

SCREENING MODELS FOR ESTIMATING VAPOR INFILTRATION TO BUILDINGS

Prepared by

Edmund A.C. Crouch, Ph.D.
Cambridge Environmental Inc.
58 Charles Street
Cambridge MA 02141
www.CambridgeEnvironmental.com

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1 Introduction and Summary

This report presents various models that, in appropriate circumstances, might be used to estimate impacts to indoor air from subsurface contamination. The models discussed here are the conservative screening models presented in U.S. EPA (1992) guidance on assessing potential impacts to indoor air from subsurface contamination, together with simple combinations and extensions of those models. The discussion focuses on benzene, since benzene is often the contaminant of most concern, but the models are applicable to other volatile compounds, in particular, to the other BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), MTBE (methyl-tert-butyl ether), other aromatic and aliphatic hydrocarbons, and tetraethyl and tetramethyl lead.

The extended models are still conservative screening models, because they ignore several important factors, including source depletion and biodegradation, that reduce emission rates and hence indoor air concentrations of contaminants. Biodegradation alone can substantially reduce long-term impacts to indoor air under practical conditions by a large factor. In order to fully model biodegradation, source depletion, and other important effects simultaneously, one must employ more sophisticated models, such as the vadose zone interactive processes (VIP) model or three-dimensional models. In special cases, a simple screening model (described here) can be used to evaluate the effect of source depletion. Should all the screening models discussed here yield estimates of indoor air concentrations that are unacceptably high, the use of such more sophisticated models should be considered, together with other approaches such as direct monitoring of soil gas and indoor air.

The physical situation that has to be modeled is sketched in Figure 1 which illustrates a cross-section through the soil column beneath a building located above a contaminated area. The source of contamination is located at the groundwater level, floating on it, or at the level of a smear zone of non-aqueous phase liquid (NAPL) just above the groundwater, some distance below the building floor. Between the groundwater and the building floor lie layers of soil that remain wet through a combination of capillary action (drawing water from the groundwater below, perhaps with evaporation from the surface above), and infiltration of rainwater from above — this region of soil above the groundwater and below the building or soil surface is termed the vadose zone. The wetness of the soil varies, from completely saturated at the groundwater surface, to somewhat drier just beneath the building, and to relatively dry at the surface of the soil outside the building. The soil wetness profile is illustrated in Figure 2 (this is for illustrative purposes only — quantitative evaluation requires further data). The wetness may change substantially at soil layer boundaries, as shown, because of the different soil hydraulic properties in each layer. On a site such as that illustrated, with a silt layer with sufficient capillarity above a sand and gravel layer, the silt layer may be wetter than the upper part of the sand and gravel layer.

From the contamination source, benzene vapors may move upwards by diffusion through the air and water in the pore spaces of the soil. The ease of such diffusion depends strongly on the amount of water in the soil — more water results in smaller air pore spaces, and less ease of diffusion, since diffusion rates through air are much higher than through water. The variation in

wetness of the soil with distance above groundwater shown in Figure 2 induces a variation in the effective diffusivity of the benzene vapor, as shown in Figure 3. The exact shape of this curve is explained further in Section 8, but the parameter values used are simply illustrative at this time.

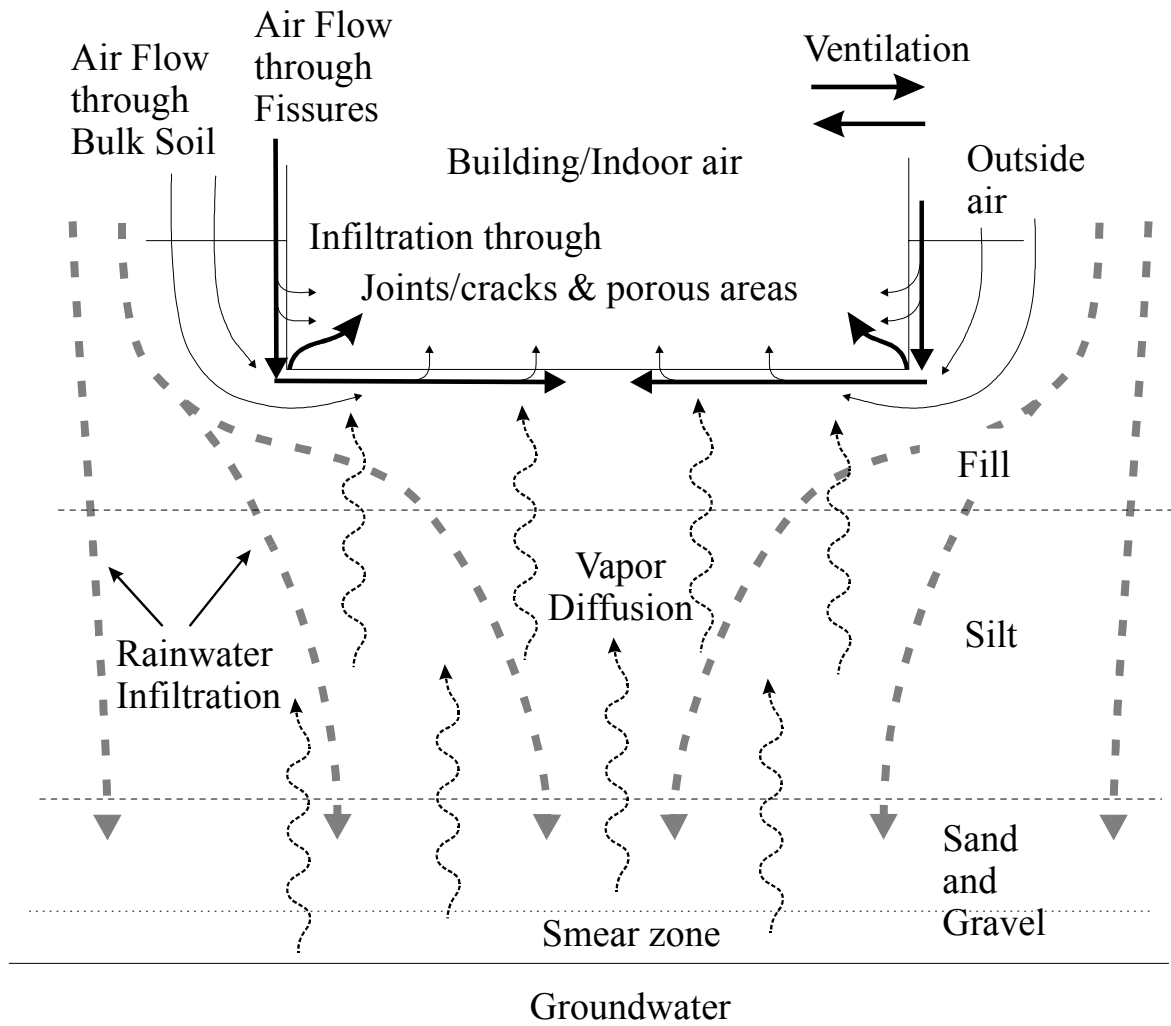


Figure 1 A sketch of the physical situation to be modeled to estimate indoor air concentration

