydrocarbon phase is free to migrate under force of gravity or other induced energy gradients only so long as its saturation is sufficiently high. At lower NAPL saturation, surface tension causes the hydrocarbon phase to break down into individual "blobs". Since these blobs are no longer continuous, the NAPL is no longer free to migrate as a separate phase. One then refers to the immobilized residual saturation. Perhaps the most important point is that a NAPL may become immobilized as a separate phase, but its individual constituents are not immobilized. Any species which is soluble in water can be leached from the immobilized NAPL which serves as a reservoir of contaminants. In fate and transport models for NAPL's, one needs to be able to estimate their residual saturations both above and below the water table. Field experience has shown that typical hydrocarbon residual saturation varies from 0.10 to 0.20 in the vadose zone, and from 0.15 to 0.50 in the saturated zone [1]. These values correspond more closely to "specific retentions", as the term is used in groundwater hydrology, rather than true residuals at large capillary pressure values.

Degradation

Degradation refers to the *in situ* loss of a chemical constituent in the subsurface. It may be due to abiotic transformations, such as hydrolysis, or it may be due to a biotic origin. Biodegradation is an important environmental pro-

cess that causes the breakdown of organic chemicals in soil. The chemical transformations are mediated through the activities of microorganisms which are naturally present. The transformation of organic carbon to inorganic carbon (CO_2) is accomplished through enzymatic oxidation. Under aerobic conditions, molecular oxygen is involved as the terminal electron acceptor; while under anaerobic conditions, the final electron acceptor is something other than molecular oxygen such as sulfate or nitrate. Mineralization refers to the complete degradation of an organic chemical to inorganic products such as carbon dioxide, water, sulfate, nitrate, or ammonia. Partial degradation is commonly used to describe a level of degradation less than complete mineralization. The degradation products may be more or less toxic than their parent compounds. Chemical compounds that are not easily degraded are said to be recalcitrant and persistent in the environment.

The rate of biodegradation is a complex function determined by the number and type of microorganisms present, the toxicity of the parent compound or its daughter products to the microorganism population, the water content and temperature of the soil, the presence of electron acceptors and the redox potential, the soil pH, the availability of other nutrients for microbial metabolism, the water solubility of the chemical, and possibly other factors. Various models for the rate of biodegradation are reviewed by Alexander and Scow [15]. For most investigations it is assumed that degradation can be described by first-order rate reactions in which the rate of loss of a chemical is proportional to the chemical concentration

$$\frac{dm}{dt} = -\lambda m \quad (8)$$

In eq. (8), λ (time^{-1}) is the first-order rate constant which is related to the half-life, $T_{1/2}$, by

$$T_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} \quad (9)$$

Measured values of $T_{1/2}$ are quite variable between the laboratory and the field, and from site to site in the field. Laboratory values tend to be measured under optimal conditions so as to assess the potential for biodegradation given the chemical characteristics, geochemistry and bacterial populations. Laboratory half-lives are not necessarily applicable to the field due to limitations in the factors described above. For a well-managed land treatment or contaminated soil bioremediation site, representative half-lives for toluene, naphthalene, and anthracene range from 1-10 days, 30-60 days, and 100-200 days, respectively.

Leaching

Chemical contaminants can be carried from the source zone to the water table through leaching by infiltrating rainwater, and directly with a NAPL which is released at sufficient rates so that it is mobile. Perhaps one of the greatest uncertainties in development of leaching models is estimation of the net water infiltration rate. Some of the water which falls on the ground surface does not infiltrate to the subsurface, but rather forms surface runoff. Most of the water that does infiltrate to the subsurface returns to the atmosphere through evaporation and transpiration by plants. Only a relatively small fraction of the yearly rainfall may infiltrate below the root zone and ultimately become groundwater recharge. In development of subsurface solute transport models one is faced with the question of estimation of the net infiltration rate and whether it is necessary to deal with the details caused by individual rainfall events. It is certain that the water content and seepage velocities are quite variable within the upper region of the soil profile containing the root zone. This in turn influences volatilization rates, degradation, and leaching itself. However, below the upper meter or so, the variability in water content and seepage rates is much less, and one might apply an average value for these variables.

