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Modelling the Migration of VOCs from Soils to Dwelling Interiors

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Modelling the Migration of VOCs from Soils to Dwelling Interiors

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ABSTRACT

Model equations are presented for calculating the migration of Volatile Organic Compounds (VOCs) from contaminated soils into dwelling interiors and ultimately to estimate human inhalation exposure. The purpose of the modelling is to provide a basis for establishing Health-Based Investigation Levels (HILs) for allowable levels of contaminant concentrations in soils. The main assumptions are that the modelling is spatially one dimensional and time dependent and based on the total concentration of a single VOC as proposed in the behaviour assessment model of Jury *et al.* (1983). The total concentration is composed of three phases of the VOC in equilibrium: gaseous phase, water-soluble liquid phase and soil-adsorbed solid phase. The free phase, or Non Aqueous Liquid Phase (NAPL), is accommodated by appearance in boundary conditions at subsurface boundaries of barriers or water tables. The model has been extended in several stages. The first stage was for a single VOC in a soil of infinite depth migrating through a soil surface boundary layer of a clear land surface to free air where the concentration immediately above the surface layer is not zero. The second stage included a house crawl space. The third stage considered a house with a crawl space or concrete slab-on-ground construction and dwelling interiors with human inhalations. The current, and final stage, considers the same housing with additional subsurface modelling of multiple subsurface soil layers, rock or dense clay barriers and water tables with capillary fringes and the presence of NAPLs, both Light Non Aqueous Phase Liquids (LNAPLs) and Dense Non Aqueous Phase Liquids (DNAPLs). The model is constrained by the need to be realistic and at the same time ensure that the soil concentrations are conservatively overestimated to provide safe, cumulative indoor human doses (CIHDs).

1 INTRODUCTION

Adequate modelling of human inhalation exposure to the large number of VOCs within dwellings located on VOC contaminated sites is currently of Australian and world importance for the establishment of acceptable levels of VOCs within soils.

The purpose of the modelling is to provide a basis for establishing Health-Based Investigation Levels (HILs) for allowable levels of contaminant concentrations in soils.

In an extensive survey of modelling requirements by Markey and Anderssen (1996), the conclusion was made that existing models being used for regulatory purposes outside Australia (eg. Johnson and Ettinger, 1991; Waitz *et al.*, 1996) and other potential models (eg. Little *et al.*, 1992; Sanders and Stern, 1994) were unsuitable in being inappropriate to cover Australian houses with crawl spaces, and largely based on steady state non-depleting sources, with a tendency to produce overly conservative HILs and attendant excessive expense in remediation. Since then a few additional models (Ferguson *et al.*, 1995; Johnson *et al.*, 1999, Labieniec *et al.*, 1996) have been presented which are also

inadequate, with the exception of the Turczynowicz and Robinson (2001) model, the first paper to demonstrate the current modelling approach outlined below.

Historically, the Australian modelling effort has been developed by Markey and Anderssen (1996) and, Anderssen and Markey (1998) in respective third and fourth National Workshops on the Health and Risk Assessment and Management of Contaminated Sites; and sponsorship by the South Australian Department of Human Services, Environmental Health Branch (EHB), formerly the South Australian Health Commission (Robinson, 1999a, 2002). The development can be broken into four stages which are now briefly reviewed.

Stage one, by Markey and Anderssen (1996), considered the literature on modelling requirements very extensively with particular emphasis on VOC sorption in soils, open field volatilisation and VOC entry into buildings and the Jury *et al*. (1983, 1984a, 1984b, 1984c, 1990) behaviour assessment modelling (BAM). Noteworthy observations were that sorption for very dry soils (< 2% moisture content) is likely to require special attention, gaseous diffusion is likely to be the dominant transportation mode for VOCs from soils to open fields, very little information could be found on passage through crawl spaces or concrete slabs, and that the most likely way forward in modelling was to build on the Jury style BAM. The first steps there were to model the soil-air interface such that the above ground VOC concentration is non-zero as would occur in a crawl space (see also, Anderssen and Markey, 1997) and to show that in this case an analytical solution for arbitrary initial concentration distributions for a soil of infinite depth could be found in terms of integrals of known mathematical functions.

Stage two, by Anderssen and Markey (1998), emphasised the inverse nature of the problem with the statement: "Determine the level of subsurface concentration of the volatile which guarantees that some particular above-ground exposure dose does not exceed some predetermined threshold". This requirement might be satisfied by forward models of different scenarios such as different subsurface concentration distributions and positions of barriers or water tables; differences in building construction; and differences in environmental degradation conditions. Also discussed were the soil-air interface condition and a first, mass-balance box type model for a crawl space which ignored ventilation rates.

Stage three, building on the two previous stages (Robinson, 1999a), was modelling work supported by EHB. The model consisted of a system of transient partial differential equations of the diffusion type in the soil of infinite depth and box mixing models above ground and in the house, ultimately producing an expression for cumulative inhalation human dose (CIHD). The mathematical method of solution of the equations used the Laplace transform procedure. This has nice features in that the algebra is straightforward for coupled layered systems and, most importantly, the large time value of cumulative dose can be obtained in explicit fashion (Robinson, 1999b). This fact not only makes sensitivity analyses simpler but also enhances the possibility of making fewer of the soil and house parameters necessarily site specific. Part of the modelling capabilities were presented by Turczynowicz and Robinson (1999, 2001) for benzene migrating from soil to a house with a crawl space.

Stage four (Robinson, 2002), also supported by EHB, extends the work of previous stages by including an arbitrary number of soil layers and also the presence of subsurface barriers and the water table. In so doing, complexities of the capillary fringe immediately

above the water table and the physical behaviour of different Non Aqueous Phase Liquids (NAPLs) need to be considered. These inclusions give rise to multiple conditions above and below the soil surface.

Above the soil surface the conditions considered are:

(A) A house with a crawl space
(B) A house with a concrete slab-on-ground construction
(C) A surface free from construction

Below the soil surface the conditions considered are

(a) A soil of infinite depth
(b) Presence of the water table along with a capillary fringe
    (i) above which may be contaminant
    (ii) in which there is a smeared zone of Light Non Aqueous Phase Liquid (LNAPL)
    (iii) and below which there may be a pool of Dense Non Aqueous Phase Liquid (DNAPL) contaminating groundwater
(c) A barrier, such as rock or dense clay, on which may be a pool of NAPL.

Conditions (A) and (B) are depicted schematically in Figure 1 and conditions (a), (b) and (c) are shown in Figure 2.

The sections to follow develop the model equations and boundary conditions and lead to directions for model simplifications along with recommendations for model improvements and requirements. Results from part of the stage three modelling are being presented in a companion paper of Turczynowicz (2002).

A requirement for model creation is to ensure that the models are conservative. This has the implication that HILs developed from the model would be higher than those experienced in reality. As an example, if one dimensional modelling of VOC migration into a house is adopted then HILs would be higher than for actual and three dimensional migration because the latter case has lateral migration which mostly will not go into the house.

