MODELING GASOLINE FATE AND TRANSPORT IN THE UNSATURATED ZONE

DANNY D. REIBLE and MARK E. MALHIET

Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803 (U.S.A.)

and

TISSA H. ILLANGASEKARE

Department of Civil Engineering, University of Colorado, Boulder, CO 80309 (U.S.A.)

Summary

Gasoline and gasoline constituents are a common source of subsurface contamination, as a result of surface spills or leaks from underground storage tanks. These materials often exist as separate non-aqueous phases for long distances or times from the source due to their low aqueous solubilities. Site assessment and remediation efforts that do not directly address the non-aqueous phase material are increasingly being recognized as unlikely to provide cost effective or timely solutions to the ground-water contamination risk.

The current work is focussed on defining the fate and transport processes of a gasoline phase from the point of spillage or leakage through the unsaturated zone. Physical processes considered include infiltration in the unsaturated zone with partitioning between the gasoline and the soil, residual water and air phases, and subsequent contamination of aquifer recharge water by a residual gasoline phase. Simple models that allow systematic and physically based estimation procedures for quantification of these subsurface processes are developed. Although the models undoubtedly oversimplify the physical situation, the result is a modeling framework that is appropriate for regulatory development or preliminary site assessment and remediation planning.

Introduction

Most efforts at controlling subsurface contamination by gasoline and gasoline constituents have been aimed at contaminants dissolved in ground water. Recent research and experience has indicated, however, that subsurface contamination is often the result of multiphase processes. Gasoline and gasoline constituents applied to the soil through leaks of underground storage tanks or surface spills are typically only sparingly soluble in water and therefore remain as a separate liquid phase some distance or time from the initial source of contamination. The separated phase material may exist as either a continuous bulk phase or as discontinuous pockets of "residual" material. Although the

direct human exposure to the non-aqueous phase liquid (NAPL) is generally minimal, the persistence of the NAPL hinders cleanup efforts and provides a long term source of ground-water contamination through leaching of the more soluble components. These problems suggest that effective control of ground-water contamination by gasoline often requires assessment and remediation of multiple fluid phases.

Guiding any assessment and remediation efforts are field data and models for the interpretation and extension of that data. Unfortunately, such models are largely unavailable. The models that have been reported in the research literature, for example those of Faust [1], Baehr and Corapcioglu [2], Abriola and Pinder [3], Osbourne and Sykes [4] and Kappusamy et al. [5] are exceedingly complex, reflecting the complex nature of the physical system. In each of the existing models, one or more species conservation equations are solved to determine the spatial and temporal variation of the saturation levels of the fluid phases (saturation = fraction of void volume containing a particular phase). Each fluid phase is considered a continuum and the various fluid phases are linked through relative permeabilities and capillary pressures that vary with the phase saturation level. Unfortunately, these data are generally unavailable, even for "clean" homogeneous media such as sand.

In addition, the objective of the complex models to define the saturation profiles of the respective fluid phases in arbitrary boundary conditions and subject to arbitrary initial saturation levels is rarely required. Models are primarily needed to indicate the magnitude of the contamination problem and to guide subsequent field investigation. As shown by Reible et al. [6], it is possible to define certain common contamination scenarios that are amenable to a much simpler analysis than afforded by the complex modeling approaches. These simpler analyses can be used as semi-quantitative approximations to the actual behavior, or if appropriate conservative assumptions are used, as a limit model of the process (i.e. a worst case scenario).

The focus of the current paper is the illustration of such an approach to describe the fate of a gasoline phase after a spill or leak onto the soil. The analysis is limited to the vadose or unsaturated zone, the near-surface environment in which both air and water initially fill the void volume. Physical processes considered include infiltration in the unsaturated zone with partitioning between the gasoline and soil or residual water and the subsequent contamination of aquifer recharge water by the residual gasoline trapped in the unsaturated zone. The assumptions about the spill or soil environment required to develop simple models of these processes are identified. To illustrate its application to a practical problem, the modeling approach is used to compare the effectiveness of water table and vapor phase underground storage tank leak detection monitors.

Model development

Gasoline infiltration in the unsaturated zone

A spill or leak of gasoline at the soil surface must typically infiltrate through the vadose or unsaturated zone. In general, the water initially contained within the pore spaces is partially displaced by the gasoline requiring development of flow models in both the gasoline and water phases to describe the infiltration. After a water infiltration event, however, soil water tends to drain rapidly to a residual saturation level that is retained by capillary forces. Reible et al. [7] indicated that essentially no displacement of this residual water occurs during the infiltration of immiscible organic phases exhibiting a high interfacial tension with water. Thus the assumption that the soil is initially drained to residual saturation with respect to water allows elimination of a separate flow equation for water and the organic phase movement is described by an analog of Richard's equation. To describe the infiltration depicted in Fig. 1, the governing equation for the fluid head, h, in cylindrical coordinates is given by

$$\frac{\partial \Theta}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}\left\{ r K(\Theta)\frac{\partial h}{\partial r}\right\} + \frac{\partial}{\partial z}\left\{ K(\Theta)\left[1 + \frac{\partial h}{\partial z}\right]\right\} = 0, \tag{1}$$

where

$$h = P/\rho g, \tag{2}$$

Θ represents the volume fraction of gasoline at any point in the medium, P the pressure in the gasoline phase, K the fluid conductivity and r and z the lateral and vertical coordinate, respectively. In eqn. (2), ρ and g are defined as the density of gasoline and acceleration of gravity, respectively. This equation applies to the zone contaminated by gasoline, the zone bound by depth Z_f and radius R_f in Fig. 1.