The usual approach in development of transport models is to assume steady-state conditions for the net water infiltration rate. In order to estimate the net infiltration rate, one may apply daily water balance models such as CREAMS or HELP, or continuous time water balance models such as PROFIL. Sensitivity studies have suggested that the net infiltration rate may be adequately estimated using either type of model. These models will provide an estimate of the yearly average infiltration rate, which in turn may be used to estimate the water content and seepage velocity. For the latter determinations, parametric models are often used rather than raw data from laboratory determinations. Parametric models relate the soil water retention parameters and relative permeability parameters to the soil texture. The most commonly used soil water retention and relative permeability models are those of Brooks and Corey [16] and Van Genuchten [17]. Using the Brooks and Corey model, one may estimate the average water content from

$$\theta_w = \theta_{wr} + (n - \theta_{wr}) \left(\frac{q_w}{K_{ws}} \right)^{\lambda/3\lambda+2} \quad (10)$$

where q_w is the net water infiltration rate, θ_{wr} is the residual water content, K_{ws} is the soil's vertical hydraulic conductivity for water, and λ is the pore size distribution index. If infiltration is uniform throughout the soil profile, then one may estimate the seepage velocity through

$$v_w = \frac{q_w}{\theta_w} = \frac{q_w}{\theta_{wr} + (n - \theta_{wr}) \left(\frac{q_w}{K_{ws}} \right)^{\lambda/3\lambda+2}} \quad (11)$$

Equation (11) may be used to estimate the seepage velocity for a given net infiltration rate and a known set of soil water retention parameters. Table 1 provides estimates of the average seepage velocity from eq. (11) for different soil textures and recharge rates. For each soil texture the average parameters determined by Carsel and Parrish [18] were used. These parameters are based on data obtained from measurements for all soils reported in SCS Soil Survey Information Reports, and were analyzed using a multiple regression equation developed by Rawl and Brakensiek [19]. It is important to note that the velocities reported in Table 1 are quite small. This suggests that the average residence time for solutes in the unsaturated zone can be very long, especially at locations where the water table is found at great depths. It also should be noted that eq. (11) and Table 1 provide a rough guide only. They are based on the assumption of steady recharge and uniform flow in a homogeneous soil profile. Rainfall events, which produce recharge, create water fluxes much higher than the average velocities. Since recharge occurs through discrete events, rather than due to average recharge rates, higher fluxes occurring over short time periods result in significantly more rapid transport through the root zone and possibly all the way to the water table. Models which rely on average monthly or annual recharge rates may adequately represent the vadose zone moisture content, but may significantly overestimate the vadose zone reten-

TABLE 1

Average solute velocities (m/year)

Soil type	Average annual recharge (m)			
	0.05	0.10	0.25	0.50
Clay	0.16	0.31	0.75	1.48
Clay loam	0.19	0.37	0.86	1.64
Loam	0.26	0.49	1.13	2.11
Loamy sand	0.53	0.99	2.25	4.16
Silt	0.21	0.39	0.88	1.64
Silt loam	0.22	0.41	0.93	1.74
Silty clay	0.16	0.30	0.74	1.45
Silty clay loam	0.16	0.30	0.72	1.37
Sand	0.68	1.27	2.86	5.27
Sandy clay	0.18	0.35	0.82	1.58
Sandy clay loam	0.25	0.48	1.12	2.12
Sandy loam	0.39	0.73	1.67	3.08

tion time. The effects of solute mixing or dispersion, macropores, and spatial variability are not included, and these affects can be very dramatic.

In recent years, it has become recognized that the effects of preferential flow are very significant in determining the residence time for solutes in the vadose zone. Even for homogeneous soil layers, experiments and theory have shown that when flow proceeds from a layer of lower permeability to one of higher permeability, then fingering will naturally occur causing preferential flow paths which channel the water through the higher permeability layer. This is shown schematically in Fig. 4. Since the same total discharge is channeled through a much smaller area, the corresponding velocities will be greater and the travel times less. In the field, naturally occurring macropores, decayed root openings, and heterogeneities will also trigger channeling of subsurface flow through the unsaturated zone.