There is a very extensive literature covering VOCs and NAPLs in general, VOC transportation, NAPL dissolution, soils and water tables, building ventilation and clean air in many journals with different discipline emphases. The references cited are meant to be pertinent but not comprehensive.
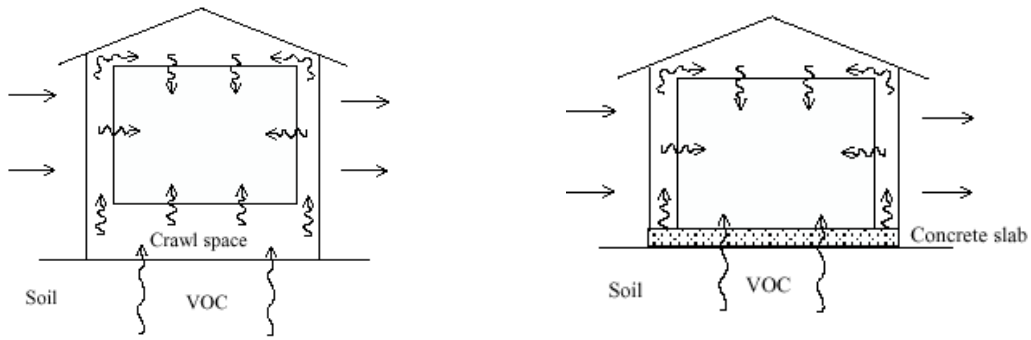
(A) House with crawl space   (B) House with concrete slab-on-ground

Figure 1.   Schematics of VOCs migrating from soil surface to dwelling interiors of commonly constructed Australian houses. Flow paths for the VOCs to the dwelling interiors are through floors, up wall cavities to roof spaces and through walls and ceilings. Ventilation through building openings provide flushing of VOCs to outdoor air.

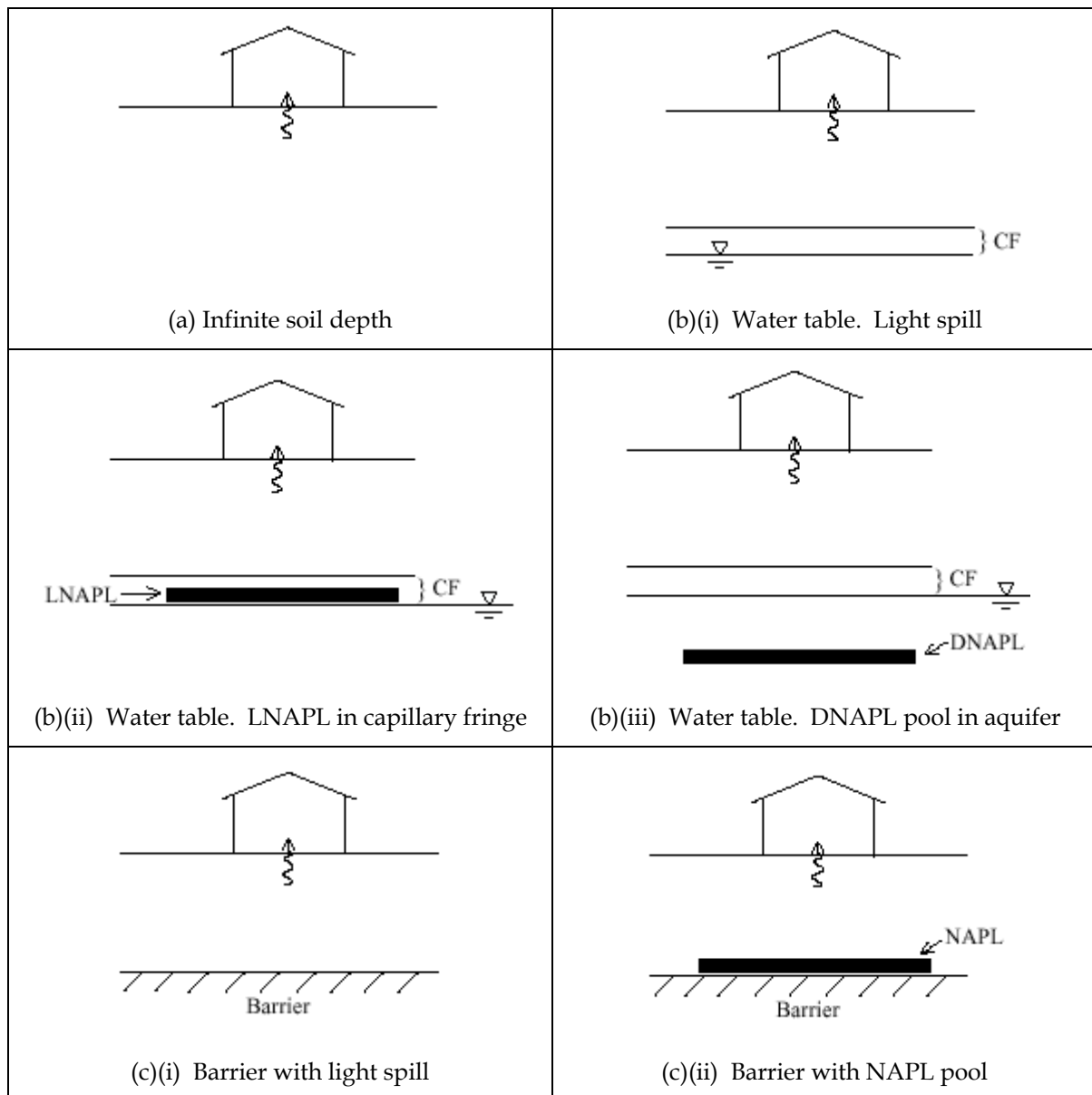| (a) Infinite soil depth	(b)(i) Water table. Light spill
(b)(ii) Water table. LNAPL in capillary fringe	(b)(iii) Water table. DNAPL pool in aquifer
(c)(i) Barrier with light spill	(c)(ii) Barrier with NAPL pool

Figure 2.   Various conditions in the soil sub-surface.

2   MODEL EQUATIONS

2.1   SOIL TRANSPORT DIFFERENTIAL EQUATIONS

VOCs are assumed to exist in three phase equilibrium in unsaturated soil as a water-soluble liquid phase, a gaseous phase and a soil-adsorbed solid phase. Migration to the surface is principally by diffusion although advection is considered. The basic equations are those of Jury *et al.* (1983, 1990) which assume that there is VOC degradation, liquid phase advection, a stagnant-air boundary layer at the soil surface with zero VOC concentration above it, an initial concentration distribution which is constant and, for a finite soil depth, constancy of transportation in a horizontal plane, and constant coefficients for equation concentrations. The physico-chemical modelling of Jury *et al.* (1983) assumed that fate and transport within the soil was by liquid advection and molecular diffusion, volatile molecular diffusion, adsorption of the liquid phase to the soil solids, and degradation associated with total concentration. The differential equation derived is also satisfied by more detailed modelling which considers liquid and vapour phase mechanical dispersion and vapour phase solid adsorption (eg., Shoemaker *et al.,* 1990) as well as volatile advection and three phase contributions to degradation (Lin and Hildemann, 1995). A detailed discussion of the inclusion of non-zero VOC air concentration was given by Anderssen and Markey (1997, 1998). Solutions to the equations in analytical form can be found in the papers of Jury *et al*. (1983) , Lin and Hildemann (1995), Anderssen, de Hoog and Markey (1997) and Anderssen and Markey (1998). The model adopted here follows the main thrust of these prior works. Initial soil concentrations are considered to be constant over each layer, although a more general distribution can be accommodated. The concrete slab is also considered to have the same transport equations as soils but for transport of the gaseous phase only (Thibodeaux and Scott, 1985). This equivalencing of concrete slab to soil layer is likely to be conservative in that gaseous diffusion through a slab would be less than through soil due to a lower pore space connectivity. If free phase liquid VOC, or NAPL, is present in the soil it is assumed to occur only in the vicinity immediately above a subsurface barrier or the water table as discussed below in Section *2.5*. The capillary fringe, immediately above the water table, is approximated by a small number of layers of constant water content.