Reible et al. [7] observed that a non-wetting organic phase such as gasoline penetrates an essentially homogeneous medium with a sharp front without
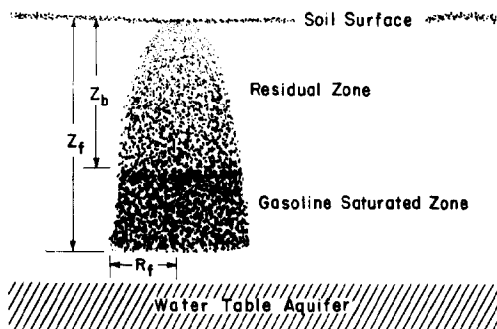

Fig. 1. Depiction of spill infiltration.

significant fingering. Assuming the gasoline infiltrates into the soil as a sharp front, Θ can be taken as zero before the front and some constant value behind the front. Denoting the gasoline volume fraction behind the front as $\tilde{\Theta}$, $K(\tilde{\Theta})$ is equal to $\tilde{K}$, a constant. $\tilde{K}$ is given by

$$\tilde{K} = (\kappa \kappa_r(\tilde{\Theta}) \rho g)/\mu, \tag{3}$$

where κ is the intrinsic permeability of the medium and κ_r is a relative permeability that accounts for the fact that not all of the pore space is available for gasoline flow due to the presence of residual water; μ is the viscosity of the infiltrating fluid, gasoline. In our model of the infiltration, water is immobile and the gasoline is displacing air from the porous medium. Compared to air, the gasoline tends to wet the water which in turn is assumed to wet the soil surface. With this view of the infiltration, gasoline is the wetting fluid during the infiltration and air is the non-wetting fluid. A commonly used relationship for relative permeability versus fluid volume fraction, that of Brooks and Corey [8], suggests that the relative permeability of gasoline is then given by

$$\kappa_r = \left[\frac{(\tilde{\Theta} - \Theta_{ir})}{(\epsilon - \Theta_{ir})} \right]^{(2+3b)/b}, \tag{4}$$

Here, Θ_{ir} is the irreducible residual gasoline fraction, ϵ is the porosity and b is a grain-size distribution parameter that varies from about 2.8 in sand to more than 10 in clays (Cosby et al. [9]). Reible et al. [6] observed that the use of the wetting fluid correlation of Brooks and Corey worked well in describing the infiltration of an automatic transmission fluid and isooctane in sand. They observed experimentally a κ_r of about 0.35 ± 0.05 with $\epsilon = 0.4$, $\tilde{\Theta} = 0.3$ (residual water fraction of 0.1) and $\Theta_{ir} \approx 0.05$. Using $b = 2.8$, substitution in eqn. (4) predicts a $\kappa_r = 0.29$, in good agreement with the experimental observations.

If the effective conductivity can be assumed constant behind the infiltrating front, eqn. (1) can be simplified to

$$\frac{1}{r} \frac{\partial}{\partial r} \left\{ r \frac{\partial h}{\partial r} \right\} + \frac{\partial^2 h}{\partial z^2} = 0 \tag{5}$$

in this region. The solution of the above equation provides the fluid head everywhere within the gasoline saturated region. The rate of infiltration can then be found through Darcy's Law as the product of the head gradient and the effective conductivity.

In general, the solution of the above equation is difficult in that the position of the front is not known but must be determined as part of the solution. In the absence of capillary forces, however, the gasoline in a homogeneous medium moves only vertically at speed $\tilde{K}/\tilde{\Theta}$ over an area of $Q/\tilde{K}$, or equivalently, a radius of
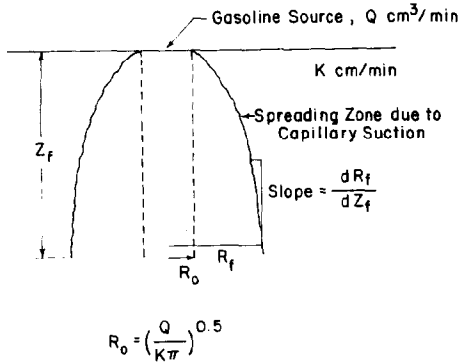
Fig. 2. Conceptual model of liquid movement.

$$R_o = \left[\frac{Q}{K\pi}\right]^{0.5} \tag{6}$$

Here Q is the volumetric fluid infiltration rate. In a medium composed of layers of different fluid conductivity, the lowest conductivity layer will typically define the radius of the infiltrating fluid.

As a result of capillary forces, the initial vertical rate of movement exceeds $\tilde{K}$ and lateral spreading occurs from the cylinder of radius R_o defined by eqn. (6). For simplicity, let us assume that the lateral rate of growth of the infiltrating gasoline plume is independent of its growth vertically. This approximation is essentially equivalent to the assumption that the lateral rate of growth of the infiltrating plume (driven by capillary forces) is much less than the vertical rate of growth (driven by both capillary and gravity forces). The conceptual model of the plume growth during the infiltration is shown in Fig. 2.