Advection, dispersion, and degradation

The aquifer processes of advection and dispersion have been greatly studied over the past few decades. As presently understood, advection refers to the average rate of advance of a solute in the aquifer; and dispersion refers to the deviation about the mean. The advection velocity is proportional to both the hydraulic conductivity and the hydraulic gradient, and inversely proportional to the porosity. Dispersion includes both the processes of molecular diffusion and mechanical dispersion. The latter process is associated with the non-uniform motion of a solute caused by the flow through the complicated pore structure of the media. For most problems of contamination of shallow aquifers, molecular diffusion plays a negligible role. On the pore scale seen in laboratory experiments, the influence of mechanical dispersion is also small. However, in the field, dispersion is used to account for the effects of aquifer heterogeneities on the transport. The solute will move faster through regions of higher permeability than through regions of lower permeability. The models recognize only the average advection velocity and account for these deviations with the dispersion term. This results in dispersion playing a much more significant role for field scale problems than for laboratory experiments. In addition, the greater the scale of the problem under investigation, the greater the range of hetero-



Fig. 4. Preferential flow through porous media.

geneities experienced by the solute and the larger the apparent magnitude of the dispersion coefficient.

Degradation processes are less rapid in the saturated zone than they are within the upper few feet near the ground surface, though they are not any less important. Groundwater transport is very slow, so that even a small degradation rate can result in a significant reduction in solute concentration before the constituent of interest reaches a potential exposure point.

Screening models

Subsurface fate and transport models may be classified as either generic models or site specific models. Generic models are based on a simplified interpretation of the hydrogeology, including generally the assumption of uniform flow in a specified direction and homogeneous conditions for other parameters. These assumptions allow the use of analytic solutions to the transport problem. Analytic solutions have the advantage of simplicity and ease of computation. Site specific models are flexible enough to deal with the individual complexity of a given hydrogeologic setting and can include almost any level of detail in the simulation of important fate and transport processes. This flexibility and ability to address great levels of complexity comes at a price. Site specific models require numerical methods and may come at a great computational expense.

Screening models are generic models in the sense that they cannot be adapted to deal with many site specific conditions. They may be used to evaluate the behavior of large numbers of chemicals in the environment. For example, the pesticide screening model of Jury et al. [20] was used to classify pesticides based on persistence categories in terms of mass remaining in the soil after 30 days [21]. The RITZ model [22] was developed as a screening model for evaluation of the fate of petroleum wastes applied at land treatment sites. EPACML [23] is an exposure assessment screening model for landfill waste. While each of these models is fundamentally different, they are similar in that they incorporate mathematical models of many important processes which affect the fate and transport of chemicals under the particular scenario for which the model was developed.

Hydrocarbon spill screening model

As an example of a model and its application, we consider the Hydrocarbon Spill Screening Model (HSSM), which is a hydrocarbon spill screening model. Hydrocarbon spills impact drinking water supplies at down gradient locations. Conventional numerical models of multiphase, multicomponent flow have extreme requirements for both computer time and site data. Site data and the intent of the modeling often do not warrant the application of such models. An alternative approach is HSSM which is based on semi-analytic models for ver-

tical product infiltration, radial spreading on the water table, and transport of aqueous phase contaminants in the aquifer. The models for these processes are linked to estimate exposure at a down gradient well. The basic set-up of the model is shown in Fig. 5.

HSSM is to be used as a screening tool. For example, the model can be used to estimate the effects of light low density non-aqueous phase liquid (L-NAPL) loadings, partition coefficients, groundwater flow velocities, etc., on pollutant transport. Since approximations are used for developing the model, the model results must be viewed as approximations. If simulation of complex heterogeneous sites is needed, or other approximations made in the model are unacceptable, then a more inclusive model should be used instead of, or in addition to, HSSM.