With coordinate *z* originating from the soil surface and positive downwards, subscripts on variables, *G* for vapour, *L* for liquid and *S* for solid, transport equations for each phase are

$$\text{vapour:} \qquad \theta_G \left(\frac{\partial C_G}{\partial t} + \mu_G C_G \right) = -\frac{\partial J_G}{\partial z} \qquad\qquad (1)$$

$$\text{liquid:} \qquad \theta_L \left(\frac{\partial C_L}{\partial t} + \mu_L C_L \right) = -\frac{\partial J_L}{\partial z} \qquad\qquad (2)$$

$$\text{solid:} \qquad \rho_B \left(\frac{\partial C_S}{\partial t} + \mu_L C_S \right) = -\frac{\partial J_S}{\partial z} \qquad\qquad (3)$$

Here, C_* are concentrations, μ_* are degradation coefficients, J_* are fluxes, θ_G is volumetric air content, θ_L is volumetric water content (porosity $\phi = \theta_G + \theta_L$) and ρ_B is bulk density. In Section 2.4, a depth dependent water content within the capillary fringe is designated θ_W. The equilibrium partitioning ignores small components of non-linear phase concentration interactions (eg. Lin and Hildemann, 1995).

The total concentration is defined by

$$C = \theta_G C_G + \theta_L C_L + \rho_B C_S \tag{4}$$

The dimensions of C, C_G and C_L are (mass/volume) and the dimension of C_S is (mass/mass).

With equilibrium phase partitioning, partition coefficients, R_*, and constant mass fractions f_*, are defined by,

$$f_G = \frac{\theta_G}{R_G}, f_L = \frac{\theta_L}{R_L}, f_S = \frac{\rho_B}{R_S} \tag{5}$$

such that

$$f_G + f_L + f_S = 1 \tag{6}$$

From these definitions of f_*, equation (4) reduces to

$$C = R_G C_G = R_L C_L = R_S C_S \tag{7}$$

R_G, R_L and R_S are determined with the procedure proposed by Jury *et al.*(1983):

$$R_L = \rho_B K_D + \theta_L + \theta_G K_H$$
$$R_G = R_L / K_H$$
$$R_S = R_L / K_D \tag{8}$$

Here, K_H is Henry's constant and the distribution coefficient, $K_D = f_{oc} K_{oc}$, where f_* is the soil organic carbon fraction and K_{oc} is the organic partition coefficient. K_H and K_D are assumed to be constant. Shoemaker *et al.* (1990) indicated that the gaseous adsorption to solids may be included by extending K_D to $K_D + K_H K_{SG}$, where K_{SG} is a positive quantity dependent on θ_L and soil type. For dry soils of $\theta_L < 0.05$, K_{SG} increases rapidly (Chen *et al.*, 2000). Further research is required before reliable estimates of K_{SG} can be used.

Summation of equations (1), (2) and (3) produces

$$\frac{\partial C}{\partial t} + \mu C = -\frac{\partial J}{\partial z} \tag{9}$$

where

$$\mu = f_G \mu_G + f_L \mu_L + f_S \mu_S \tag{10}$$
$$J = J_G + J_L + J_S \tag{11}$$

Fluxes J_G, J_L and J_S are defined by

$$J_G = -D_G^E \frac{\partial C_G}{\partial z} - V_G^B C_G \tag{12}$$

$$J_L = -D_L^E \frac{\partial C_L}{\partial z} + V_L^B C_L \tag{13}$$

$$J_S = -D_S^E \frac{\partial C_S}{\partial z} \simeq 0 \tag{14}$$

Magnitudes of D_*^E are $D_G^E \gg D_L^E \gg D_S^E$ (Bird *et al.* 1960) and so solid phase flux, J_S, is omitted (see also Cohen and Ryan, 1989). D_G^E and D_L^E are effective diffusivities which consider the respective diffusivities in air, D_G^{air}, and water, D_L^{water}, and then take into account the soil tortuosities, which in turn depend on θ_* and ϕ by the Millington-Quirk relationships (Millington and Quirk, 1961)

$$D_G^E = \left(\theta_G^{10/3}/\phi^2\right) D_G^{air} \tag{15}$$

$$D_L^E = \left(\theta_L^{10/3}/\phi^2\right) D_L^{water} \tag{16}$$

V_G^B is the upward bulk vapour velocity and V_L^B is the downward leaching, bulk water velocity.

The effective diffusivities could be augmented by dispersion effects:

$$\begin{aligned} D_G^E &\rightarrow D_G^E + \alpha_G \left|V_G^B\right| \\ D_L^E &\rightarrow D_L^E + \alpha_L \left|V_L^B\right| \end{aligned} \tag{17}$$

as suggested, for example, by Mendoza and Frind (1990) for D_G^E and by Shoemaker *et al.* (1990) for D_L^E, with dispersion coefficients α_G and α_L. Liquid dispersion is expected to be very small and gaseous dispersion small. Reliable values need to be found, particularly for α_G.

D_G^E, D_L^E, V_G^B, V_L^B could all be taken as functions of (z,t) but are here assumed to be constant.

For the slab-on-ground construction only gaseous phase migration is considered. Krylov and Ferguson (1998) indicate that the effective diffusivity for gaseous flow is determined by that for the concrete slab alone, the contributions from sub-concrete bedding and plastic sheet and above surface covering being negligible. With the presence of concrete cracks, the effective gaseous diffusivity is represented by

$$D_G^E + \tau_{dust} \frac{A_c}{A_F} D_G^{air} \tag{18}$$

where the latter term is for dust filled cracks (Hers *et al.*, 2000) with A_c the area of cracks and A_F the floor area and τ_{dust} a tortuosity factor. Estimates for A_c, are difficult to assess as is τ_{dust}. However, using typical concrete values of $\phi = 0.068, \theta_G = 0.034$ (Krylov and Ferguson, 1998) and $\tau_{dust} A_c / A_F$ ranging from 0.000075 to 0.001 (Hers *et al.*, 2000), the ratio of diffusivities of (dust cracks)/(solid concrete) ranges from 0.027 to 0.363. Further research is required to find better estimates of diffusivities for both the solid concrete and dust filled cracks.

With the definitions of J_* in (11), (12), (13), and (14), the relationships between C_* in (7), then the single transport equation which is to be solved follows from (9) as

$$\frac{\partial C}{\partial t} + \mu C = D \frac{\partial^2 C}{\partial z^2} - \upsilon \frac{\partial C}{\partial z} \tag{19}$$

where

$$D = \frac{D_G^E}{R_G} + \frac{D_L^E}{R_L} \tag{20}$$

$$\upsilon = -\frac{V_G^B}{R_G} + \frac{V_L^B}{R_L} \tag{21}$$

V_G^B can also be considered as an equivalent seepage velocity $\left(-K_H V_G^B\right)$, following from equations (8) and (21).