Vertical movement

Reible et al. [6] considered the one-dimensional vertical motion of an infiltrating nonaqueous phase. This section essentially summarizes the approach presented there.

Neglecting lateral movement, the fluid head in the infiltrating gasoline phase is given by (from eqn. 5)

$$\frac{\partial^2 h}{\partial z^2} = 0, \tag{7}$$

which suggests that the fluid head variation is linear with height. By using Darcy's Law, the vertical movement with time, t, is then given by

$$w = \tilde{\Theta}\frac{dZ_f}{dt} = \tilde{K}\frac{dh}{dz} \approx \tilde{K}\frac{\Delta h}{\Delta z}. \tag{8}$$

The change in head between the source and the leading edge of the front can be taken to be the sum of the average capillary suction head at the front (denoted by H_f) and the gravity head (denoted by the position of the front relative to the surface, Z_f). Reible et al. [6] observed that the fluid saturation profile at the leading edge of the infiltrating front, which gives rise to the capillary suction effect, was approximately independent of time. Therefore the capillary suction can be adequately represented by its average value. Thus the vertical movement of the gasoline phase is given by

$$\tilde{\theta}\frac{\mathrm{d}Z_f}{\mathrm{d}t} \approx \tilde{K}\frac{H_f + Z_f}{Z_f} \tag{9}$$

This is analogous to the classic approach of Green and Ampt [10] to water infiltration in the unsaturated zone.

The ponded depth of the spilled liquid at the surface is neglected in equation (7). If a ponded depth exists, the driving head in eqns. (8) and (9) should include this depth. If the gasoline has completely infiltrated (no ponded depth at the surface), a drainage front with an associated capillary suction forms. The location of the drainage front is at location Z_b in Fig. 1. Assuming that the drainage front is also sharp and that the effective capillary suction at that front is H_b, the vertical movement of the gasoline is given by

$$\tilde{\theta}\frac{\mathrm{d}Z_f}{\mathrm{d}t} \approx \tilde{K}\frac{(H_f - H_b) + (Z_f - Z_b)}{(Z_f - Z_b)} \tag{10}$$

H_f and H_b can be estimated directly from infiltration experiments or indirectly through capillary pressure and relative permeability versus saturation measurements in a manner analogous to that used by Morel-Seytoux and Khanji [11] to describe an effective capillary suction head during water infiltration in the unsaturated zone. Reible et al. [6] have also indicated that these parameters can be approximated by the air-entry head in the two phase flow of organic and air in the unsaturated zone, or equivalently, an effective capillary rise height (H_{cr}). Kessler and Rubin [12] also indicated that the capillary suction versus saturation curve for a non-aqueous phase is approximately given by that for water times the ratio of the interfacial tensions. Thus the effective capillary suction for a gasoline phase can be approximated by the effective capillary suction for water (capillary rise height) by the relation

$$H_{f,4} \approx (\sigma_4/\sigma_2)H_{f,2} \tag{11}$$

Here, σ_4 and σ_2 refer to the surface tensions of the gasoline and aqueous phases, respectively. Although an air-entry head or an effective capillary rise height can be difficult to define in a soil medium, residual water tends to wet the soil surface and fill the fine pores of the medium, effectively providing a more homogeneous pore size distribution for a non-aqueous phase liquid [6]. In a ho-

mogeneous pore size medium, an entry pressure or effective capillary rise height can be easily defined due to the typically sharp capillary pressure versus saturation profile observed. In a sandy loam with an approximate water air entry pressure of 25 cm, Reible et al. [6] reported an effective $H_f \approx H_{cr} \approx 5$ cm for isooctane and 8 cm for an automatic transmission fluid.

The effective capillary suction at the drainage front (H_b) would, in general, be different from H_f due to hysteresis in the wetting and drainage portions of the capillary pressure versus saturation relationships. In the absence of experimental values for H_b, however, the neglect of hysteretic effects and the assumption that $H_f \approx H_b$ may be necessary. In the same sands reported above, Reible et al. [6] found an effective $H_b \approx 8$ cm for isooctane and 11 cm for automatic transmission fluid.

The back or drainage front location in eqn. (10) can be eliminated with a statement of conservation of volume

$$HO = \tilde{\Theta}(Z_f - Z_b) + \Theta_{or} Z_b \tag{12}$$

where Θ_{or} is the residual gasoline content of the soil (i.e. the gasoline immobilized by capillary forces after passage of the saturated plug) and HO is the height of the soil zone that would be saturated with gasoline as a result of the spill or leak.

By using eqn. (12), eqn. (10) can then be integrated from an initial fluid front location, Z_{f0}, at time 0 to a final fluid front location, Z_f, at time t

$$t = \frac{\tilde{\Theta}}{\tilde{K}}\left[Z_f - Z_{f0} - A \ln\left\{ \frac{Z_f - HO/\Theta_{or} + A}{Z_{f0} - HO/\Theta_{or} + A} \right\} \right] \tag{13}$$

where

$$A = \frac{\Theta_{or} - \tilde{\Theta}}{\Theta_{or}}(H_f - H_b) \tag{14}$$

If $H_f \approx H_b$, or if $H_f \ll Z_f$, eqn. (13) reduces to simply

$$t = \frac{\tilde{\Theta}}{\tilde{K}}[Z_f - Z_{f0}] \tag{15}$$

Equation (15) confirms that the rate of vertical movement of an infiltrating fluid in the absence of capillary forces is $\tilde{K}/\tilde{\Theta}$, i.e. the head gradient is unity.