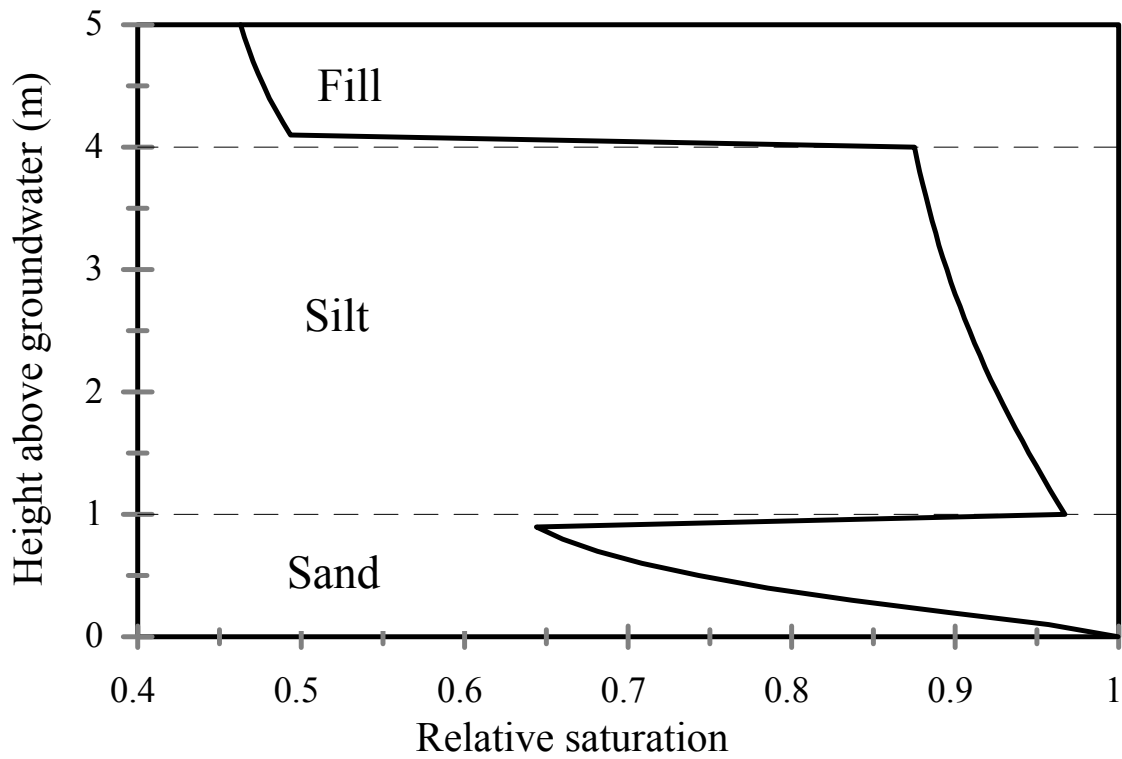


Figure 2 Variation of wetness of the soil with height above groundwater

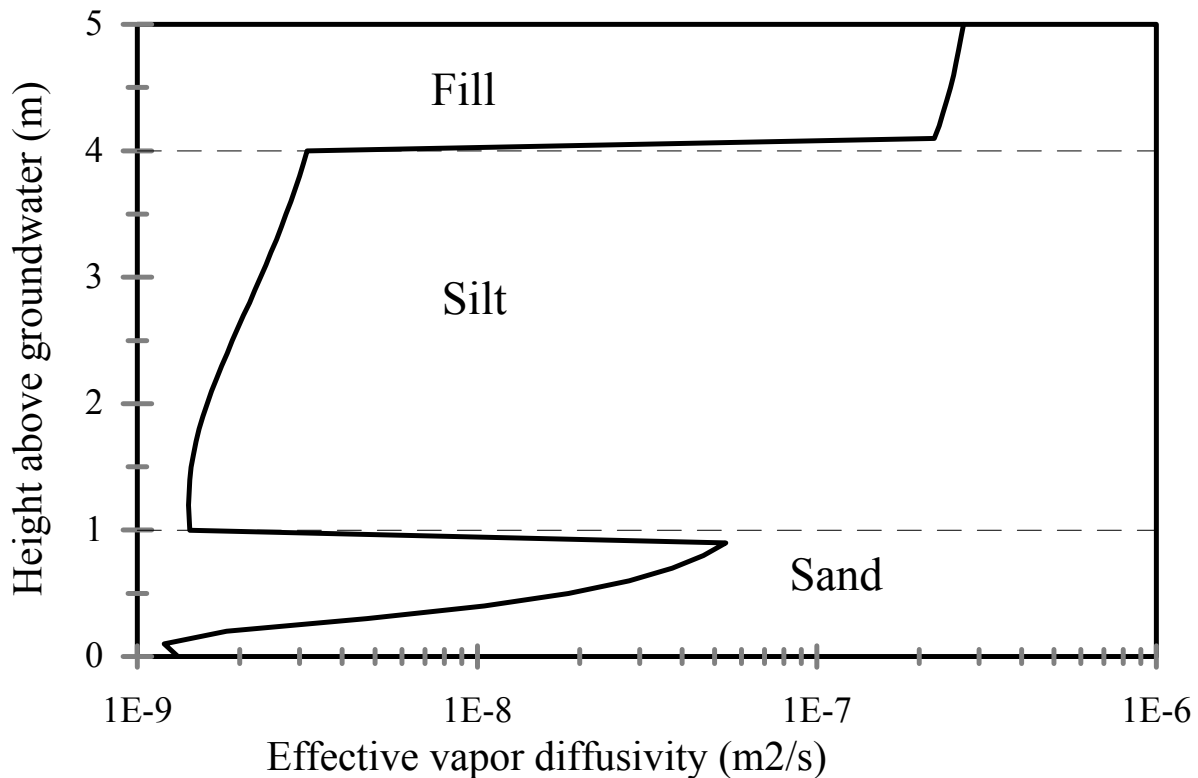


Figure 3 Variation of effective diffusivity of benzene in soil with height above groundwater

Most of the resistance to diffusion in the vadose zone comes from the wettest regions of the soil. The wettest region is usually just above the contamination source, closest to the groundwater, a region often called the “capillary fringe.” For a site with a silt layer above sand and gravel, as illustrated, the silt layer may have a substantial effect on the resistance to contaminant diffusion. In fact, the wetness of the soil continues varying with distance above groundwater. In analytical models of soil wetness, there may be no particular region that can be identified as a distinct capillary fringe, but in real soils there may be a layer of soil that is completely saturated — indeed, it is possible to have layers of completely saturated soil separated by layers with lower water content. Analysis of the physical situation has to take account of variation of soil wetness over the entire vadose zone, from groundwater to surface (or building underside).

While vapor diffusion tends to allow benzene vapor to move upwards, the downward flow of infiltrating rainwater, in addition to increasing the wetness of the soil, has a much larger, direct, effect on the net rate of movement of benzene. As it flows downwards, water will dissolve benzene vapor, and carry benzene back downwards in solution. The opposite can also occur —

if water is evaporating from the surface, there will be a net upward flow of water that carries benzene up.

Close beneath a building, benzene vapors diffusing upwards may become entrained in an air flow driven by the difference in pressure between the interior of the building and the outside, and flowing into the building through cracks or porous places in the building walls or floor. Very often, the inside of a building is at slightly lower pressure than outside (because of temperature differences and/or forced ventilation in the building), so that air flows (shown by arrows in Figure 1) are inward, into the building. If the air flow is small enough (that is, if the sub-surface building walls and floors are sufficiently air-tight), the air flow may be too small to entrain all the diffusing benzene vapor, and the vapor will be partially diverted around the building. However, such an effect is unlikely, unless the building is specifically designed to be airtight below the soil surface, and the usual effect is for all the benzene diffusing from below to be swept into the building. In practice, for most buildings, most of any air flow probably channels through fissures in the soil at the junction between soil and building, rather than flowing through the bulk of the soil. Even in situations where the flow is through the bulk soil, the flow of air is confined to a narrow region near the floor or walls.¹

The physical situation is thus fairly complex, and generally no attempt is made to include all the complications in models. Guidance by U.S.EPA (1992) suggests some screening models for estimating indoor air concentration due to groundwater contamination. In the U.S. EPA guidance, the screening models are (partially) separated into those used to estimate the contaminant flux through the soil, and models that are used to estimate indoor air concentrations, with each of the latter models usually relying on one of the former. Simple versions of these models, with some enhancements and additions, have been implemented in spreadsheets available from the U.S. EPA. The spreadsheets are documented in a Users Guide (U.S. EPA, 1997). Other, similar, models are available. For example, the BP RISC model incorporates a version of the Johnson and Ettinger model (Spence and Walden, 1997) The treatment here is unified, and examines models that may be labeled as:

- the Farmer model
- the Farmer model modified to take account of the capillary fringe, and
- the Johnson and Ettinger heuristic² model.

¹ If the smear zone extended up into the region of air flows, the modeling might become much more complex than described here. An example of such a situation is considered in Section 10.5, to illustrate an alternative simple screening model for such a circumstance.

² Johnson and Ettinger describe their model as "heuristic," because it does not precisely model the physical situation, but should incorporate the major parameters in approximately the correct way. For example, only air flow through bulk soil is considered, while any air flow through the fissures between soil and building wall or floor is ignored.

These models, by their simplicity, over-estimate indoor air concentrations. For example, because the Farmer model "ignores all possible attenuating factors, it is likely this model overpredicts the contaminant flux" (U.S.EPA, 1992).

The first, the Farmer model, ignores many of the physical processes shown in Figure 1, including the variation of soil wetness with depth, mass transport downwards by infiltrating rainwater, and the air flows near the building floor. Each distinguishable soil layer is treated as being of constant wetness throughout its entire thickness, with the assumption that all the benzene vapor diffusing upwards enters any building above the contamination source. The calculations performed by BP RISC for estimating indoor air calculations from soil contamination treat the vadose zone in this way also.

The second EPA screening model, a modified Farmer model, incorporates the effect of the capillary fringe; indeed it can account for the variation in wetness all the way through the vadose zone. It thus takes account of the wetness of the soil caused by capillary effects, but ignores the increase in wetness and the mass transport due to infiltration of rainwater. It also does not account for the air flows near the building floor. As described in U.S. EPA (1992), the modified Farmer model would require highly accurate measurements of the soil wetness near the groundwater level. The components of the BP RISC model used for estimating indoor air concentration from groundwater treat the vadose zone in this way also.

The last EPA screening model, the Johnson and Ettinger model, has as its major emphasis an attempt to take some account of the air flows. The EPA formulation of the Johnson and Ettinger model may be used together with the Farmer model or the modified Farmer model — there is no explicit selection or proscription of either one, although the examples present only the original Farmer model. Even with these modifications, the effects of infiltrating rainwater on soil wetness and on mass transport are ignored. The BP RISC model also incorporates the Johnson and Ettinger heuristic treatment of air flows and infiltration into a basement.