The system of second order equations for each layer can be defined in general terms by

$$\left[D_i \frac{\partial^2}{\partial z_i^2} - \upsilon_i \frac{\partial}{\partial z_i} - \mu_i \right] C_i\left(z_i, t\right) = \frac{\partial C_i\left(z_i, t\right)}{\partial t}, \qquad i = 1, \ldots, n \tag{22}$$

where n is the number of subsurface layers above the water table or impermeable barrier or semi-infinite soil section of zero initial VOC concentration, if it is required. For the ith layer, $C_i\left(z_i, t\right)$ is the total concentration, υ_i is the effective aqueous seepage velocity, μ_i is the linear degradation rate constant and z_i is the local vertical coordinate system, positive downwards, $0 \leq z_i \leq x_i$, with x_i being the thickness of the layer. Should the semi-infinite section pertain, then the equation is the same as (22) with subscripts $n + 1$.
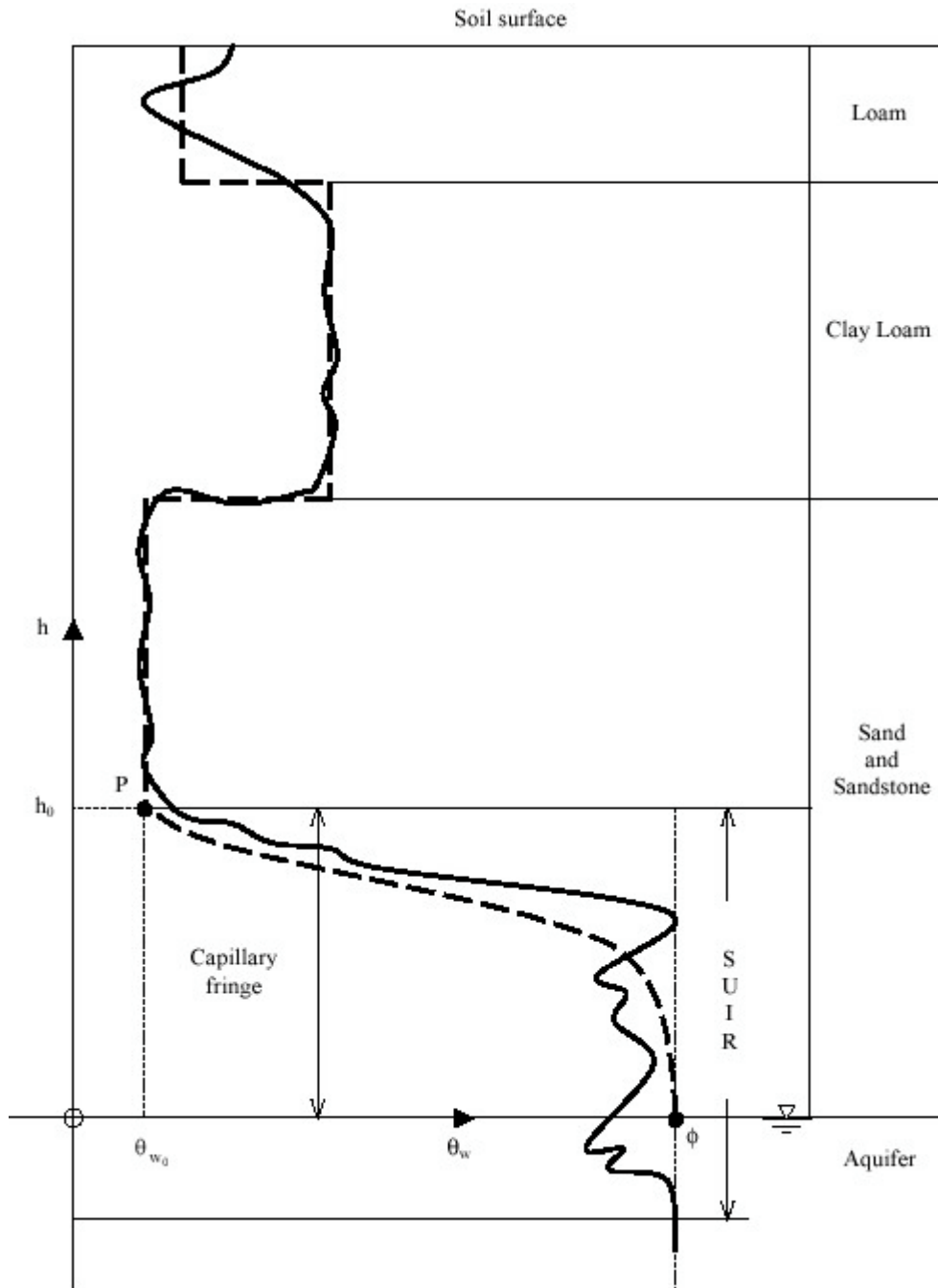
Figure 3   Stylised realistic and idealised height-water content, $h - \theta_w$, curves between soil surface and aquifer are depicted for a typical three-layered soil. Realistic curves are bold continuous lines and idealised curves are bold dashed. The changes in soil type create demarcations in water content above the saturated-unsaturated interface region (SUIR). In this region are the water table and capillary fringe (Ronen *et al.*, 2000). The transition curve from water content θ_{w_0} to maximum ϕ (porosity) is non-monotonic in this case. The idealised curve of van Genuchten type is constructed by measuring the depth of the point $P(\theta_{w_0}, h_0)$ (approximating the top of the capillary fringe), the water table depth and using the curvature parameter, *N*, dependent on soil type.

2.2   BOUNDARY AND INITIAL CONDITIONS FOR MULTIPLE LAYERS

The initial concentration condition for each layer can be quite general. One form of sufficient generality is the polynomial $C_i(z_i,0) = \sum_{j=0}^{P} C_{i,j} z_i^j$ of order P. However, the constant concentration condition will be used here:

$$C_i(z_i,0) = C_{i,0} \tag{23}$$

At the lower surface of the ith layer, continuity of concentrations and fluxes between layers requires

$$C_i(x_i,t) = C_{i+1}(0,t)$$

$$\left[D_i \frac{\partial}{\partial z_i} - v_i \right] C_i(x_i,t) = \left[D_{i+1} \frac{\partial}{\partial z_{i+1}} - v_{i+1} \right] C_{i+1}(0,t), \quad i=1,...,n-1 \tag{24}$$

2.3   BOUNDARY CONDITION FOR SOIL-AIR INTERFACE

The condition for flux, $J_1 = J_1(z,t)$ at the soil-air interface is (Markey and Anderssen, 1996; Anderssen and Markey, 1997, 1998)

$$-J_1(0,t) = \left[D_1 \frac{\partial}{\partial z_1} - v_1 \right] C_1(0,t) = H_1 C_1(0,t) - H_a C_a(t) \tag{25}$$

with

$$H_a = \frac{D_G^{air}}{d_{air}}, \qquad H_1 = \frac{H_a}{R_G} \tag{26}$$

$C_a(t)$ is the air concentration immediately above the stagnant soil surface boundary layer of thickness d_{air} and transfer coefficient H_a. A more fundamental representation of boundary layer behaviour, taking into account surface roughness, gaseous vertical velocity, and above boundary air speed is possible (eg. Brutsaert, 1975; Grifoll and Cohen, 1994), but not likely to yield better results than the direct experimental results of Jury *et al.* (1984c).