Lateral movement

In sandy materials, the capillary head gradients are generally much smaller than the gravity head gradient that drives the vertical motion. The geometry of the contaminated zone can thus be approximated as a cylinder slowly growing with depth from an initial radius, R_o, given by eqn. (6). Assuming that the

vertical gradient in fluid head is unity as implied by eqn. (15), eqn. (5) can be written

$$\frac{1}{r}\frac{\partial}{\partial r}\left\{r\frac{\partial h}{\partial r}\right\} = 0 \tag{16}$$

subject to

$$
\begin{aligned}
h &= z - H_f &&\text{at} &&r = R_f \\
h &= z &&\text{at} &&r = R_o
\end{aligned}
\tag{17}
$$

Here R_f is the radial extent of contaminated zone at any time. The solution to this equation gives the fluid head as a function of radius in the cylindrical zone of contamination,

$$h = -\frac{H_f}{\ln(R_f/R_o)}\ln(r/R_o). \tag{18}$$

Again by using Darcy's Law, eqn. (18) can be used to estimate the rate of lateral growth of the contaminated zone

$$\tilde{\Theta}\frac{dR_f}{dt} = -\tilde{K}\frac{dh}{dr}\bigg|_{R_f}, \tag{19}$$

or

$$\tilde{\Theta}\frac{dR_f}{dt} = \tilde{K}H_f[R_f\ln(R_f/R_o)]^{-1}. \tag{20}$$

By recognizing once again that the rate of vertical growth of the infiltrating plume is $\tilde{K}/\tilde{\Theta}$, the ratio of the lateral to vertical growth is given by

$$R_f\ln(R_f/R_o)\frac{dR_f}{dZ_f} = H_f, \tag{21}$$

or

$$\frac{R_f^2}{2}\ln(R_f/R_o) - \frac{R_f^2}{4} + \frac{R_o^2}{4} = H_f(Z_f - Z_{f0}). \tag{22}$$

This formula gives the radius of the contaminated zone as a function of the depth of penetration of the gasoline front. Equation (22) is convenient in that the volume of contaminated soil is often desired. The volume, V, of the contaminated zone is given by

$$V = HO(\pi R_o^2) + \int_{Z_{f0}}^{Z_f} \pi R_f^2(z)\,dz, \tag{23}$$

where $HO\,(\pi R_{f0}^2)$ is the initial volume of the contaminated soil.

Vapor movement

Let us now consider the movement of gasoline vapors in the unsaturated zone. Vapor movement away from the liquid contaminated zone is assumed to occur by diffusion, that is vapor pumping by liquid movement or by temperature and/or pressure variations is neglected. Since gasoline is quite volatile (vapor pressures of 0.1–0.3 bar at 20°C) and can be detected at very low absolute concentration levels, the detectable extent of gasoline vapors moves rapidly. At distances far from the source, the geometry of the source is unimportant. Let us assume that the source is a hemispherical region of radius a below an impermeable surface. This represents the minimum extent of the liquid source region for the vapors. The conceptual model of the vapor movement is shown in Fig. 3. The vapor partial pressure, $\mathscr{P}$, away from the source is given by

$$\theta_1 \frac{\partial \mathscr{P}}{\partial t} = D_{\text{eff}} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial \mathscr{P}}{\partial r}, \tag{24}$$

subject to

$$\mathscr{P}(r \leq a, t) = \mathscr{P}_{\text{eq}}, \qquad \mathscr{P}(r = \infty, t) = 0$$

$$\mathscr{P}(r, t = 0) = 0, \qquad \frac{\partial \mathscr{P}}{\partial z}(z = 0) = 0.$$

Here θ_1 is the void fraction available for vapor transport. The solution to this equation can be shown to be [13]

$$\mathscr{P} = 2\mathscr{P}_{\text{eq}} \frac{a}{r} \text{erfc} \left\{ \frac{r-a}{2} \left[\frac{\theta_1}{D_{\text{eff}} t} \right]^{0.5} \right\}. \tag{25}$$

Erfc(ξ) represents the complementary error function $(1 - \text{erf}(\xi))$. The factor of 2 arises from the impermeable surface and indicates that a permeable surface would decrease the observed concentrations by the same factor. The effective diffusivity, D_{eff}, can be estimated from the relation presented by Bruell and Hoag [14], which is essentially the model of Millington and Quirk [15]

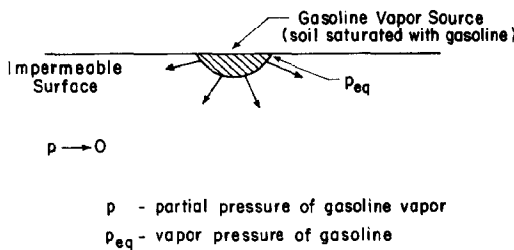$$D_{\text{eff}}/D = \theta_1 \frac{\theta^{2.34}}{\epsilon^{2.0}}. \tag{26}$$

Fig. 3. Conceptual model of vapor movement.