Complex models, however, may not always be the most desirable tool for a given problem. Such models require large amounts of computer time and available memory. Further, there may be a significant investment in training the users to set up the model and run it properly. Additionally, a large amount of field data is required to run such a model because the expense of running the model is not warranted if adequate site data are not available. In addition to the parameters for aqueous phase solute transport (such as hydraulic conductivity, dispersivity, sorption parameters), multiphase transport parameters are needed (interphase partition coefficients, capillary pressures and relative permeabilities) for each different zone or material present in the field. The latter properties are not well understood and are difficult to obtain for field problems. Site data is usually incomplete because of monetary, safety and regulatory limitations. Historical records of pollutant releases are often non-existent, although such knowledge should be precisely defined in a model. Sampling limitations often result in situations where the total mass of contaminants cannot be defined. These limitations are likely to require approximations to be made even when running a complex model. Certain problems may warrant the use of alternative simplified models.

HSSM has an advantage in some of these areas; the model executes rapidly

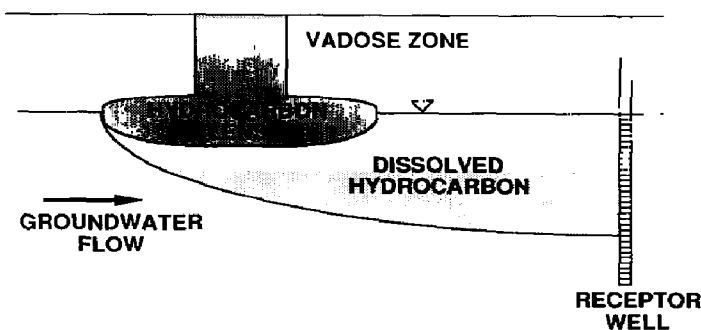


Fig. 5. Hydrocarbon spill screening model (HSSM).

on small computers, requires little memory and is designed to be run easily. The advantage is that HSSM is based on semi-analytic approaches, which do not require discretization of the domain nor iterative solution of the non-linear governing equations. These advantages are achieved at the cost of flexibility in accommodating heterogeneities and other phenomena. Clear recognition should be made that for the sake of efficiency and robustness, accuracy and/or the ability to simulate various situations is sacrificed. At some point, there is a limit to the phenomena that can be treated in a simplified context; beyond that limit, the complex models must be used.

A detailed discussion of the model assumptions is presented by Weaver and Charbeneau [24], and only a brief description is given here. The spill or release of the L-NAPL phase may be simulated in three ways. First is a release of a known L-NAPL flux for a specified duration. The release occurs at the ground surface. Based on an approximate capillary suction relationship, some of the L-NAPL may run off at the surface if the flux exceeds the maximum effective L-NAPL conductivity. Second, a constant depth of ponded L-NAPL, for a known duration, may also be specified. This case represents a slowly leaking tank, or a leaking tank within an embankment. Lastly, a known volume of L-NAPL may be placed over a specified depth of the soil. This last scenario represents either a land treatment operation or a landfill containing a known amount of contaminants at the beginning of the simulation.

Transport of the NAPL through the unsaturated zone is assumed to be one-dimensional. Capillary pressure gradients are neglected except as they influence the infiltration of NAPL into the soil. The resulting equations for NAPL flow are hyperbolic and are solved by the generalized method of characteristics. When relatively large amounts of L-NAPL are released, downward transport of the L-NAPL (say gasoline) is the primary mechanism for downward transport of hydrophobic chemicals (e.g., benzene, toluene, and xylene). Assumptions concerning aquifer recharge are relatively unimportant in this case. If a large enough volume is supplied, the L-NAPL reaches the water table. If sufficient head is available, the water table is displaced downward, lateral spreading begins, and the oil lens part of the model is triggered. Spreading is assumed to be radial, and the thickness of the lens is determined by buoyancy only (Ghyben-Herzberg relations). The shape of the lens is given by the Dupuit assumptions, where the flow is assumed horizontal and the gradient is independent of depth.