2.4   WATER TABLE AND CAPILLARY FRINGE

The water table is designated as the position below the soil surface where the hydrostatic pressure corresponds to atmospheric pressure. It has depth variations spatially and also in time due to seasonal rainfall, evaporation and aquifer variations. The region immediately above it, where there are rapid changes in water content, is known as the capillary fringe. For homogeneous soils it is assumed that saturation begins below the water table and under saturation above the water table. It has been found that, under ideal homogeneous soil conditions, the relation between the height above the water table, *h*, and moisture content, θ_w, can be well approximated by various empirical relationships such as those of Brooks and Corey (1964), Campbell (1974), van Genuchten (1980) and various modifications of them (eg. Sillers and Fredlund, 2001). The height to reach a roughly constant plateau of water content usually is in the range 20 cm to two metres depending on the soil type. It is also found that with rising and falling water tables the $h-\theta_w$ curve

may alter in shape, the degree being less for slow changes (Hinz, 1998). These behaviours are observed mostly in laboratory studies. However, in field studies, heterogeneity is prevalent and there is departure from the ideal smooth transition from unsaturated to saturated conditions (Ronen, 1997, 2000) as shown in Figure 3.

When there is NAPL present, the general shapes of the $h - \theta_w$ curves prevail but are reduced in height due to reductions in capillary surface tensions. In the case of a heavy spill, DNAPLs will pass through the water table and pool at some depth below it. LNAPLs on the other hand will form a 'smear zone' immediately above and below the water table, whether the LNAPL has originated on-site or off-site. For a homogeneous soil, the LNAPL would tend to form a continuous layer just above the water table, but due to the fluctuating water table level and inhomogeneities of field soils, pockets of LNAPLS (blobs/ganglia) are found above and below the water table (eg. Lee *et al.,* 2001; Reddi *et al.,* 1998).

All NAPLs are soluble and degradable to some extent, even if only slightly, but the rate of dissolution may be extremely slow (tens to thousands of years (eg. Grathwohl, 2000)). NAPL dissolution is an active area of research but currently it does not seem possible to predict accurately the rate of dissolution of a particular VOC (Khachikian and Harmon, 2000).

Realistic modelling of NAPLs and the fluctuating water table with its capillary fringe is not an easy task. For the fluctuation factor it is possible to transform a diffusion-advection-degradation equation for a time varying domain size to another with time varying coefficients over a fixed domain for simplified layer geometries by scaling depth coordinates with the total variable depth (Reddi *et al.*, 1998). However, only in exceptional cases is the transformed problem analytically tractable (Sanders, 1960). Approximation schemes must be adopted to solve either the transformed or untransformed equations of this moving boundary problem.

The simplifications adopted in the modelling are as follows. The water table is assumed to be at an average and constant depth for all time. The $h - \theta_w$ curve follows the van Genuchten (1980) and Mualem (1976) relationship

$$\theta_w = \frac{\phi}{\left[1 + \left(\beta^* h\right)^N\right]^M}, \quad \beta^* = \gamma\beta, \quad M = 1 - \frac{1}{N}, \quad \theta_{w0} \le \theta_w \le \phi, \tag{27}$$

ϕ is porosity (at the water table, and for practicality assumed constant across the capillary fringe) and γ a modifying factor to account for change to aqueous surface tension by the VOC (Leverett, 1941; Parker *et al.*, 1987). θ_{w0} is the plateau level of water content, β is a factor which controls the height of the $h - \theta_w$ curve and exponent N determines the curvature between the plateau θ_{w0} and saturation at $\theta_w = \phi$.

It is tempting to set up a table of values of both β and N for a soil classification scheme. Both Carsel and Parrish (1988), and Sillers and Fredlund (2001) have done this for many hundreds of data sets and calculated averages and variations. Although the average value of N for a particular soil type is within reasonable variation bounds, average β values are unacceptably variable. This variability is principally due to pore size variations. To reduce the uncertainty in forming an $h - \theta_w$ curve the proposed scheme relies on the site measurement of the average water table depth and the average height above the water

table where the plateau θ_{w0} approximately begins. With known ϕ, θ_{w0}, $h_0 = h$ at θ_{w0} and an exponent N dependent on given soil type, β^* can be determined from

$$\beta^* = \frac{1}{h_0}\left[\left(\frac{\phi}{\theta_{w0}}\right)^{1/M} - 1\right]^{1/N} \tag{28}$$

An extra advantage of this procedure is the direct measurement of β^* rather than an attempt to estimate β at a contaminated site and then apply a theoretical surface tension factor γ.

Figure 3 depicts a schematic of an $h - \theta_w$ curve that is typical of field sites and the proposed simplified $h - \theta_w$ curve for modelling based on equations (27) and (28).

A further approximation of the model $h - \theta_w$ curve is made by representing it as a number of piecewise constant segments so that each segment can be treated as a soil layer with constant $\theta_w = \theta_L$

Values of N for different soil types, K_{soil}, range from a low of 1.1 for clay (< 60%) to a high of 2.7 for sand, based on results of Carsel and Parrish (1988). Although these results were obtained from North American soils with differences in particle size distributions (thence pore size distributions) from those of averaged Australian soils, there will be little difference in *N* for the same soil type classification from one region to another.

2.5   BOTTOM BOUNDARY CONDITIONS

At the bottom of the nth layer, the boundary conditions required for the six different conditions depicted in Figures 2 are the following. The height of the capillary fringe above the water table is designated as $h_{WT} = h_0$ and the depth below the soil surface to a barrier as h_B.

(d) A semi-infinite lower soil section requiring continuity equations for concentrations and fluxes between layers:

$$C_n(x_n, t) = C_{n+1}(t)$$

$$\left[D_n \frac{\partial}{\partial z_n} - v_n\right]C_n(x_n, t) = \left[D_{n+1}\frac{\partial}{\partial z_{n+1}} - v_{n+1}\right]C_{n+1}(0, t) \tag{29}$$

(e) Presence of the water table with

   (i)   A small NAPL site spill and no LNAPL in the smear zone assuming a zero flux condition

$$\left[D_n \frac{\partial}{\partial z_n} - v_n\right]C_n(x_n, t) = 0 \tag{30}$$

This is a conservative condition in that small amounts of VOCs in the aqueous phase will diffuse through the water table into groundwater.

   (ii) A large NAPL on-site or off-site spill with LNAPL floating in the capillary fringe zone immediately above the water table.

$$C_n(x_n, t) = C_w e^{-\lambda t} \tag{31}$$

C_w is the aqueous saturation concentration for the LNAPL dissolution of the VOC and λ is a dissolution rate constant to take account of the decrease in dissolution rate with time. The LNAPL layer thickness relative to the thickness of the capillary fringe is small and not taken into account.

    (iii) A DNAPL pool in the aquifer below the water table assuming that the concentration of DNAPL dissolved in water, $C_A(t)$, is measurable

$$C_n(x_n, t) = C_A(t) \tag{32}$$

It will be assumed that $C_A(t) = C_A$, a constant. This condition would then be the same form as (31) with $\lambda = 0$.

(f) A subsurface barrier which may have above it
    (i) A light spill with zero flux condition

$$\left[D_n \frac{\partial}{\partial z_n} - \upsilon_n \right] C_n(x_n, t) = 0 \tag{33}$$

This is also a conservative condition in that there will be small amounts of VOC diffusing into the barrier. Although this is the same as the water table condition (29) of (b)(i), the presence of the capillary fringe will provide a different VOC migration behaviour within the soil.

    (ii) A NAPL pool just above the barrier is assumed to have the same saturated concentration condition of (b) (ii):

$$C_n(x_n, t) = C_\square e^{-\lambda t} \tag{34}$$

Again, a capillary fringe will create a difference in the two scenarios.