For a typical air diffusivity (D) of an organic compound of 0.1 cm^2/s, and with a residual water fraction of 0.1 and a total porosity of 0.40, the effective diffusivity, D_{eff}, is about 0.0112 cm^2/s.

Gasoline partitioning in the unsaturated zone

Let us now examine the constituents of the gasoline to define their fate. Benzene and toluene are the constituents of gasoline that pose the greatest threat to ground-water supplies and will be the only constituents considered here.

Let us first estimate the activity coefficient of these constituents in gasoline. Generally, the non-aqueous phase is assumed to be ideal but this assumption is strictly valid only for a mixture of similar compounds. A variety of estimation methods are available, but let us employ Scatchard–Hildebrand's theory due to its applicability to nonpolar mixtures such as gasoline, the availability of the necessary parameters, and its simplicity. Scatchard–Hildebrand theory suggests that the activity coefficient of benzene or toluene in the gasoline phase can be estimated by eqn. (27) [16],

$$\Gamma_i = \exp\left\{\frac{\nu_i \phi_j (\delta_i - \delta_j)^2}{RT}\right\}. \tag{27}$$

Here, δ_i and δ_j represent the solubility parameters for the constituent of interest (e.g. benzene, $\delta = 9.2$ [cal/cc]$^{1/2}$) and gasoline (taken as n-octane, 7.5 [cal/cc]$^{1/2}$), respectively, and ν_i is the molar volume of the constituent (benzene, $\nu_i = 89$ cc/mol). ϕ_j is the ratio of the mole fraction weighted molar volume of gasoline to the mole fraction weighted molar volume of the mixture. Since benzene is present in only small quantities (typically 1% by weight), $\phi_j \approx 1$ for this constituent. R and T are the ideal gas constant and the absolute temperature, respectively (1.987 cal/(mol K) and 298 K). Substituting for each of these values, Γ_i for benzene is about 1.54. A similar calculation for toluene yields $\Gamma_i \approx 1.36$.

Partitioning into the aqueous phase

This activity coefficient can be used to estimate the aqueous solubility or the partition coefficient between the non-aqueous and aqueous phases. At equilibrium, the fugacity of the gasoline and aqueous phases are equal. Fugacity can be thought of as a "corrected pressure" equal to the partial pressure of that component in a mixture of ideal gases but incorporating the effect of non-idealities under other conditions. The equality of fugacities can be expressed in terms of activity coefficients as shown in eqn. (28).

$$(X_i \Gamma_i P_i^{\text{sat}})_4 = (x_i \gamma_i p_i^{\text{sat}})_2. \tag{28}$$

The subscript 2 again represents the aqueous phase and 4 the gasoline phase

(subscripts 1 and 3 represent the air and soil phases, respectively). Thus the activity coefficient in the gasoline phase is represented by Γ_i while the activity coefficient in the aqueous phase is γ_i. $P_i^{sat} = p_i^{sat}$, since these terms represent the pure component pressures at the same temperature, pressure and *phase* as the mixture, and both phases are liquids. We may also assume that the sparingly water-soluble benzene and toluene follow Henry's Law (linear partitioning) in the aqueous phase and thus γ_i is simply the inverse of the aqueous solubility expressed in mole fraction units (for benzene, $\gamma_i = 2430$). Thus the mole fraction based water–gasoline partition coefficient for benzene is

$$K_{24} = X_i/x_i = \gamma_i/\Gamma_i \approx 0.00062. \tag{29}$$

A similar calculation for toluene suggests that $K_{24} \approx 0.00014$. The low magnitude of these numbers suggest that the mole fractions of benzene and toluene in the gasoline phase will be much higher than those in the aqueous phase. On a weight basis (ratio of grams component per gram phase), these partition coefficients are 0.0039 for benzene and 0.00089 for toluene. If the gasoline contained 1 wt.% benzene this suggests that the residual water in the soil would contain, at equilibrium, 39 ppm benzene. If the gasoline contained 10% toluene, the residual water in the unsaturated zone would contain about 89 ppm toluene. Thus a small but potentially significant quantity of the gasoline constituent would be contained within the water in the unsaturated zone. Note that these aqueous concentrations are small enough (much less than their aqueous solubilities) to justify the assumption of linear partitioning between the aqueous phase and adjacent phases.

Partitioning into the soil phase

There also exists the possibility that the benzene and toluene would be adsorbed onto the soil. The partitioning between the gasoline and a wet soil phase is given by

$$K_{34} = K_{32}/K_{42} \approx \begin{cases} 0.007 \text{ for benzene} \\ 0.003 \text{ for toluene} \end{cases}, \tag{30}$$

where K_{32} represents the soil–water partition coefficient for benzene or toluene which can be estimated via standard methods [16]. Equation (30) assumes that the partitioning is controlled by the water film that wets the surface of the soil particles. Assuming a soil organic carbon content of 1%, for example, gives a K_{32} of 1.8 and 3.8 for benzene and toluene, respectively. Here K_{32} was taken as equal to the product of the organic carbon based partition coefficient (K_{oc}) and the fraction organic carbon in the soil (f_{oc}). K_{oc} was assumed to be adequately correlated with a compound's aqueous solubility (S) by [18]

$$\log K_{oc} = -0.54 \log S + 0.44. \tag{31}$$

Since the residual water is assumed immobile during the infiltration of the

gasoline phase, the soil matrix and the residual water can be treated as a single phase. The effective partition coefficient between the gasoline and the combined phases, defined on the basis of only the soil mass, is given by

$$K_{4\text{eff}} \equiv \frac{\text{gr/gr gasoline}}{\text{gr/gr soil}} = \frac{K_{42}}{K_{32} + W/S}, \tag{32}$$