The L-NAPL is treated as a two-component mixture. The L-NAPL itself is assumed to be soluble in water and sorbing. Due to the effects of the recharge water and contact with the groundwater, the L-NAPL may be dissolved. The L-NAPL's transport properties (density, viscosity, capillary pressure, relative permeability), however, are assumed to be unchanging. The second component is a chemical constituent which can partition between the L-NAPL phase, water phase and the soil. This constituent of the L-NAPL is considered the

primary contaminant of interest. The mass flux of the second constituent into the aquifer comes from recharge water being contaminated by contact with the lens and from dissolution occurring as groundwater flows under the lens. The concentration of the chemical in the aquifer is limited by its water solubility.

The aquifer transport of the dissolved contaminant is simulated by using a two-dimensional, vertically averaged analytic solution of the advection-dispersion equation. The vertical extent of the contaminant is estimated from the recharge rate, groundwater seepage velocity and vertical dispersivity, rather than assuming the contaminant is distributed over the entire aquifer thickness. The boundary conditions are placed at the down gradient edge of the lens and take the form of a Gaussian distribution with the peak directly down gradient of the center of the lens. The peak concentration of the Gaussian distribution adjusts through time so that the simulated mass flux from the lens equals that into the aquifer. Although the size of the lens varies with time, a constant representative lens size is used for the aquifer source condition. In many cases the lens reaches its maximum size rather rapidly compared with the transport in the aquifer, so that the use of the maximum lens size will not introduce large errors.

The required input parameters include parameters specifying the type, extent and magnitude of the L-NAPL release, the residual oil contents for the unsaturated and saturated zones, the residual water content of the oil lens, the transport properties of the water and L-NAPL (density, viscosity, surface tension), the aquifer and soil water retention characteristics (vertical and horizontal hydraulic conductivities, porosity, irreducible water content, pore size distribution index, and air entry head), the dissolved constituent characteristics (initial concentration within the L-NAPL, aqueous solubility, and the soil-water and oil-water partition coefficients), and the aquifer transport characteristics (vertical, longitudinal and transverse dispersivities, hydraulic gradient, half-life of the constituent within the aquifer). Other parameters control the simulation characteristics and locations where exposure concentrations are calculated.

To show the type of output one can obtain, a spill of 1,500 gallons (5400 L) of gasoline over a sandy aquifer was simulated. The area of the the release has a radius of 2 m and the duration of the release is 1 day. The water table is at a depth of 5 m and the aquifer has a seepage velocity of 0.9 m/day. The simulation results show that the gasoline first reaches the water table at a time of 2.6 days, and after 4.3 days sufficient gasoline has accumulated in the capillary fringe to cause the lens to start to spread. Spreading occurs over a period of 68 days with a final lens radius of 3.6 m.

Benzene, toluene, and xylene were separately considered as constituents within the gasoline. Benzene is assumed to have a concentration of 8.2 g/L (1.14% bymass) in the gasoline. Toluene is assumed to have a concentration of 43.6 g/L (6.07% by mass). Xylene is assumed to have a concentration of

71.8 g/L which is 10% of the gasoline. Partition coefficients are based on an assumed fraction of organic carbon in the soil and aquifer of $f_{oc}=0.005$ and with gasoline having a molar concentration of 7 mol/L. With eq. (4), the soil-water distribution coefficients for benzene, toluene, and xylene are 0.415, 1.50, and 4.15 L/kg, respectively. The corresponding aquifer retardation factors for these chemicals are 2.66, 7.0, and 17.6 for benzene, toluene, and xylene. Equation (5) gives oil-water partition coefficients of 312, 1200, and 4240 for benzene, toluene, and xylene, respectively, by using the idealized gasoline mixture presented by Corapcioglu and Baehr [6].

Figure 6 shows the calculated benzene concentrations at the receptor wells located at distances of 50, 100, 200, and 500 m from the spill location. The peak concentration at 50 m is about 3.7 mg/L and occurs 0.7 years after the spill. At 500 m, the peak concentration is 0.7 mg/L and occurs at a time of 4.5 years after the spill. This decrease in peak concentration with distance is associated with mixing in the aquifer since the biodegradation of benzene was neglected in the model. Figure 7 compares the concentrations of benzene, toluene and xylene at the 50 m receptor well. The peak concentrations of these chemicals are similar (3.7, 5.8, and 2.5 mg/L for benzene, toluene, and xylene, respectively) even though they were present in far different concentrations in the