All the boundary conditions of (b) and (c) can be put in the general form

$$\left[\beta_1 \frac{\partial}{\partial z_n} + \beta_2 \right] C_n(x_n, t) = C_F(t) \tag{35}$$

Coefficients β_1, β_2 and $C_f(t)$ are defined by obvious associations with the appropriate equations of (b) and (c). If the Laplace transform process is applied to all equations, the semi-infinite case (a) can also be put in the same form as the Laplace transformation of (35).

It is assumed that for the floating LNAPL condition there will be some LNAPL present for the whole of the human life time. If this were not the case, such as with a so called moderate spill, the time at which the last of the LNAPL had dissolved (numerically, at a sufficiently small $\exp(-\lambda t)$) would require a switch to the zero flux boundary condition and a restarting of the problem with all concentrations throughout the soil and house taken as initial conditions. This can be solved but it is desirable to consider this aspect as a refinement.

2.6 CRAWL SPACE TRANSPORTATION

For a dwelling with a crawl space, assuming diffusion and advection are negligible and the concentration $C_a(t) = C_{CS}(t)$ is uniform throughout the crawl space, a mass balance equation of box model type is

$$\Omega_{CS}\left[\frac{\partial C_{CS}}{\partial t}+\mu_a C_{CS}\right]+\Omega_{CS} X_{CS} C_{CS}=-A_F J_T(0,t) \tag{36}$$

which becomes, with equation (25) for $J_1(0,t)$,

$$\frac{\partial C_{CS}}{\partial t}+\left(\mu_a+X_{CS}+\frac{A_F}{\Omega_{CS}}H_a\right)C_{CS}=\frac{A_F}{\Omega_{CS}}H_1 C(0,t) \tag{37}$$

The initial value of $C_{CS}(t)$ is $C_{CS}(0)=0$

Here, the crawl space has volume Ω_{CS}, ground area the same as floor area of A_F, air degradation coefficient μ_a and ventilation air exchange rate X_{CS}. If X_{CS} is measured with a gas tracer then the degree of mixing of a VOC with air is accounted for, assuming equivalence of mixing of VOC and gas tracer in air. If some other method of measurement is used, then the degree of mixing will need to be incorporated in X_{CS} (Bowes *et al.*, 1993; Jayjock, 1994; Nicas, 1996).

To account for ambient VOC concentrations, a term $\Omega_{CS} X_{CS} C_{amb}$ can be subtracted from the left side of (37) and initial condition $C_{CS}(0)=C_{amb}$.

2.7   DWELLING TRANSPORTATION

For a dwelling construction with a crawl space, similar assumptions to those of the crawl space produce a mass balance equation for dwelling space concentration $C_D(t)$ of

$$\Omega_D\left[\frac{\partial C_D}{\partial t}+\mu_a C_D\right]+\Omega_D X_D C_D+S C_D=Q_{CSD} C_{CS} \tag{38}$$

The initial value of $C_D(t)$ is $C_D(0)=0$

Here, the dwelling space has volume Ω_D, air degradation coefficient μ_a, ventilation air exchange rate X_D and volumetric flow rate of air from crawl space to dwelling space of Q_{CSD}. The path of airborne VOC from crawl space to dwelling space may be any or all of pathways: through the floor or into wall cavities and through walls or into the roof via wall cavities and then through the ceiling. S is the sum of all sinks and sources (negative quantities). Mostly the interest will be on sinks as humans inhaling contaminated air.

Again, ambient ventilation concentrations C_{amb} may be included with a term $\Omega_D X_D C_{amb}$ subtracted from the left of (38) and initial condition $C_D(0)=C_{amb}$.

For a slab-on-ground construction, the equation takes the same form as equation (37) but with C_D replacing C_{CS} and a sink term added:

$$\frac{\partial C_D}{\partial t}+\left(\mu_a+X_D+\frac{S}{\Omega_D}+\frac{A_F H_a}{\Omega_D}\right)C_D=\frac{A_F H_1}{\Omega_D}C_1(0,t) \tag{39}$$

Ventilation in crawl space and dwelling interior and flow from crawl space to dwelling interior are very important considerations in the convective transport of VOCs above ground. To attempt to use a fundamental detailed approach with flow through all openings and cracks (including floor boards) is a very complicated process, as indicated

in Figure 1, which needs to be validated on a house by house basis. An alternative approach, adopted here, is to use measurements of flow rates on typical Australian houses (Biggs, Bennie and Michell, 1987; Delsante *et al.*, 1998a, 1998b; Olweney *et al.*, 1998).

2.8   HUMAN CUMULATIVE DOSE

With an assumed inhalation rate of $I(t)$, the cumulative dose over time t for a human in the dwelling space is

$$Dose(t) = \int_0^t I(\tau) C_D(\tau) d\tau \tag{40}$$

Current practice for $I(t)$ is to assume constant but different values for children, female adults and male adults (Langley, 1991) and to define the age of a child as up to 12 years (USEPA, 1997).

An approximation of (40), of the type used by Sanders and Stern (1994) and Sanders and Talimcioglu (1997), may be found by assuming that $\frac{\partial C_D}{\partial t} = 0$ and μ_a and S are negligible in equations (38) and at (39) to give

$$Dose(t) \approx \frac{I Q_{CSD}}{X_S \Omega_D} \int_0^t C_{CS}(\tau) d\tau \tag{41}$$

for a dwelling with a crawl space, or

$$Dose(t) \approx \frac{I A_F H_1}{X_S \Omega_D} \int_0^t C_1(0,\tau) d\tau \tag{42}$$

for a dwelling with slab-on-ground construction and neglecting $H_a C_D(t)$.

3   SUMMARY OF EQUATIONS

A summary of the equations developed in Section 2 is as follows.

For the ith layer, of depth x_i, for a total of n initial finite depth layers, the diffusion-advection-degradation equation for unsaturated conditions is

$$\frac{\partial C_i}{\partial t} + \mu_i C_i = D_i \frac{\partial^2 C_i}{\partial z_i^2} - \upsilon_i \frac{\partial C_i}{\partial z_i} \tag{43}$$

where $C_i(z_i,t)$ is the total VOC concentration with contributions from concentrations of a water-soluble liquid phase, a gaseous phase and a soil-adsorbed solid phase, all in equilibrium.

The simplest initial condition to adopt for first phase modelling is that at zero time there is a constant concentration, $C_i(z_i,0) = C_{i,0}$ to a depth x_i. More complex concentration distributions can be adopted if necessary.