, where W/S is the weight ratio of the residual water to the adsorbing soil. When the effective partition coefficient is defined in this manner, the residual water serves only to enhance the sorptive capacity of the soil. This allows a retardation coefficient for the components in the non-aqueous phase to be defined identically to that used for aqueous phase movement. That is, the velocity of a non-diffusive, non-aqueous phase contaminant front (V_{cont}) is related to the bulk phase front velocity (V_4) by the relation

$$V_{\text{cont}} = \frac{\epsilon}{\epsilon + \rho_b K_{4\text{eff}}} V_4. \tag{33}$$

Partitioning into the vapor phase

Since gasoline constituents are volatile, significant quantities are partitioned into the vapor phase. By using the fugacity concept and assuming that the vapor phase is ideal, the partial pressure of a compound in the vapor phase in equilibrium with the gasoline phase is given by

$$\mathscr{P} = (x_i \Gamma_i p_i^{\text{sat}})_4 = (x_i \Gamma_i P^{\text{v}})_4, \tag{34}$$

where P^{v} is the pure component vapor pressure. If the gasoline phase could be assumed ideal, this would reduce to Raoult's Law. Once away from the envelope contaminated by the non-aqueous phase liquid, the partial pressure of the component is defined by equilibrium with the soil and water phases. Thus

$$\mathscr{P} = (x_i \gamma_i p_i^{\text{sat}})_2 = (x_i \gamma_i P^{\text{v}})_2 = H x_i, \tag{35}$$

where H is a Henry's Law coefficient.

The effective diffusivity given by eqn. (26) would be reduced by retardation associated with the sorption of the vapors into the soil and water phases. For dry soils, direct sorption onto the soil phase can be very large. In the presence of water, however, much of the soil surface is covered by moisture and the partitioning between phases is controlled by the water phase. That is,

$$D_{\text{ret}} = D_{\text{eff}}/\alpha, \tag{36}$$

where

$$\alpha = \Theta_1 + \Theta_2/H + \rho_b K_{32}/H. \tag{37}$$

Here, Θ_w represents the volumetric water content, ρ_b the bulk density of the soil, K_{32} the partition coefficient between the water film and soil and H the

partition coefficient between the water film and the soil vapor space. This equation assumes that sorption into the soil phase occurs only after dissolution into the water film at the surface. Thus water insoluble vapors such as the bulk hydrocarbon vapors from gasoline would be essentially unretarded by sorption while the more soluble vapors such as benzene could be significantly retarded. In dry soils, however, when direct sorption of the vapors can occur, these compounds would also be significantly retarded.

Contamination of recharge water

The initial infiltration of the gasoline gives rise to a residual gasoline level. Because the gasoline is typically non-wetting compared to water, much of this residual can be displaced by water infiltration, for example after rainfall events. In sand column experiments, Reible et al. [6] observed an initial residual fraction of isooctane (a surrogate for gasoline) of approximately 10% and displacement of about half of this amount by subsequent water infiltration. Much of the mobile gasoline residual was displaced immediately by an advancing water front. Continued water infiltration, however, was only marginally effective at removing more gasoline. As indicated by Wilson and Conrad [19], a gradient far exceeding the natural gravity-driven infiltration gradient would normally be required to purge the soil of the residual chemical. The rate of movement of the water and gasoline phase during this period is truly a multiphase flow phenomena that requires, in general, solution of conservation equations in each of the fluid phases.

As indicated above, much of the gasoline will be redistributed after the initial rainfall event to an essentially irreducible volume fraction. The existence and magnitude of an irreducible fraction is uncertain but as indicated above may be of the order of 50% of the initial residual fraction in sand.

The level of contamination of the recharge water upon redistribution of the gasoline can presumably be found by the same methods described for estimating the contamination of the residual water during the gasoline infiltration. Equilibration of the various phases is an appropriate assumption in the absence of short-circuiting due to medium heterogeneity. Thus the net movement of the water soluble contaminants in gasoline can be related to the volume of recharge waters and their net movement as defined by conventional aqueous phase models. A retardation factor ($R_f = \epsilon/[\epsilon + \rho_b K_{32}]$) would apply to the movement of constituents in the recharge water. The aqueous phase retardation factor for benzene and toluene is about 5 and 10, respectively, with a soil bulk density of 2.5 g/cc, a porosity of 35% and a soil organic carbon content of 1%.