While all the models are considered usable by U.S. EPA (1992), the resultant over-estimates of indoor air concentrations may not be adequate on a particular site. The models can be improved by taking better account of actual field conditions and phenomena, but using the same input information. These improved models will give more accurate, but still conservative, results. The improvements shown in this report allow

- explicit inclusion of the capillary fringe (here meaning the variation in soil wetness through the entire vadose zone) in the Johnson and Ettinger model,
- inclusion of both the capillary fringe and infiltrating rainwater in the Johnson and Ettinger model, and
- use of data on soil properties to accurately account for the variation in soil wetness.

Since there may be a "smear zone" of contamination, where non-aqueous phase liquids (NAPL) have been left in the vadose zone above the groundwater level, this report also

- describes the effects of a smear zone of NAPL.

The simplest way to describe all these effects is to incorporate them simultaneously into an extended model, as is done in Section 2 of this report, although even this extended model omits the effects of the air flow through fissures between the soil and building wall or floor. The extended model reduces, under the appropriate conditions, to the EPA screening models, demonstrating equivalence in such conditions. Similar solutions for particular conditions allow illustration of the effect of omitting the capillary fringe, or infiltrating groundwater.

The modified Farmer model (including the effect of the capillary fringe — Section 4) and the Johnson and Ettinger heuristic model (Section 5) both augment the original Farmer model. The capillary fringe principally affects vapor transport near the bottom of the vadose zone, while the resistance of floors or walls incorporated into the Johnson and Ettinger modification affects vapor transport at the top of the vadose zone. Both modifications are incorporated in the extended model of Section 2. The extended model also incorporates the dual effects of infiltration of rainwater (or evaporation from the soil surface) — modification of the wetness of the soil, and downward (or upward) transport of benzene in dissolved form. The extension to include infiltration of groundwater is relatively simple,³ involving the same type of calculations as used in the capillary fringe modification. The treatment of a smear zone of NAPL (acting as the source of contaminant vapors) can also be incorporated in all of these models (Section 7). The extended model in Section 2 is formulated in such a way that the presence of layers of soil with different properties is automatically taken into account — all the soil properties can vary with depth in the formulation given there.

The results of incorporating the capillary fringe into the Farmer model are examined in Section 8, and the results of incorporating the effects of a building floor (the Johnson and Ettinger model) into the Farmer model are examined in Section 9. The capillary fringe modification incorporated in the U.S. EPA (1992) guidance documents takes account only of the water content of the soil, not the infiltration of water (due to rainfall) into that soil. As mentioned, the effect of rainwater infiltration can be incorporated into the Farmer and Johnson and Ettinger models, but incorporating biodegradation (in addition to the variation in soil wetness) requires the use of a more complex numerical approach.⁴ To avoid this complexity, all the models examined here ignore biodegradation (as do the EPA screening models and BP RISC).

³ That is, just as easy to implement in a spreadsheet as the effect of the capillary fringe.

⁴ Implementation of such a numerical approach is impractical in spreadsheets. Practical approaches that incorporate biodegradation have been described in cases where the soil water content is assumed to be constant throughout the vadose zone.

2 The physical problem and its mathematical formulation

All the simple models discussed by the EPA (1992) have as their basis analytic or very simple numerical solutions for one-dimensional steady-state transport of a volatile contaminant in the vadose zone, with equilibrium partitioning between all phases present. The simplification to one dimension is required to obtain such simple solutions. It is also a reasonable representation of the physical situation if the soil column and the surface are everywhere reasonably uniform in the horizontal direction — there should ideally be no surface obstructions such as houses that occupy only parts of the surface and provide a barrier to vapor diffusion or rainwater infiltration. We examine here the one-dimensional problem, and later consider qualitatively the effect of partial obstructions. The steady-state assumption is justified for all depths below about a meter — disturbances at the surface (such as rainfall, temperature fluctuations, and pressure fluctuations) are exponentially damped with depth in soil, the damping being higher for higher frequency disturbances, so that the vadose zone tends to have very constant properties (Section 11). The assumption about equilibrium partitioning is justified by comparison of the short time scales for local equilibration (Section 11) within the pore spaces of the vadose zone compared with time scales of interest in emission rate estimates (months to years) or even sampling events (minutes to hours).

The transport of a volatile contaminant in the vadose zone occurs primarily through diffusion in the vapor form, and mass transport dissolved in flowing liquid water. The wetness of the soil is thus a critical controlling factor, since the vapor diffusivity depends strongly on the amount of air pore space available,⁵ while movement of water within the vadose zone is affected by the soil wetness. Infiltration of rainwater thus has two major effects on the transport of contaminants in the vadose zone. First, the additional water increases the wetness of the soil above that expected when there is no infiltration, reducing the effective air pore space and hence reducing the effective diffusivity. Second, the downward flow of water contributes to the downward flux of any soluble contaminant. The calculations described later show that the second effect is dominant.

In view of this strong effect of water, the soil wetness has first to be modeled, and that is done in Section 2.1. With the soil wetness known, the diffusion of the contaminant vapor and the mass transport in dissolved form may be modeled as described in Section 2.2.

⁵ There may be other soil components or liquid contaminants present, such as NAPL, in addition to water, that reduce the amount of pore space available to vapors or gases. Water will also be present in vapor form, moving by diffusion.

2.1 The water capillary head and saturation

The governing equation⁶ for the water capillary head h in the one-dimensional system in steady state is

$$K \left(\frac{\partial h}{\partial z} - 1 \right) = -Q \quad (1)$$

where

- K is the unsaturated hydraulic conductivity of the soil (LT^{-1}),
- h is the capillary head (L) (this is the negative of the water pressure head, and is a positive quantity in the vadose zone),
- z is the height above the groundwater level (L), and
- Q is the downward volumetric infiltration rate of rainwater (LT^{-1})

A computationally convenient way to write the solution to this equation is

$$h = z - Q \int_0^z ds / K(s) \quad (2)$$

where the hydraulic conductivity K varies with the height above groundwater, through its dependence on the soil saturation. A convenient way of representing this dependence on wetness is to use the van Genuchten relationship between unsaturated and saturated hydraulic conductivity:

$$K = K_s S^{1/2} \left(1 - (1 - S^{1/M})^M \right)^2 \quad (3)$$

where the terms are:

- K_s saturated hydraulic conductivity (LT^{-1}),
- M a parameter of the model (dimensionless) — see below, equation (5),
- S relative saturation, given by

$$S = \frac{\theta - \theta_r}{\theta_s - \theta_r} \quad (4)$$

- θ the pore water volume fraction (dimensionless) at head h ,
- θ_r the residual water volume fraction (dimensionless) under completely drained conditions, and

⁶ This formulation is similar to that given in the EPA's MULTIMED model documentation (Salhotra *et al.*, 1993), although care has to be taken to match the sign of h and the direction of measurement of z .

θ_s the saturated water volume fraction.⁷

Other expressions have been proposed for estimating the relative hydraulic conductivity K/K_s (for a review, see Mualem, 1986). However, other estimates for K/K_s usually have little effect on the overall estimate of benzene flux or indoor air concentration.

Salhotra *et al.* (1993) note that good results for the solution of equation (1) may be obtained by a backward difference scheme. Equivalently, good results are obtained for equation (2) when the integral is approximated using the trapezoidal rule, using the beginning of the interval to estimate the size of the integrand. A step size of 0.1 meters is often sufficient to give adequate accuracy, but this can readily be altered.

The variation of connected pore water fraction with depth may be obtained from the soil properties at the site. The van Genuchten (1976) model is widely used to predict how soil water content varies with the pressure head. The van Genuchten model may be expressed as

$$S = \left(1 + (\alpha h)^N\right)^{-M} \quad (5)$$

where the terms are

S the saturation (dimensionless) at capillary head h ,
 α an empirical constant for the soil (L^{-1}),
 N an empirical constant for the soil (dimensionless), and
 $M = 1 - 1/N$.

2.2 Contaminant transport in the presence of infiltration

The one-dimensional transport of a contaminant through the vadose zone, with the contaminant in local partitioning equilibrium between soil, NAPL phase, water, and air, and above any region where the NAPL phase may be considered a source, may be modeled by the mass balance/diffusion equation

$$n_e \frac{\partial C}{\partial t} + \beta n_e C = \frac{\partial}{\partial z} \left(\frac{Q}{H} C + D \frac{\partial C}{\partial z} \right) \quad (6)$$

where the undefined terms are

C the concentration of contaminant in vadose zone air (ML^{-3}),
 t time (T),

⁷ This exposition differentiates between total water content of the soil, represented by θ (with various subscripts), and the connected part of the water (and air) content, denoted by n (with various subscripts).

z height (L) above groundwater ($= L_t - x$, where x is the depth below ground surface and L_t is the depth of the groundwater).

n_e an effective pore air volume fraction (dimensionless), given by

$$n_e = n_a + (\kappa\rho + n_w) / H + n_o / P_{ao} \quad (7)$$

n_a the connected part of the pore air volume fraction (dimensionless),

n_w the connected part of the pore water volume fraction (dimensionless),

n_o the pore NAPL volume fraction (dimensionless)

κ the soil/water partition coefficient for the contaminant ($M^{-1}L^3$),

ρ the soil dry bulk density (ML^3),

H the Henry's law constant for the contaminant (dimensionless air/water partition coefficient),

P_{ao} the air/oil partition coefficient for the contaminant,

β the decay coefficient for the contaminant (T^{-1}), incorporating biodegradation,

Q the (downward) mass infiltration rate of water (LT^{-1}), and

D the effective air diffusivity of the contaminant (L^2T^{-1}), estimated by

$$D = \frac{D_a n_a^{10/3} + D_w n_w^{10/3} / H + D_o n_o^{10/3} / P_{ao}}{n^2} \quad (8)$$

D_a the diffusivity of the contaminant vapor in air (L^2T^{-1}),

D_w the diffusivity of the contaminant dissolved in water (L^2T^{-1}),

D_o the diffusivity of the contaminant dissolved in the NAPL (L^2T^{-1}),

n the total connected pore volume fraction.