At the top surface the flux $J_1(z_1,t)$ is given by

$$-J_1(0,t) = D_1 \frac{\partial C_1(0,t)}{\partial z_1} - v_1 C_1(0,t) = H_1 C(0,t) - H_a C_a(t) \tag{44}$$

For the ith layer, continuity of concentrations and fluxes is required between layers $i-1,i$ and $i+1$. For the latter case these equations are

$$C_i(x_i,t) = C_{i+1}(0,t)$$

$$\left[D_i \frac{\partial}{\partial z_i} - v_i \right] C_i(x_i,t) = \left[D_{i+1} \frac{\partial}{\partial z_{i+1}} - v_{i+1} \right] C_{i+1}(0,t), \qquad i = 1,...,n-1 \tag{45}$$

At the bottom of the nth layer the boundary condition for all water table or barrier conditions takes the general form

$$\left[\beta_1 \frac{\partial}{\partial z_n} + \beta_2 \right] C_n(x_n,t) = C_F(t) \tag{46}$$

Coefficients β_1, β_2 and $C_F(t)$ are different for each boundary condition as shown in Section 2.5. For pools of NAPLs, basic assumptions made are that they lie as thin horizontal layers of negligible thickness and that their dissolution rate is prescribed. When the soil is of infinite depth, an $(n+1)^{th}$ layer is defined from the bottom of the nth layer to infinite depth, with the same properties of the nth layer but zero initial concentration. The conditions required are then continuity equations (45) and $C_{n+1}(\infty,t) = 0$

The coupled equation for soil and crawl space concentrations is

$$\Omega_{CS} \left[\frac{\partial C_{CS}}{\partial t} + \mu_a C_{CS} \right] + \Omega_{CS} X_{CS} C_{CS} = A_F \left[H_1 C_1(0,t) - H_a C_{CS}(t) \right] \tag{47}$$

For preliminary modelling, crawl-space concentration $C_{CS}(t)$ is $C_{CS}(0) = 0$, which assumes that an inhabited house exists when the initial soil concentration is prescribed. $C_{CS}(t) = C_{amb}$ can be accommodated subsequently to investigate the effects of ambient air concentrations.

For the convective migration from crawl space to dwelling interior, the coupled concentrations equation is

$$\Omega_D \left[\frac{\partial C_D}{\partial t} + \mu_a C_D \right] + \Omega_D X_D C_D + S C_D = Q_{CSD} C_{CS} \tag{48}$$

Initially the dwelling concentration $C_D(t)$ is $C_D(0) = 0$. Ambient air concentrations can also be included subsequently.

For the slab-on-ground construction,

$$\Omega_D \left[\frac{\partial C_D}{\partial t} + \mu_a C_D \right] + \Omega_D X_D C_D + S C_D = A_F \left[H_1 C_1(0,t) - H_a C_D(t) \right] \tag{49}$$

Finally there is human cumulative dose, for an inhalation rate, $I(t)$, given by

$$Dose(t) = \int_0^t I(\tau) C_D(\tau) d\tau \tag{50}$$

Dose(*t*) becomes the essential quantity to assess the impact of the VOC on human health.

A summary of the primary model parameters can be placed in the following groups:

Soil: $\left[\phi_i, \theta_L, \rho_B, f_{oc}, V_L^B \left(\text{or} V_G^B \right), \alpha_G, K_{SG}, K_{\text{soil}} \right]_i, d_{air}$

Volatile: $\left[K_{oc}, K_H, D_G^{\text{air}}, D_L^{\text{water}}, C_{0,i}, x_i, \mu_i, \mu_a, C_W, \lambda \right]$

House: $\left[A_F, \Omega_{CS}, \Omega_D, X_{CS}, X_D, Q_{CD}, S, A_c, \tau_{\text{dust}} \right] \tag{51}$

Secondary parameters, D_i, υ_i depend on primary parameters. In many cases the parameters in one layer, i, are the same as those in other layers. Parameter h_{WT} is equivalent to x_n and barrier depth $h_B = \sum_{i=1}^n x_i$. Excluded from these groups are the inhalation *I*, being part of the sink *S*, and also C_{amb}, to avoid the complication of ambient concentrations.

These groups are useful to have when carrying out sensitivity studies to look at their relative importance. From the work done so far on homes with crawl spaces and neglecting the water table, it appears that changes in the house parameter group may cause the greatest changes to *Dose*(*t*), and the soil group the least effect (Turczynowicz, 2002; Turczynowicz and Robinson, 2001).

4   SOLUTION METHODS

The model equations proposed are all of linear form. In first phase modelling for a soil layer, coefficients *D* and υ in the soil transport equations are assumed constant in space and time over a layer and the initial concentrations constant, but not necessarily so.

For a specified $C_a(t)$, a single layer of initial concentration, constant or variable, above a soil of infinite depth, total concentration in the soil $C(t)$ can be found analytically in terms of known functions and integrals of them. For $C_a(t) = 0$ solutions may be found in (Jury *et al.*, 1983; Lin and Hildemann, 1995) and for $C_a(t) \neq 0$ see (Anderssen, de Hoog and Markey, 1987; Robinson 2000). With $C_a(t) = 0$ and two layers above an infinite depth there are complicated analytical expressions involving infinite series of integrals (Liu and Ball, 1998).

When there is a lower soil boundary, as in conditions (b) and (c), it is theoretically possible to obtain infinite series solutions for all concentrations in soil and above ground. Shan and Stephens (1995) recognised this for a two layer system with $C_a(t) = 0$ and lower boundary condition that of a water table with zero thickness of capillary fringe, ie. the same condition as a barrier with light spill (c)(i). However, they declined the challenge of finding requisite, infinite residue series and developed an approximate infinite series instead. Such infinite residue series appear in finite domain problems of the many

examples given for diffusional equations in Carslaw and Jaeger (1959). However, the theoretical nicety of series solutions is often attained at greater analytical and computational effort relative to robust numerical inverse Laplace transform methods.

The standard numerical methods for solving the model equations are to use finite differencing (eg. Anderssen and Latham, 1997) or Laplace transformation with numerical inverse transformation. The Laplace transform method has several advantages in that initial soil concentrations which may be discontinuous spatially are more readily handled, the algebra for multiple layers is straightforward and repetitive and efficiently handled in successive chaining, and analytical derivation of long term *Dose*(*t*) values is possible. Also if the transform variable is time, *t*, model parameters with time dependent behaviour, such as seasonal variations in θ_L and V_G^B, can also be accommodated. The writer has successfully used the Laplace transform approach in Robinson (1999a, 1999b, 2000, 2002) and Turczynowicz and Robinson (2001). Public domain software for robust inversions is available in Piessens and Huysmans (1984) and D'Amore *et al.* (1998).
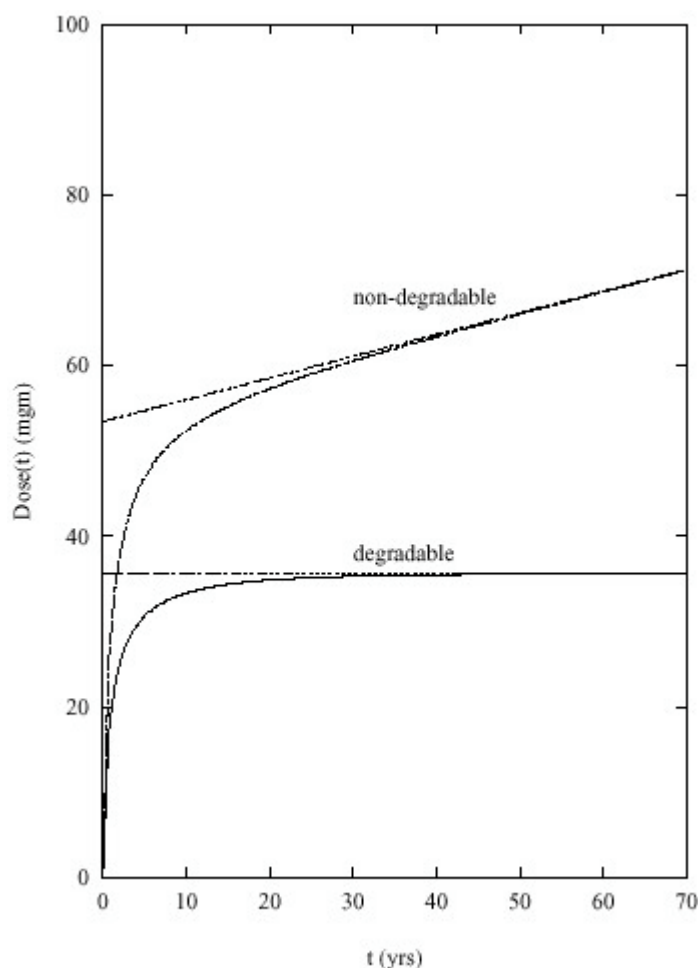

Figure 4   Typical Dose-Time Curves for Degradable and Non-Degradable Sources

5   TOWARDS SIMPLIFIED MODELS

The cumulative dose at very large time reaches a predictable form

$$Dose(t \to \infty) = a + bt \tag{52}$$

where the constants a and b are functions of all the parameters.