Example application

Leak detection monitor effectiveness

To illustrate the applicability of the approach described here to practical problems in assessing or regulating subsurface contamination by non-aqueous

TABLE 1

Leaking underground storage tank scenario soil and leak parameters

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Soil Characteristics
Type: Homogeneous sandy soil
Aquifer: Water table aquifer — 6 m depth
Zone: Extent of interest — 6 m × 6 m × 6 m
     (zone within which monitors are located)
Surface: Paved (Impermeable)
    $b = 2.8, \epsilon = 0.40$
    $K = 10^{-3}$ cm/s (saturated conductivity)
    $H_f = 10\text{-}20$ cm, $\tilde{\Theta}_{wr} \approx 10\%, \tilde{\Theta}_{or} \approx 10\%$

Leak
Material: Gasoline containing 1% benzene and 10% toluene by weight
Location: Surface
Rate: 0.2 gal/h (Minimum detectable leak rate called for in proposed regulations)
Monitors: Vapor — Located within zone of interest
       Water table — Located at 6 m depth

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phase liquids, consider the performance of underground storage tank leak detection methods. The EPA rules for leak detection monitoring (EPA-OUST [19]) identify six methods for leak detection monitoring. Two of these methods, water table monitoring and vapor phase monitoring, are release detection methods designed to detect the presence of contamination as a result of the leak. To analyze the performance of each of these monitors in a specific underground storage tank leak scenario, assume the tank is located in a homogeneous sandy soil with a saturated gasoline conductivity of 10^{-3} cm/s. In the absence of fluid–soil interactions the gasoline conductivity can be estimated from the medium's intrinsic permeability by eqn. (3). A water table will be assumed located 6 m below the surface. Other soil and leak parameters are included in Table 1.

Vapor monitor

Let us first consider the vapor monitor and determine its performance, defined as the time required before detection of a leak. Under the proposed regulations, the vapor monitor is required to be used in a subsurface environment which has a low background total volatile organic carbon (VOC). Leak detection occurs when VOC levels significantly higher than background are observed. The specific concentration that is significant is dependent upon the monitor and the normal fluctuation of background levels. Let us assume for the purposes of this discussion that the significant level is a change of 100–500 ppm VOC. We will assume that the Reid vapor pressure of the stored gasoline is about 0.5 atm. This approximately corresponds to a vapor pressure of 0.15

atm at an assumed soil temperature of 15°C. This vapor pressure would be maintained wherever separated phase gasoline existed within the subsurface, so let us assume that the gasoline is confined to the minimum area surrounding the leak; i.e. a hemisphere extending from the surface. The radius of this hemisphere (which we will denote with the symbol a) grows with time according to

$$\dot{q} = \tilde{\Theta}(\tfrac{2}{3}\pi a(t)^3), \tag{38}$$

where $\tilde{\Theta}$ is the volume fraction available for the gasoline and q is the liquid leak rate. For a 0.2 gal/h leak, the saturated liquid zone would extend over a hemispherical radius of 95 cm. The average radius over the time of the leak would be 75 cm.

Vapor movement away from the liquid contaminated zone is assumed to occur by diffusion. Since the essentially insoluble bulk hydrocarbon vapors are of interest here, partitioning into the residual water and soil phases will be neglected. The soil surface will be assumed impermeable and we neglect the presence of the storage tank allowing the concentration profiles away from the source to be governed by eqn. (25).

Let us now calculate the concentration at the edge of the zone of interest (maximum distance, $r - a$, of 5.25 m regardless of leak source location) from a 30 day gasoline leak. 30 days is the proposed monitoring frequency in the regulations. Equation (25) gives the predicted concentration as 8700 ppm. Thus, easily detectable concentration changes occur throughout the zone of interest even though several conservative assumptions (e.g. radial liquid movement, no reflection at tank wall) were used.

Water table monitor

Let us now compare these results to the response of the water table monitor. As described in the proposed regulations, a water table monitor should be capable of detecting a layer of 0.125″ of free gasoline floating on a water table no more than 20″ below the surface. The volume of leak required to achieve this gasoline level is essentially the volume of gasoline contained within the overlying unsaturated zone (i.e. the volume of gasoline in a 0.125″ layer can be neglected). The rate of infiltration of gasoline is most rapid if the leak is of sufficient size to result in a saturated plug of gasoline infiltrating through the unsaturated zone. Regardless of the saturation level at the infiltration front, however, the region behind the front is at least residually saturated with gasoline. The minimum volume of gasoline that must leak before detection at the water table is thus the residual saturation fraction times the volume contaminated. The residual gasoline fraction can be as high as 10% of the total soil volume or more (Wilson and Conrad [19], Reible et al. [6]) and 10% will be used here. Due to spatial variability of the soil, the average residual saturation level may be much less than this figure (e.g. CONCAWE [21] suggests an

average residual saturation of 1.25%). The lower estimates of residual saturation are appropriate for calculations aimed at determining the earliest arrival time of any gasoline at the water table, while the larger may be more appropriate for determining the ultimate retention of gasoline by the soil as we are using it here.

The problem of determining the time until detection of a floating gasoline layer on the water table thus becomes that of determining the total volume of soil contaminated by the gasoline and estimating the leak time required to fill that volume to a residual saturation level of 10%. Let us consider a leak near the soil surface which requires infiltration through the entire depth of the unsaturated zone. The volume of the contaminated zone is given by eqn. (23). If H_f is taken to be aproximately 20 cm, the radial extent of the leaked gasoline plume upon arrival at the water table (6 m below the surface) would be 1.4 m (R_f). If H_f were taken to be 10 cm, approximately consistent with the values found by Reible et al. [6] in a fine sand, R_f would be 1.1 m. The volume of the contaminated zone, again by using $H_f = 20$ cm, is 22 m^3. Using a residual gasoline fraction of 10%, approximately 2.2 m^3 of gasoline must be leaked before the detection by a water table monitor. At a leak rate of 0.2 gal/h, as called for in the proposed regulations, this would require in excess of 4 months (121 days). Although the assumptions of the model is such that it may not accurately define the actual time of water table monitor detection, it would suggest that the water table monitor would be inadequate under some circumstances.