Even in uniform soils, the terms D and n_e depend on the height above groundwater z because of the variation in water content of the soil with depth, so that n_a , n_w and n_o all vary with height above groundwater.

In the steady state (so that the partial derivative with respect to time in equation (6) vanishes) and in the absence of any biodegradation (so that $\beta = 0$) it is possible to analytically integrate this equation in terms of one quadrature that may readily be computed. In non-steady-state conditions, or in the presence of biodegradation, more complex methods (or numerical calculations) are necessary. Under such simplifying conditions, the left hand side of equation (6) vanishes, and the first integral of the equation may obtained as

$$\frac{Q}{H} C + D \frac{\partial C}{\partial z} = -E \quad (9)$$

where E is the vapor emission flux from the soil surface ($ML^{-2}T^{-1}$). In turn, equation (9) may be analytically integrated to obtain the relation between concentration $C(z)$ in soil air at height z above groundwater, concentration in soil air at the depth of the groundwater $C(0) = C_0$, and the emission flux:

$$C_0 - C(z) \exp\left(\frac{Q}{H} \int_0^z ds/D(s)\right) = \frac{EH}{Q} \left(\exp\left(\frac{Q}{H} \int_0^z ds/D(s)\right) - 1 \right) \quad (10)$$

For example, if $C(L_i) = 0$ (no surface obstructions, ambient air concentration zero or negligible), then this reduces to

$$E = \frac{QC_0/H}{\exp\left(\frac{Q}{H} \int_0^{L_i} dz/D(z) - 1\right)} \quad (11)$$

Equations (10) and (11) may be simplified for the case of no rainwater infiltration ($Q = 0$) to obtain the various screening models discussed in U.S.EPA (1992).

3 Farmer model

Various screening models that may be obtained by specializing the above approach are listed in the *Air/Superfund National Technical Guidance Study Series: Assessing Potential Indoor Air Impacts for Superfund Sites* (U.S.EPA, 1992). The simplest model is the "Farmer model," in which the soil column is assumed to be uniform in properties over the entire vadose zone, the soil is assumed to have constant water content from the depth of the groundwater up to the building floor, and the infiltration rate of rainwater is assumed to be zero. In that case, equation (10) simplifies to

$$C_0 - C_i = E \frac{L_i}{D} \quad (12)$$

where

- C_i is the concentration of the contaminant in the soil gas at the interface between the soil and the bottom of the building (ML^{-3}), and
- L_i is the depth to groundwater (L).

Since there is assumed to be no depth-dependence of any of the terms, D is the same at any depth in this approximation.

A simple elaboration of the Farmer model is to apply it to multiple soil layers. Then, equation (10) simplifies to

$$C_0 - C_i = E \sum_{j=1}^N \frac{L_j}{D_j} \quad (13)$$

where

- N is the number of layers,
- L_j is the thickness of layer j , $j=1\dots N$, and

D_j is the diffusivity in layer $j, j=1\dots N$.

The simplest screening approach is to assume that the bottom of the building presents no resistance whatever to vapor flow, so that the concentration C_i at the interface of the soil and the building is equal to the concentration C_b inside the building due to the flux E — that is, the relation between the concentration at the interface and the concentration in the building is given by:

$$C_i = C_b \quad (14)$$

In that case, the flux is related to the indoor air concentration by

$$EA_b = C_b Q_b = C_i Q_b \quad (15)$$

where the terms are:

Q_b total air flow rate (ventilation rate) through the part of the building into which the infiltrating soil gas mixes ($L^3 T^{-1}$), and
 A_b total floor area of the building at ground level (L^2),

Combining (12) and (15) gives the ratio r_F (subscript for Farmer model) of the concentration of the contaminant in indoor air to the concentration in the soil gas just above the groundwater as

$$r_F = \frac{g_1}{1 + g_1} \approx g_1 \quad (16)$$

where the dimensionless group g_1 is given by

$$g_1 = \frac{DA_b}{Q_b L_t} \quad (17)$$

In the simplest screening approach, the term $1 + g_1$ in the denominator of equation (16) is simply replaced by 1, as indicated in the approximation shown. This corresponds to using the approximation $C_i = 0$ to estimate the flux in equation (12).

The usual way of using the Farmer model is to make the following simplifying assumptions:

- (A) The groundwater is moving sufficiently rapidly that the effective dispersivity in the groundwater itself is high, and the resistance to mass transfer within the groundwater is low compared with the resistance to mass transfer in the soil layer. Under these conditions, the contaminant concentration in the soil gas just above the groundwater is given by

$$C_0 = HC_t \quad (18)$$

where the terms are:

C_l the contaminant concentration in the groundwater (ML^{-3}), and
 H the dimensionless Henry's law constant.

- (B) The effective diffusivity in the vadose zone is due to vapor diffusion through the soil gas alone, and is given by equation (8) with D_w and D_a set to zero. The assumption of uniformity in the vadose zone is incorporated by taking n_a and n to be constants in equation (8) in this case.
- (C) The system is in steady state, and remains that way. This implies (1) an infinite source of contaminant in the groundwater, and (2) that sufficient time has passed that the vadose zone has come to a steady state. This steady state implies both local equilibration at the scale of soil particles (a rapid process) and the achievement of a steady-state concentration distribution through the vadose zone (a slow process).

4 The modified Farmer model (with capillary fringe)

The *Air/Superfund Technical Guidance* (U.S.EPA, 1992) discusses a way of relaxing the assumption of constant air pore volume fraction — labeled (B) in Section 3 — and the U.S. EPA (1997) spreadsheets incorporate a modification to partially account for this. In the vadose zone, the water content is not constant with depth, but increases near the groundwater (and, indeed, reaches saturation at the groundwater level). It follows that the air pore volume fraction must decrease near the groundwater, so that the effective diffusivity is much lower near the groundwater. As shown in the example of Figure 2, the diffusivity can also vary substantially with depth within and between the different soil layers, depending on the properties of those soil layers and the water content.

The way in which the water content varies with depth may be calculated as described in Section 2.1 — and an example of a possible profile shape is shown in Figure 2 (see Section 8 for a description of the illustrative parameter values used to obtain this figure). The effective diffusivity may then be calculated using equation (8), with the result for the given example shown in Figure 3 (again, see Section 8 for a description of the parameter values used).

The region of high water content near the groundwater level shown in Figure 3 is called the capillary fringe, although strictly the variation in water content and hence the variation in effective diffusivity extends over the whole vadose zone. This is particularly true for a layered soil situation, where, as in the illustrated example, a “capillary fringe” may exist in more than one soil layer. The effect on the diffusion of vapor may be taken into account as in Section 2.2, equation (10), where an integral is performed over the required depth range. If rainwater infiltration is assumed to be negligible, the effect is to produce an equation identical in form to equation (12), except that the constant effective diffusivity used in equation (12) is replaced by a correctly weighted average D_T (the harmonic average) over the vadose zone:

$$D_T = L_t \left(\int_0^{L_t} \frac{dz}{D(z)} \right)^{-1} \quad (19)$$

This result may be obtained from equation (10) with $Q = 0$. The integral in this equation may be considered a total resistance to diffusion. The depth dependence of the effective diffusivity is generally estimated by taking account of the diffusivity of the contaminant in both air and water, and incorporating the depth dependence of the soil pore air volume fraction and soil pore water volume fraction as in equation (8).

With these definitions, the estimated ratio r_T of contaminant concentration in indoor air to contaminant concentration in the soil gas just above the groundwater is given by (just as for the original Farmer model, in Section 3):

$$r_T = \frac{g_1}{1 + g_1} \quad \text{where now} \quad g_1 = \frac{D_T A_b}{Q_b L_t} \quad (20)$$

5 Johnson and Ettinger heuristic model

The second screening model discussed in U.S.EPA (1992) (and implemented in U.S. EPA, 1997) is the heuristic model of Johnson and Ettinger (1991). Assumptions **(A)** and **(C)** of Section 3, used in the formulation of the Farmer model, are applicable to this model also — the groundwater is assumed to be moving fast enough, and the dispersivity in the groundwater is high enough that the resistance to evaporation of the contaminant from groundwater is small compared with the resistance to vapor diffusion presented by the soil layer; and the system is assumed to be in steady state.