When $b = 0$, the initial soil concentrations have all been dissipated either as degradations or migrations to the house. This will occur in the subsurface conditions (a), (b)(i), (c)(i) for light NAPL spills and in heavier NAPL conditions (b)(ii) and (c)(ii) if the dissolution rate constant λ is non-zero. $b \neq 0$ for (b)(ii) and (c)(ii) if $\lambda = 0$ and (b)(iii) for DNAPL pooling. Both a and b can be calculated by means of Laplace transform properties. Typical curves for $Dose(t)$ are shown in Figure 4 for the cases $b = 0$ and $b \neq 0$.

First note that a general expression for the Laplace transform $F(p)$ of a function $f(t)$ can be defined by (Carslaw and Jaeger, 1959)

$$F(p) = \mathsf{L}\{f(t)\} = \int_0^\infty \exp(-pt) f(t) dt \tag{53}$$

and for $Dose(t)$

$$U_{Dose}(p) = \mathsf{L}\{Dose(t)\} \tag{54}$$

Particular properties of interest are

$$\mathsf{L}\{a + bt\} = \frac{a}{p} + \frac{b}{p^2} \tag{55}$$

and

$$f(\infty) = \left[pF(p) \right]_{p \to 0} \tag{56}$$

When $b = 0$, the calculation of $Dose(\infty)$ is given by,

$$Dose(\infty) = \left[pU_{Dose}(p) \right]_{p \to 0} \tag{57}$$

When $b \neq 0$

$$b = \left[p^2 U_{Dose}(p) \right]_{p \to 0}$$
$$a = \left[p \left(U_{Dose}(p) - \frac{b}{p^2} \right) \right]_{p \to 0} \tag{58}$$

When $Dose(t \leq 70\,\mathrm{yrs.}) \approx Dose(\infty)$ then use of asymptotic limits enables sensitivities to be calculated much more quickly than using a numerical procedure valid for all t. Numerical values generated from the model by Turczynowicz (2002) for BTEX, napthalene and aromatics and aliphatics EC $\leq$ 16, for a crawl space house on a soil of infinite depth all show asymptotics limits reached at < 10 years.

For the infinite depth case and a house with a crawl space on a single layer of initial constant concentration, an explicit expression for $Dose(\infty)$ can be found in Robinson (1999b) and Turczynowicz and Robinson (2001). The same case with a double soil layer under crawl space or single layer under concrete slab was considered in Robinson (1999b).

As an example, the final result for a house with crawl space and a single soil layer can be expressed as

$$Dose(\infty) = I\, T_D\, T_{CS}\, U_1 \tag{59}$$

I is constant and the expressions for T_D, T_{CS} and U_1 are

$$T_D = \frac{Q_{CD}}{\Omega_D \left(\mu_a + X_D + S/\Omega_D\right)} \tag{60}$$

$$T_{CS} = \frac{A_F\, H_1/\Omega_{CS}}{\left[\mu_a + X_{CS} + A_F H_a/\Omega_{CS}\right]} \tag{61}$$

$$U_1 = \frac{K_1\, C_{1,0}}{\left[1 - T_{CS}K_2\right]} \tag{62}$$

and K_1 and K_2 are

$$K_1 = \frac{\left(D_1 R - \tfrac{1}{2}V_1\right)}{\mu_1\left(\tfrac{1}{2}V_1 + H_1 + D_1 R\right)}\left(1 - e^{-\left(R + \frac{V_1}{2D_1}\right)L}\right) \tag{63}$$

$$K_2 = \frac{H_a}{\tfrac{1}{2}V_1 + H_1 + D_1 R} \tag{64}$$

where

$$D_1 R = \sqrt{V_1^2/4 + \mu_1 D_1} \tag{65}$$

In the limiting case, $\mu_1 \to 0$, then $\left(D_1 R - V_1/2\right)/\mu_1 \to D_1/V_1$.

Having the explicit expression (59), a sensitivity analysis can be conducted on varying all the parameters which directly affect $Dose(\infty)$ as shown in equation (59) as well as all the supporting parameters used to calculate them as shown in the parameter groups (51).

A general expression for finding the sensitivity of changes in $Dose(t)$ with respect to any of the parameters, designated g_i, $i = 1, \ldots, Np$ (the total number of parameters), is

$$g_i \frac{\partial Dose(t)}{\partial g_i} \tag{66}$$

relative to some base values of all parameters g_i. The sign of the evaluated expression will denote an increasing effect for positive values and vice versa for negative values. The magnitude will enable a ranking of parameter sensitivity.

Sensitivity analyses have been carried out for a crawl space house for benzene (Turczynowicz and Robinson, 1999, 2001) and for further aromatics as well as aliphatics in the paper of Turczynowicz (2002).

Thus, with the sensitivity ranking capability and the apparent dominance of the importance of house parameters, there is the likelihood of presetting some site parameters and providing simplified formulae derived from those like (59).

6   CONCLUDING REMARKS

For the models to be useful in setting HILs, some general statements can be made about the models presented here: They need to be exercised with parameter values for different

forward modelling scenarios, they need to be simplified wherever possible and conversely extended in scope, and they need to be validated to ensure that they will provide conservative estimates of HILs.

Desirable extensions to the modelling which follow the modelling framework developed are:

- Soil and VOC
  - Depth variable initial VOC concentrations which account for both time of VOC deposit and building habitation.
  - Seasonal variation in parameters which are held constant over a season, eg. θ_L and υ.
  - Values for gaseous phase dispersion.
  - Values for gaseous contributions to soil-adsorbed solid phases.
  - Improved assessments of NAPL dissolution and degradation.
  - Including the moderate spill case of a NAPL on top of a barrier or water table with a dissolution period of less than 70 years.
  - Improved assessment of VOC degradation in soils.
  - Allowing for the interactions of migrating VOC mixtures.
- Building
  - Seasonal variations in air exchange rates.
  - Inclusion of background VOC concentrations from ambient air.
  - Improved estimates for diffusivities in concrete and cracks.
  - Adjusting inhalation rates as a function of time.
- Sensitivity Analysis and Model Simplification
  - Ranking of parameters for degree of sensitivity in base case scenarios and subsequent reduction of site-specific parameter measurements and model simplifications.

A start on exercising the models has been made for crawl space houses with aromatics and aliphatics (Turczynowicz, 2002; Turczynowicz and Robinson, 2001).

Some validation is currently being investigated by Len Turczynowicz in monitoring crawl space and house migration flow paths to dwelling interior for a crawl space surface layer treated with xylene.

Clearly, much needs to be done.

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