As can be seen from the above calculations, a single vapor monitor in the zone of interest would be expected to perform adequately and provide leak detection within the 30-day period suggested in the proposed regulations. Even a perfect water table monitor (i.e. one that detects free product at the instant of its arrival at the water table), however, might not indicate a leak for more than 4 months. While these estimates were made for a single tank and soil configuration, it is expected that the conclusions can be generalized. In particular, these results suggest that water table monitoring may not provide an indication of a storage tank leak until long after significant environmental damage has occurred. Perhaps for these reasons, the regulations limit the use of a water table monitor to very permeable soils ($K > 0.01$ cm/s).

Conclusions

These calculations demonstrate that crude but useful estimates of the subsurface fate and transport behavior of non-aqueous contaminants can be made. Although research should continue to improve the understanding of such processes, the scientific basis currently exists to provide guidance for regulatory or remediation planning for non-aqueous phase subsurface contamination.

Although the calculation procedures identified here are simple, the models are consistent with the limited database generally available and with the lim-

ited, semi-quantitative predictions, which are generally the objective of preliminary risk and site assessment calculations for the purposes of regulatory development.

Acknowledgements

References

1   C.R. Faust, Transport of immiscible fluids within and below the unsaturated zone: A numerical model. Water Resour. Res., 21 (1985) 587.
2   A. Baehr and M.Y. Corapcioglu, A predictive model for pollution in soils and groundwater, in: Petroleum Hydrocarbons and Organic Chemicals in Ground Water. Natl. Water Well Assoc., Washington, OH, 1984, p. 144.
3   L.M. Abriola and G.F. Pinder, A multiphase approach to the modeling of porous media contamination by organic compounds 1. Equation development, Water Resour. Res., 21 (1985) 11.
4   M. Osbourne and J. Sykes, Numerical modeling of immiscible organic transport at the Hyde Park landfill. Water Resour. Res., 22 (1986) 25.
5   T. Kappusamy, J. Sheng, J.C. Parker and R.J. Lenhard, Finite element analysis of multiphase immiscible flow through soils, Water Resour. Res., 23 (1987) 625.
6   D.D. Reible, T.H. Illangasekare, D.V. Doshi and M.E. Malhiet, Infiltration of immiscible contaminants in the unsaturated zone, submitted to Ground Water, (1989).
7   D.D. Reible, T.H. Illangasekare, D.V. Doshi and I.F. Ayoub, Development and experimental verification of a model for transport of concentrated organics in the unsaturated zone, in: Proc. of Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration. Natl. Water Well Assoc., Dublin, OH.
8   R.H. Brooks and A.T. Corey, Hydraulic properties of porous media. Colorado State University, Hydrology Paper No. 3, Boulder, CO, March 1964, p. 27.
9   B.J. Cosby, G.H. Hornberger, R.B. Clapp and T.R. Ginn, A statistical exploration of the relationships of soil moisture characteristics to the physical properties of soils, Water Resour. Res., 20 (1984) 682.
10   W.H. Green and G.A. Ampt, Studies on soil physics, J. Agri. Sci., 4 (5) (1911) 1.
11   H.J. Morel-Seytoux and J. Khanji, Derivation of an equation of infiltration, Water Resour. Res., 10 (1974) 795.
12   A. Kessler and H. Rubin, Relationships between water infiltration and oil spill migration in sandy soils, J. Hydrol., 91 (1987) 187.
13   J. Crank, The Mathematics of Diffusion. Oxford Press, London, 1975.
14   C.J. Bruell and G.E. Hoag, The diffusion of gasoline range hydrocarbon vapors in porous media. Experimental methodologies, Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection and Restoration. Natl. Water Well Assoc., Washington, OH, 1986.

15 R.J. Millington and J.P. Quirk, Permeability of porous solids, Trans. Faraday Soc., 57 (1961) 1200.

16 J.M. Prausnitz, Molecular Thermodynamics of Fluid-Phase Equilibria. Prentice-Hall, Englewood Cliffs, NJ, 1969.

17 W.J. Lyman, W.F. Reehl and D.H. Rosenblatt, Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York, NY, 1983.

18 S.W. Karickhoff, D.S. Brown and T.A. Scott, Sorption of hydrophobic pollutants on natural sediments, Water Resour. Res., 13 (1979) 241.

19 J.L. Wilson and S.H. Conrad, Is physical displacement of residual hydrocarbons a realistic possibility in aquifer restoration?, in: Petroleum Hydrocarbons and Organic Chemicals in Ground Water. Natl. Water Well Assoc., Washington, OH, 1989, p. 274.

20 EPA-OUST, Underground Storage Tanks, Final Rules. Federal Register, 9/23/88, Vol. 53, 185, 37194, Washington, DC.

21 CONCAWE, Protection of groundwater from oil pollution. Report No. 3/79, The Hague, Netherlands, 1979.