Johnson and Ettinger's (1991) model approach for the behavior of the vadose zone yields an equation similar to equation (12); however, they did not specify that the diffusivity has to be uniform with depth. Equation (12) can be used for a non-uniform vadose zone with no rainwater infiltration provided the harmonic mean given by equation (19) is used.

The principal change from the Farmer model is in the relation adopted between the concentration C_i at the interface between soil and building, and the concentration C_b inside the building. In place of equation (14), Johnson and Ettinger (1991) used the flux relation

$$EA_b = Q_s C_i + \frac{Q_s (C_i - C_b)}{\exp(Q_s L_c / D_c A_c) - 1} \quad (21)$$

where the terms not previously defined are:

Q_s rate of flow of soil gas into the building through cracks or porous areas in the building floor or walls ($L^3 T^{-1}$),

- A_c area of cracks or porous areas in the building walls or floors through which the soil gas infiltrates (L^2),
- L_c the effective distance through the cracks or porous areas, usually close to the thickness of the building wall or floor (L),
- D_c the effective vapor-pressure-gradient diffusivity for the cracks or porous areas through which the soil gas is infiltrating ($L^2 T^{-1}$).

This flux relationship comes from the solution of the differential equation for linear, one-dimensional contaminant vapor diffusion together with advection within cracks or pores in the bottom of the building. The diffusivity D_c corresponds to that applicable within the cracks or pores through which the soil gas is flowing into the building. Johnson and Ettinger (1991), in their examples, suggest the use of the effective diffusivity of soil beneath the building, using the assumption that any cracks in the underside of the building are probably partially filled with soil.

Equating the fluxes given by equations (12) and (21) allows evaluation of an estimate r_{JE} (subscript *JE* for Johnson and Ettinger) for the ratio of contaminant concentration in indoor air to contaminant concentration in soil gas just above the groundwater as

$$r_{JE} = \frac{g_1}{1 + g_1 e^{-g_2} + g_1 g_3 (1 - e^{-g_2})} \quad (22)$$

where the dimensionless group g_1 is given by equation (17) (for a uniform vadose zone) or equation (20) (for a non-uniform vadose zone with no rainwater infiltration), and dimensionless groups g_2 , and g_3 are given by

$$g_2 = \frac{Q_s L_c}{D_c A_c} ; \quad g_3 = \frac{Q_b}{Q_s} \quad (23)$$

Equation (22) reduces to equation (16) if $g_2 = 0$ with g_3 finite, corresponding to the floor acting as no barrier at all — all the vapor diffusing upwards gets swept into the building. For g_2 large with g_3 finite (*e.g.* a relatively thick floor) it reduces to

$$r_{JE} \rightarrow \frac{g_1}{1 + g_1 g_3} \quad \text{as} \quad g_2 \rightarrow \infty \quad (24)$$

and in fact, since $g_3 > 1$ (the building ventilation rate must exceed the rate of air infiltration, since the former includes the latter),

$$\frac{g_1}{1 + g_1 g_3} \leq r_{JE} \leq \frac{g_1}{1 + g_1} \quad \text{for any } g_2 \quad (25)$$

One further limit is of some interest. When $Q_s \rightarrow 0$, so that all vapor transport through the underside of the building is by diffusion through the cracks, then

$$g_2 \rightarrow 0 \quad \text{but} \quad g_2 g_3 = \frac{Q_b L_c}{A_c D_c} = G \quad \text{is finite} \quad (26)$$

and then

$$r_{JE} \rightarrow \frac{g_1}{1 + g_1 + g_1 G} \quad (27)$$

6 Incorporating rainwater infiltration into the Johnson and Ettinger model

Rainwater infiltration may be incorporated into the Johnson and Ettinger model by using the flux relation given by equation (10) in place of equation (21). Then the ratio r_I of contaminant concentration in indoor air to contaminant concentration in soil gas just above the groundwater can be obtained as

$$r_I = \frac{g_1 e^{-g_4}}{(1 - e^{-g_4}) / g_4 + g_1 e^{-g_2} + g_1 g_2 (1 - e^{-g_2})} \quad (28)$$

where

$$g_4 = \frac{QL_t}{HD_T} \quad (29)$$

and equation (19) has been used to represent the integral in equation (10). Equation (28) is a generalization of equation (22), and reduces to it if $g_4 = 0$ (*i.e.* if the rainfall infiltration rate Q vanishes).

An assumption that there is no rainwater infiltration is strictly only correct in the middle of a large area that is covered by a water-impermeable surface, or very close below that area. For obstructions the size of houses, water infiltration (groundwater recharge) occurs below the house at sufficient depth. Rainwater infiltrating into the soil at the side of a building will spread sideways under that building, and flow downwards below the building. A typical “open field” infiltration rate might correspond to 20% or more of the rainfall rate. Under the center of a typical house, the infiltration rate may be reduced by another factor of 10 or more a meter or more below the house — but at least a 2-dimensional calculation is required for this estimate. Even such low infiltration rates may have a substantial effect on the vapor emission rates, and hence indoor air concentrations, of benzene, because of the exponential dependence of emission rate on infiltration rate (see equation (28)).

7 Calculation methods, and accounting for a smear zone

The formulations described in the previous sections can be used to calculate emission rates as a function of groundwater depth and thickness of any smear zone. To complete these calculations, two simple numerical integrations are necessary. The first obtains the water content of the soil, and the second obtains the resistance to diffusion, with the second contingent on the first through the dependence of effective diffusivity on soil water content. The first integration, in equation (2), is straightforward to evaluate using the method described in Section 2.1 — a step length of 0.1 meters often gives sufficient accuracy, although a smaller step size may be desirable for some circumstances (*e.g.* very shallow groundwater or smear zone). This gives the capillary head as a function of the distance above groundwater, and hence (through equation (5)) the water content of the soil as a function of distance above groundwater.⁸

The second integral, in equation (19), may then also be numerically evaluated as a function of distance above groundwater. A trapezoidal rule integration using a the same step length as for the capillary head calculation, and the average of the integrand at each end of the step, usually gives sufficient accuracy. The effective diffusivity D_T that is used in all the equations may then be readily evaluated as a function of depth to groundwater L_t .

In the presence of a smear zone, with the assumption that the smear contains sufficient contaminant (benzene) to maintain constant the contaminant concentration in pore air at the top of the smear, it is straightforward to verify that the only real change necessary is in the definition of D_T — equation (19) is replaced by:

$$\begin{aligned} D_T &= (L_t - L_s) \left(\int_{L_s}^{L_t} ds/D(z) \right)^{-1} \\ &= (L_t - L_s) \left(\int_0^{L_t} ds/D(z) - \int_0^{L_s} ds/D(z) \right)^{-1} \end{aligned} \quad (30)$$

where

L_s is the height (L) above the groundwater at which the soil concentration has its fixed, known value given by equation (18), usually the top of the NAPL smear zone.

⁸ The integration is used in this step to evaluate the change in water content of the soil due to rainwater infiltration. Occasionally that integration can be omitted without a large error, since the change in soil water content may be small for the typical rainfall infiltration rates in some soil types. Omitting the integration, $h = z$; to incorporate the integration, equation (2) should be used.

The definitions of g_1 and g_4 should also be modified equivalently, so that now

$$g_1 = \frac{D_T A_b}{Q_b(L_t - L_s)} \quad \text{and} \quad g_4 = \frac{Q(L_t - L_s)}{HD_T} \quad (31)$$

The calculation of water pressure head as a function of depth is unchanged (provided the NAPL smear does not affect the water content), since the smear and water content interpenetrate. Since the numerical integration provides the integral in equation (19) as a function of height above groundwater, the modifications of equations (30) and (31) may be obtained directly by taking differences of values already calculated.

8 The effect of the capillary fringe

An example was constructed to illustrate the variations in water content and diffusivity that might occur at a site with three soil layers above groundwater — a bottom layer containing sand and gravel extending to 1 meter above groundwater, a middle silt layer 3 meters thick, and a top 1 meter thick fill layer. For this illustration, the following values of the parameters for the van Genuchten model of equation (5) were used:

		Fill	Silt	Sand and Gravel	
θ_s	=	0.43	0.43	0.38	
θ_r	=	0.078	0.07	0.1	
α	=	1.5	0.3	2.7	m ⁻¹ ,
N	=	1.5	1.35	1.5	
n	=	0.43	0.43	0.38	
K_s	=	2.89E-06	5.56E-08	3.33E-07	m/s

It is emphasized that these are for illustrative purposes only — actual calculations for any particular site require evaluation of these parameters based measurements on the site soils or of samples from the site soils.

The connected parts of the air and water volume fractions are given by:

$$\begin{aligned} n_a(z) &= \theta_s - \theta(z) \\ n_w(z) &= n - n_a(z) \end{aligned} \quad (32)$$

It is assumed here that the connected part of the pore space is equivalent to the total pore space, since this assumption is conservative (it over-estimates diffusion rates). If the connected part of the pore volume fraction is smaller than the total pore volume fraction, the formulation given by equation (32) effectively assumes that the difference is incorporated in the residual fraction θ_r .