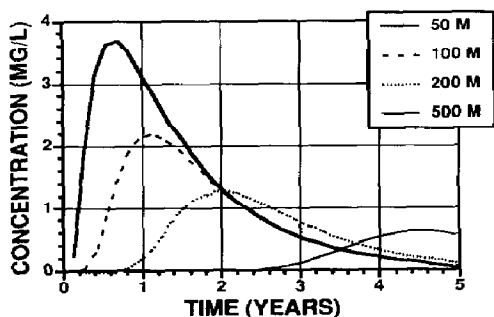


Fig. 6. Benzene concentrations mg/L at receptor wells located 50, 100, 200, and 500 m from the spill.

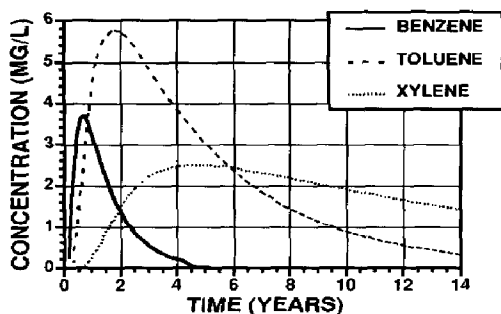


Fig. 7. Benzene, toluene and xylene concentrations (mg/L) at a distance of 50 m from the spill.

gasoline. This behavior is due primarily to the oil-water partition coefficients. Benzene is leached most rapidly from the oil lens. Toluene is leached less rapidly than benzene, but because it was present at much higher concentrations in the gasoline, the receptor concentration is higher. Xylene, which is present in gasoline at the highest concentrations, is leached so slowly from the lens that its concentrations are diluted due to mixing with the groundwater and the resulting exposure concentrations are less.

Discussion

This article has provided an overview of the important processes which affect the subsurface fate and transport of chemicals. Significant parameters have been noted and discussed. Unfortunately, the uncertainties in parameter estimation for model applications are very great. Even for the flow of water, the uncertainties are large. In the unsaturated zone one may anticipate that preferential flow may play an important role, though it is unlikely that one will be able to locate the flow paths (a particularly important point for vadose zone monitoring). In groundwater aquifers, one rarely knows the hydraulic conductivity to within an order of magnitude. This implies that estimates of seepage velocities are often good only to within an order of magnitude unless they are determined directly through use of tracers. The mixing parameters will also remain elusive, though the importance of dispersion is probably less important for many applications.

The parameters which determine the partitioning of chemicals in a multi-phase system can in principle be estimated with greater accuracy. Use of hydrophobic theory should lead to estimates of the soil-water distribution coefficient which are good to within plus or minus fifty percent. A similar level of accuracy could be achieved for the oil-water partition coefficient except that the composition of the NAPL phase is generally poorly known and varies with location. Henry's law constants can probably be estimated with the greatest accuracy. Estimation of degradation parameters may also be expected to face considerable uncertainty both because of the first-order rate equation may not be appropriate and because the controls are poorly known and vary with location in the subsurface.

In light of these uncertainties, one may question the use of mathematical models for subsurface fate and transport. One should not expect that models can predict actual concentrations to be found at a field site with any great level of accuracy. However, models can show the relative importance of the various processes which affect fate and transport, and identify the most significant parameters upon which attention may then be focused. Such uses of models highlights the role of models in developing a conceptualization of contaminant behavior at a site. Of ultimate value is the understanding of contaminate behavior developed by the engineer or geologist from regional and local scale

hydrology, contaminant properties and distribution, model use, etc. Properly calibrated models then become useful in analysis and design of alternate remedial systems. In general, models play an especially important educational role in training and developing our intuition as to how to interpret and understand field observations from complex environmental systems, and in classification of chemicals in terms of their general fate and transport behavior.

Disclaimer

Although the participation of the second author in the work described in this article has been supported by the United States Environmental Protection Agency, the article has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred. The mention of trade names or commercial products does not constitute endorsement or recommendation for use. The work described in this article did not involve environmentally related measurement and thus did not participate in the Agency's quality assurance program.

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