The variation of water pore fraction and total diffusivity of benzene with height above groundwater may be seen in Figure 2 and Figure 3. The curve of Figure 2 represents the solution to Equation (1) or (2) using the parameters just given, together with an infiltration rate

of 2 inch/year. This value was again chosen for illustrative purposes, and is deliberately low to correspond to infiltration beneath houses. Obtaining an accurate estimate for the effective infiltration rate below a surface obstruction is not straightforward, and requires at the least the use of a 2-dimensional computer code (*e.g.* HYDRUS 2-D) to solve the 2-dimensional analog of equation (1).

Figure 3 shows the total diffusivity for benzene in soil, assuming the soil water content shown in Figure 2. As indicated in Equation (8), it is the sum of two parts — that due to diffusion through air and that due to diffusion through water. The terms in Equation (8) have been evaluated from Equations (32), (4), and (5), using the solution of Equation (1). It is clear that in this example the high water content of the soil has a substantial effect on the effective diffusivity close to the groundwater, and in the silt layer.

9 The effect of building floor resistance

A building floor may present an appreciable resistance to penetration by contaminant vapor if it is well constructed — for example, an intact concrete slab with well-sealed edges. The Johnson and Ettinger model takes account of the resistance of the building floor to vapor intrusion, but this extra resistance is often negligible, particularly when the capillary fringe is also correctly taken into account.

For an estimate of the soil gas infiltration rate, we adopt the approach taken by Johnson and Ettinger (1991), and assume that there is an open crack (*e.g.* a joint between floor slab and wall, or between pieces of the floor slab) of a total length equal to the perimeter of the floor slab (or piece of floor slab), buried some depth beneath the soil, and effectively filled with soil through the full floor thickness. The flow of soil gas into the slab may be approximated (Johnson and Ettinger, 1991) by

$$Q_s = \frac{2\pi\Delta P k X_c}{\mu \ln(2Z_c/r_c)} \quad \text{provided} \quad \frac{r_c}{Z_c} \ll 1 \quad (33)$$

where the terms are:

X_c	length of the crack (L),
r_c	effective radius of the crack (L),
Z_c	depth of burial of the crack (L),
k	soil permeability to gas flow (L ²)
μ	viscosity of air (ML ⁻¹ T ⁻¹ , 1.82 × 10 ⁻⁵ kg/m-s),
ΔP	wind and temperature driven average pressure drop (ML ⁻¹ T ⁻²).

Equation (33) is the solution for a flow to a cylinder of length X_c and radius r_c located a depth Z_c below ground surface. The air permeability k could be measured directly, or estimated from the soil hydraulic conductivity.

The Farmer model and the Johnson and Ettinger models give estimates of indoor air concentration of rC_0 , where the ratio r is given by equation (16), (20), or (22). The benzene concentration C_0 in soil air just above the groundwater (or just above the NAPL plume, or just above the NAPL smear) may be estimated from the concentration C_l of benzene in soil water using equation (18), and C_l may in turn be estimated from the mass fraction of benzene in the NAPL using Raoult's law:

$$C_l = \frac{M_o}{M_b} m \quad (34)$$

where the terms are:

S	solubility (ML^{-3}) of benzene in water (1,721 mg/liter at 20°C),
M_o	average molecular weight (M) of the oil,
M_b	molecular weight (M) of benzene (78.11), and
m	mass fraction of benzene in the NAPL (dimensionless).

10 Complications of the real world

The models discussed so far in this report correspond to a one-dimensional simplification of the real world, in which soil is assumed to be homogeneous and isotropic, all fluxes are in steady state, and any inconvenient obstacles to flow like buildings have been incorporated heuristically. The real world is three-dimensional, non-homogeneous, non-isotropic, and time-varying, and there are buildings present. We here further examine qualitatively or semi-quantitatively some of these complications, delaying some of the discussion of time-variation to Section 11.

10.1 Biodegradation

Biodegradation has been ignored in all the calculations performed in this report, in order to obtain simple solutions to the physical problem defined in Section 2. In practice, biodegradation of both the benzene vapor and the NAPL may have a substantial effect on emission rates of benzene from the plume, and hence increments in indoor air concentrations.

There is one situation in which the effect of biodegradation in Equation (6) may be evaluated easily. If the source of benzene is biodegrading at the same rate as the benzene vapor, then the concentrations of benzene in both soil and air, and the emission rate of benzene, decrease with time exponentially at the biodegradation rate. However, for NAPL sources, such an occurrence is unlikely since biodegradation of benzene depends strongly on the availability of oxygen. Near-soil-surface biodegradation rates tend to be substantially higher than deep subsurface rates.

The potential magnitude of the effect of biodegradation may be appreciated by examination of typical biodegradation rates for benzene vapor and NAPL in soil. Near-surface biodegradation rates for benzene vapor are typically around 10% per day, while the biodegradation rate for the NAPL plume might be as low as 10^{-4} per day or lower. If these rates were applied to the

(assumed steady-state) concentrations obtained using the models described in this report, 30-year average concentration estimates would be reduced by factors of 1,000 fold to 1.6 fold respectively. This simple calculation shows that biodegradation could have a very substantial effect.

10.2 Rainwater infiltration rates below buildings

Equation (28) shows an exponential effect of infiltration of rainwater on the estimated indoor concentration. This effect is due to the downward mass transport of dissolved benzene in infiltrating water, not the effect of infiltrating water on the water content of the soil (although that also reduces the upward transport of benzene). Accurate estimates of benzene vapor infiltration into houses thus require estimates of water infiltration rates below buildings.

While buildings may be considered impervious to rainwater, the infiltration rate below them is not zero. Rainwater infiltrating to either side of the house (which may be locally enhanced by the disposition of rainwater from the building) will also travel sideways beneath the house as it infiltrates downward, giving an effective downward infiltration rate below the house. This effect is enhanced by the nature of the recharge — occurring as short periods of saturation of surface layers during rain — and the lack of evapo-transpiration from the area covered by the house. Any open soil fractures (see also Section 10.3) may conduct water below houses, and increase the effective infiltration rate.

Accurate estimates of the average infiltration rates below houses require the use of 2-dimensional or 3-dimensional modeling for water infiltration, for example using HYDRUS 2-D or a similar model.

10.3 Soil fracture effects

Some soils contain fractures within them, and such fractures provide decreased resistance to both horizontal and downward water flow. Indeed, horizontal groundwater flow rates may be largely controlled by such fractures. The advective flow resistance through such cracks is very much lower than the advective flow resistance through the bulk soil.

Fractures may also have some effect on movement of vapor in the sub-surface. However, such effects will be confined to diffusive flow — for there should be little or no advective gas flow in most of the vadose zone, where the principal resistance to vapor migration occurs, as discussed in Section 10.4.

The relative effect of cracks in soil on advective flow of water, and on diffusive flow of vapor, may be appreciated by considering values taken from one particular site, using vertical 1 mm cracks as an example. At this example site, the bulk hydraulic conductivity of the un-cracked soil is 3.92 cm/day (per unit gradient of water head), or 4.62×10^{-11} m³-s/kg in absolute units. Poiseuille flow through a crack gives an absolute hydraulic conductivity through the crack of

$$\frac{b^2}{12\mu} \quad (35)$$

where

b is the width of the crack (L), and
 μ is the viscosity of water ($\text{ML}^{-1}\text{T}^{-1}$, 0.001 kg/m-s).

For a 1 mm crack, the absolute hydraulic conductivity calculated from equation (35) is $8.33 \times 10^{-5} \text{ m}^3\text{-s/kg}$, giving a crack/bulk ratio of conductivities of 2×10^6 . Thus, cracks will dominate advective flow if their area exceeds about one-millionth of the cross-sectional area perpendicular to the flow direction.

On the other hand, for diffusive flow, the equivalent crack/bulk ratio is that of the minimum diffusivity within the vadose zone (which was about $1.5 \times 10^{-9} \text{ m}^2/\text{s}$, close to the diffusivity through water) and the diffusivity of benzene in air ($8.69 \times 10^{-6} \text{ m}^2/\text{s}$). This crack/bulk ratio is about 6×10^3 , a factor that is 300-fold lower than the crack/bulk ratio for advective flow. Thus, at the example site, cracks of this width have a much larger effect on advective flow than on diffusive flow — the average crack size would have to be 17-fold narrower for the effects to be equal.

This rough calculation has been performed for relatively wide, continuous, vertical cracks. The calculation suggests that, for the example site, if such cracks have a cross-sectional area exceeding about 1/6,000 of the total area, diffusive flow through them might dominate diffusive flow through the bulk soil. However, such a conclusion would be true only if the soil fractures were effectively vertical, and extended far enough vertically without being sheared or pinched off, which is unlikely although highly site-specific. However, such cracks (whether or not sheared or pinched off) would also have a major effect on the rate of rainwater infiltration beneath a house, by providing a major conduit for advective transport of water from outside the shadow of the house. The downward water flow beneath the house due to such infiltrating rainwater would reverse any diffusive (upward) vapor transport of benzene.

Thus, the net effect of cracks, at least on the example site discussed, would likely to be to *reduce* vapor emissions. The presence of cracks increases the transport of water from around a house to below a house, increasing the effective water infiltration rate below the house, and so substantially reducing net upwards benzene transport.

10.4 Air flow beneath buildings

The heuristic model of Johnson and Ettinger uses the solution of a one-dimensional advection/diffusion equation *within porous regions or cracks in the wall* to derive the flux relation given by equation (21). No account is taken of the three-dimensional shape of the air flow beneath the house — the only flow assumed to occur is through the walls. The actual flow of air is complicated, and depends strongly on building construction details. If most flow is through cracks in the wall/floor joints, then most of the air flow will be confined to a narrow region around the perimeter of the building, as indicated in Figure 1 — ambient outside air will flow down into the soil near the house, and then into the cracks at the wall/floor joint, with the flow field confined to a few wall thicknesses or less sideways and downwards. In practice, most flow would probably occur at the soil/wall interface, where moisture and temperature fluctuations open fissures between soil and wall.

It is also important to realize that all the air sucked through the soil and into the house originates in the outside air, and will thus carry contaminant concentrations similar to, if not identical with, those in outside air. If a large fraction of this outside air flows through the bulk soil (rather than through fissures in the soil beside the wall or under the floor), there may be a buffering effect reducing temporal fluctuations of concentrations, due to adsorption on the soil. There may also be biodegradation in the soil of this adsorbed contaminant.

To reach the cracks in the floor, or to reach porous floors, air has to flow from the outside down underneath the house. Once again, however, most of the air flow will be confined to a narrow layer very close to the underside of the building floor, probably principally through fissures at the interface between floor and soil. Any flow in the bulk soil will be confined to the upper layers, where the soil resistance to air flow is lowest (due to the lower water content, and hence higher air pore volume fraction).

The net effect of such flows is that vapor diffusing up from below a building, and from below the region of air flow, will be swept into the building, unless the air flow rate is small compared with the vapor diffusion rate. This is what is predicted by equation (25) — the Johnson and Ettinger model has no practical effect when the controlling resistance for vapor diffusion is that of the soil.

The confinement of air flows to the upper layers of the soil also ensures that the estimates for vapor diffusion through the vadose zone are good approximations in the case where the NAPL and any smear zone are below the region of air flow — there is no mass air flow to take into account in the lower regions of the vadose zone where the principal resistance to diffusion occurs.

If, on the other hand, the smear zone extends up into the region where there are mass air flows, then the modeling approach used throughout most of this report is no longer valid for the part of the smear zone affected by air flows. The major transport mechanism for benzene in that region

will be advective transport of vapor entrained in the air flow, probably leading to rapid depletion of benzene in that part of the smear.

The quantity of benzene in the upper part of the smear zone is limited however (see Section 10.5), and it may be possible to use a mass balance approach to evaluate the worst possible effects of any such situation. Section 10.5 presents such a mass balance approach applied to a smear zone, where soil measurements allow direct estimates of the amount of benzene available. In general, a similar approach could be applied to the fraction of the smear zone (if any) extending into the region of air flows in the soil.

10.5 Source depletion, and advective flow in the contaminated region

None of the calculations performed so far in this report take any account of depletion of benzene at its source (the NAPL plume, or the NAPL in the smear zone) due to continued benzene emission. If the effective source is a NAPL plume floating on the groundwater, such an assumption is often justified, since the maximum emission rates of benzene correspond to depletion times that substantially exceed the assumed exposure times. However, if the effective source of benzene is instead the NAPL in the smear zone, the assumption of no depletion is not necessarily justified. For the highest emission rates (usually corresponding to the thickest smear zones and highest indoor air concentration), the concentrations of NAPL, and hence of benzene, present in the smear zone may yield much shorter depletion times, in which case the models discussed here will overestimate long-term average indoor-air concentrations.

In addition to assuming no depletion, all the modeling discussed so far has been based on the assumption that any NAPL is not near enough to the bottom of a building to be within the region of advective air flows, so that the major impediment to benzene transport is the resistance to vapor diffusion in the soil. If any NAPL extends into the region of advective air flows, then such an assumption may be incorrect.

Under certain circumstances, a very simple, model-independent approach based on conservation of mass can be used to evaluate the worst-case implications for long-term average indoor-air concentrations. This model-independent approach uses the measured concentrations of total petroleum hydrocarbons (TPH) or benzene in soil, or NAPL thickness and benzene concentration in NAPL. It may be used to evaluate the effect of source depletion over long exposure periods, or to estimate an upper bound on the average exposure concentration over any exposure period.

Suppose that the only source of benzene is NAPL floating on the surface of groundwater, or present in a smear zone above the groundwater, and that this source is effectively not moving.⁹ Thus, the only source of benzene below any house is that present in the contamination below the house, and the maximum amount of benzene that can get into the house cannot exceed the total amount initially below the house — that is, the mass per unit area of benzene emitted into the house cannot exceed the mass per unit area of benzene originally in the source. The total mass per unit area of benzene below the house may be estimated by examination of

- for a NAPL plume, the thickness of the plume and the concentration of benzene in the NAPL.
- for a smear zone, the concentration of benzene in a soil sample, and the thickness of the smear zone; or the total petroleum hydrocarbon (TPH, assumed to all be the same composition as the NAPL plume) concentration in the smear zone together with the benzene concentration in the NAPL plume.

For an emission rate e (mass/unit area/unit time) into the house, the air concentration in the house would be

$$C = \frac{e}{ah} \quad (36)$$

where

- a is the air change rate (air changes/unit time), and
- h is the height of the well-mixed volume of the house.

Integrating this equation over all time allows an overestimate of lifetime average concentration C_{avg} for any individual as

$$C_{avg} = \frac{1}{T} \int C dt = \frac{m}{ahT} \quad (37)$$

where

- m is the total mass/unit area emitted into the building, and
- T is the length of a lifetime.

This is an overestimate of lifetime average concentration because it implicitly assumes that all the benzene is emitted during the individual's residence, and moreover assumes that individual to be present in the well-mixed volume of the house the entire time that benzene is emitted. If either assumption is not true (*e.g.* if the individual spends any time out of the well-mixed

⁹ An example of such a situation is where most of a release may have passed beneath a building, carried by groundwater flow, but there is some NAPL (resistant to leaching by groundwater movement) left in the vadose zone or on the surface of the groundwater beneath the house.

volume, or if the benzene is emitted over a period exceeding the residence period of the individual), then the lifetime average dose to the individual would be lower than that given by equation (37). The lifetime risk estimate depends only on the lifetime average exposure¹⁰ — it is not necessary to know the exact pattern of exposure.

This calculation is based simply on conservation of mass. It provides an upper bound for any configuration of soil and NAPL below the house, including situations where the NAPL may be within a soil zone containing advecting air. The only requirement is that the whole source of benzene for a particular house be initially below the house; so for example, it does not apply if there is some other source and the benzene is swept below the house by groundwater flow.

For example, consider a NAPL plume (stationary below the house) that has benzene concentrations of 1000 mg/kg, NAPL density 780 kg/m³, and thickness 20 cm measured in soil with total pore volume fraction of 0.4. The mass/unit area of benzene in the NAPL plume would then be 62,400 mg/m². Using an estimate of air change rate of 0.5 per hour (1.39×10^{-4} air changes/sec), a well-mixed building height of 2.5 m, and a standard lifetime of 70 years (2.2×10^9 seconds), the upper-bound lifetime average indoor air concentration would be $0.082 \text{ mg/m}^3 = 82 \text{ } \mu\text{g/m}^3$.

As another example, consider a smear zone with a measured TPH of 1,000 mg/kg extending over a depth range of 1 meter above groundwater, in soil of bulk density 1,600 kg/m³. If the TPH has an average benzene concentration of 100 mg/kg (so a soil sample of this smear zone would have a benzene concentration of 100 $\mu\text{g/kg}$), the benzene source corresponds to 160 mg/m³. With the same assumptions as above, the lifetime average concentration in the building could not exceed $0.2 \text{ } \mu\text{g/m}^3$.

¹⁰ Upper bound estimates of lifetime carcinogenic risk from exposure to contaminants in air are generally estimated using

$$R = UC_{ave}$$

where

U is an upper bound estimate on the carcinogenic unit risk of the contaminant, and
 C_{ave} is the exposure concentration of benzene ($\mu\text{g/m}^3$) averaged over a lifetime.

11 Time variations

The modeling described in this paper makes various steady-state assumptions. In particular:

- there is phase equilibrium on the scale of soil pore spaces,
- temperature variations are negligible,
- variations in infiltration rate are small, and
- there are no rapid fluctuations in concentrations of benzene in soil air

Here, we give some justification for some of these assumptions, with methods that are applicable to all, and show that the subsurface below about 1 meter depth is extremely constant in time — concentrations of contaminants in soil gas should be very constant with time, pressure changes are negligible, temperature changes are negligible, and soil moisture changes are negligible. The analysis presented is not complete, because the fine details can become extremely complex. However, it conveys the essential elements of the situation.

The modeling also requires a further steady-state assumption:

- the equilibration time for the vadose zone concentration gradients is small compared with exposure times,

so that the vadose zone may be treated as being in steady-state. This assumption is not necessarily correct, but it results in overestimates of emission rates, and so is conservative.

11.1 The generic diffusion equation for fluctuations

In what follows, we examine the behavior in the vadose zone of physical quantities, Ψ , (for example, concentration fluctuations, water content fluctuations, temperature fluctuations) that satisfy a linear partial differential equation of the form

$$\frac{\partial \Psi}{\partial t} = \gamma \frac{\partial^2 \Psi}{\partial z^2} + \mu \frac{\partial \Psi}{\partial z} - \nu \Psi \quad (38)$$

where γ , μ , and ν are real functions of distance z above groundwater, and γ is positive. It generally turns out that μ and ν are small in a certain sense compared with γ , so that only the first term on the right of equation (38) needs to be taken into consideration.

Under the conditions stated, with γ , μ , and ν not dependent on Ψ (and hence also independent of t), Equation (38) is linear in the quantity Ψ , so small fluctuations in Ψ about a steady-state solution satisfy the same equation. If γ , μ , and ν are dependent on Ψ , then equation (38) may be linearized for small fluctuations of Ψ about a steady-state solution; and we shall assume that equation (38) represents such a linearized form.

Now any fluctuations in Ψ may be fourier analyzed in time, and the linearity of equation (38) allows the addition of solutions for each fourier component separately. We examine solutions that have the form

$$\Psi \sim \exp(i(\omega t - kz)) \quad (39)$$

corresponding to fluctuations at real angular frequency ω , using the usual complex number approach to keep track of phase relationships. Inserting this into equation (38), assuming that locally k may be treated as independent of z (*i.e.* ignoring gradients of k), and solving the resulting quadratic for k gives

$$k = \pm \left[\frac{a}{2\gamma} + i \frac{b \mp \mu}{2\gamma} \right] \quad (40)$$

where the \pm signs are co-ordinated and

$$a = \sqrt{\frac{\sqrt{(\mu^2 + 4\gamma\nu)^2 + 16\gamma^2\omega^2} - (\mu^2 + 4\gamma\nu)}{2}} \quad (41)$$

$$b = -\sqrt{\frac{\sqrt{(\mu^2 + 4\gamma\nu)^2 + 16\gamma^2\omega^2} + (\mu^2 + 4\gamma\nu)}{2}}$$

As previously stated, μ and ν are often small enough to be ignored in these solutions, in which case equation (40) simplifies to

$$k \approx \pm(1-i)\sqrt{\frac{\omega}{2\gamma}} \quad (42)$$

This is the form we require. Substituting equation (42) it back into equation (39) shows that fluctuations with angular frequency ω propagate as a wave into the soil, with local wave vector $\sqrt{\omega/2\gamma}$, but with a decaying exponential amplitude. The amplitude decreases by a factor $\exp(2\pi) \approx 535$ -fold for each wavelength traveled.

11.2 The infinite half-plane solution

A second special solution to equation (38) is also useful. For γ constant, and μ and ν negligible, change variable to $x = L - z$, where L is the depth to groundwater, so that x measures the distance below the surface. Then equation (38) becomes simply

$$\frac{\partial \Psi}{\partial t} = \gamma \frac{\partial^2 \Psi}{\partial x^2} \quad (43)$$

If groundwater is ignored, and we simply examine an initial condition in which the soil is uniformly contaminated at a value Ψ_0 to infinite depth at time zero, but the value of Ψ is kept fixed at zero at $x = 0$, the solution for Ψ at finite time is given by

$$\Psi = \Psi_0 \operatorname{erf}\left(\frac{x}{\sqrt{4t\gamma}}\right) \quad (44)$$

where erf is the error function. It is straightforward to extend this solution to include a term linear in the first space derivative in equation (43), but equation (44) captures the essence. Moreover, while this solution has been stated in terms of diffusion of a contaminant through soil, it is more widely applicable — all that is necessary is an equation of the form of equation (43) with the correct boundary conditions.

11.3 Equilibrium within pores, but not across the vadose zone

Equation (44) may be used to demonstrate equilibration within soil pore spaces in short times. Within the pore space, water forms a film on the soil particles. For an average particle size of order 400 μm (in sand, for example), the water film might be perhaps 1/10th that since the pore spaces will typically be smaller than the particles, and water does not completely fill the pores. The controlling differential equation is the diffusion equation as in equation (43), with γ equal to the diffusivity in water (around 10^{-9} m^2/s) Thus the typical time constant for equilibration is obtained, using equation (44) from

$$\frac{x}{\sqrt{4t\gamma}} \sim 1 \quad (45)$$

which gives a time of order 0.4 seconds. A similar result applies for diffusional equilibration across the air in the pore space, only using the diffusivity in air, giving an equilibration time about 4 orders of magnitude shorter.

On the other hand, the time for diffusive equilibration across the whole vadose zone will be given by the same formula, but now with $x \approx 4$ m (for a typical vadose zone depth), while equation (6) governs, so that γ is the ratio of an effective diffusivity within the vadose zone (in the range 10^{-9} to 10^{-6} m^2/s) to an effective pore space (taking account of adsorption to soil and organic carbon). With negligible adsorption to soil components and a very open soil (*e.g.* a dry sand), the time for equilibration is of the order of months. With tighter and/or wetter soil and more adsorption, the time for equilibration may extend into the tens of years to centuries.

11.4 Concentration fluctuations

For fluctuations in contaminant concentrations, equation (6) governs. Comparing with equation (38), γ is the ratio of an effective diffusivity within the vadose zone (in the range 10^{-9} to 10^{-6} m^2/s) to an effective pore space (taking account of adsorption to soil and organic carbon). In this case, it is straightforward to show that the μ and ν terms of equation (38) are indeed negligible for any potential infiltration rate. The fluctuations of most interest are those induced by actions at the soil surface, which are likely to have a major frequency components ranging from 1/day to 1/year, corresponding to angular frequencies ω of 7×10^{-5} per second to 2×10^{-7} per second. For an effective diffusivity in the vadose zone of order 2×10^{-9} m^2/s (e.g. the silt layer in Figure 3), and an effective pore volume fraction of perhaps 5 (including adsorption to soil organic carbon), the effective wave vector $\sqrt{\omega/2\gamma}$ ranges from 300 per meter to 16 per meter, corresponding to wavelengths of 2 cm (for daily fluctuations) to 40 cm (for annual fluctuations). Since the fluctuation intensity is reduced about 535-fold for each wavelength, surface effects on a time-scale of years or less will have no practical effect for depths below 1 meter.

11.5 Other effects

Similar methods may be applied to fluctuations in temperature (governed by the diffusive heat equation), pressure fluctuations, and soil wetness fluctuations. Soil wetness is governed by extending equation (1) to include variation in time, with the result

$$\frac{\partial}{\partial z} \left(K \left(\frac{\partial h}{\partial z} - 1 \right) \right) = - \frac{\partial Q}{\partial z} = - \frac{\partial \theta}{\partial t} \quad (46)$$

which, while a diffusion equation, is highly non-linear, since K and h are functions of θ . Nevertheless, it may be linearized by expanding about a steady-state solution. Details (which are somewhat complex) and numerical results are omitted here. Initial estimates for the soil wetness show that the result depends strongly on the soil type and soil wetness — silt, for example, at a relative saturation below about 0.9 has propagation wavelengths below 1 m for daily fluctuations, whereas sand has much longer wavelengths even when relatively dry. Such results are expected from common experiences. Annual or shorter temperature fluctuations do not propagate substantially below 1 m depth.

12 Conclusions

U.S. EPA has proposed various screening models for estimating the effect on indoor air concentrations of volatile contaminants in groundwater or at the groundwater/vadose zone interface. This report shows that these models can be derived from a consistent theoretical analysis of the physical situation involved, and readily extended to incorporate important physical effects ignored by U.S. EPA. In particular, the effects of the variation of soil wetness throughout the vadose zone, and the infiltration of groundwater, both of which are extremely influential, are not incorporated in the simplest implementations of the U.S. EPA screening models.

This report has shown how the extensions to the screening models to incorporate the capillary fringe and infiltrating groundwater may be implemented, and the extra computation is not difficult. The parameter values used are those commonly available from site investigations.

Further extensions to the screening procedures would be desirable, in particular to incorporate biodegradation and source depletion, since both may drastically reduce the emission rates of volatile compounds from soil. Unfortunately, it does not seem possible to use similar simple computational procedures to incorporate either source depletion or biodegradation.¹¹ Application of more complex schemes, such as the VIP model, are necessary. Furthermore, a two- or three-dimensional modeling procedure might also be the optimum way to handle the problem of rainwater infiltration below a house.

Given the complexities of the modeling, careful implementation and application are needed, and there are situations where much simpler models are adequate to demonstrate negligible potential emissions, as shown by the hypothetical example in Section 10.5.

¹¹ A simple procedure to incorporate source depletion is described in U.S. EPA (1992), applicable if the time-scale for source depletion is long compared with the diffusion time of vapor through the vadose zone, and if the effective diffusivity does not depend on depth. Computational evaluation on other sites has shown that the time-scales for source depletion and diffusion through the vadose zone may not be very different, while this report shows that the diffusivity is depth-dependent. The procedure of U.S. EPA (1992) is thus inadequate for the general case.

13 References

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