

# A SCREENING MODEL TO ESTABLISH REMEDIATION OBJECTIVES BASED ON SOIL GAS CONCENTRATIONS

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## Abstract

This screening model was developed to establish remedial action objectives (RAOs) for soils contaminated with volatile organic compounds (VOCs) based on soil gas concentrations that are protective of groundwater quality. As described below, application of the model is limited to sites with relatively low net infiltration and where vadose zone soil gas concentrations are expected to persist for times significantly greater than the groundwater travel time beneath the contaminated area. The model also assumes that soil gas concentrations near the water table have stabilized, contaminant transport in the vadose zone is relatively rapid compared to contaminant transport from the vadose zone to the water table, and that no mobile NAPL is present. The case of a declining water table, as found in many arid subbasins, is analogous to infiltration of contaminated water and can be accounted for by the model. Application of the model to a hypothetical site is provided, and the sensitivity of model predictions to assumed input parameters is also discussed.

## Transport Theory

In order for contaminants in the vadose zone to affect groundwater quality, these contaminants must be transported from vadose zone soils, across the capillary fringe, and into the saturated zone. Within the vadose zone, contaminants may occur in the soil gas, dissolved in pore water, adsorbed onto soil solids, and as nonaqueous-phase liquid (NAPL). Within the capillary fringe contaminants partition among the same phases, although the mass of contaminants in the soil gas phase is greatly reduced. In the saturated zone there is no soil gas phase. A schematic diagram of the distribution of the various contaminant phases in these three zones is presented in Figure 1.

Assuming mobile NAPL is not present in the system, contaminants can only move from the vadose zone into the saturated zone either by direct dissolution from the gas phase into the groundwater, or by dissolving into soil water infiltrating through the vadose zone to the capillary fringe. Assuming that the concentrations of VOCs in soil gas and pore water are in equilibrium, they can be described by the nondimensional form of Henry's Law:

$$H_D = C_G / C \quad (1)$$

where  $C_G$  is the concentration in the soil gas (ug VOC / L soil gas)  
 $C$  is the aqueous concentration (ug VOC / L water)  
 $H_D$  is the dimensionless Henry's Coefficient

The dimensionless Henry's Law coefficient can be computed from standard tables of Henry's Law coefficients by:

$$H_D = H / RT \quad (2)$$

where  $H$  is the Henry's coefficient (atm-m<sup>3</sup> / mol)  
 $R$  is the universal gas constant (8.2057 x 10<sup>-5</sup> atm-m<sup>3</sup> / mol-K)  
 $T$  is the temperature in degrees Kelvin (K) (293.15 K = 20 /C)

Once dissolved in the soil water, these VOCs can be transported across the capillary fringe and into the groundwater by the following processes:

- 1) advection by infiltrating soil water,
- 2) aqueous-phase molecular diffusion, and
- 3) mechanical dispersion.

Advective transport of contaminants from the vadose zone into the saturated zone may result from steady or periodic infiltration of meteoric water, anthropogenic water sources such as irrigation return flows or urban runoff collection systems, or by drainage of soil water under falling water table conditions. Most screening models consider infiltration to be the only transport process from the vadose zone to the saturated zone (e.g. ADEQ, 1996; Ravi and Johnson, 1997).

Net infiltration can vary significantly from site to site, especially in arid climates, depending on soil type, vegetation, land slope, and land use. A frequency distribution of empirically estimated net infiltration rates as a percentage of precipitation on arid sites under natural land use is shown in Figure 2 (data from Scanlon et. al, 1997). Based on these data, the median net infiltration rate is approximately 3% of annual precipitation, which for the Phoenix or Tucson basins would range from 0.2 to 0.4 inches per year.

Advective transport due to a falling or fluctuating water table has received little attention in the literature, and is typically disregarded. When the water table falls, the originally saturated soil becomes unsaturated allowing contaminated soil gas to enter the pores and contact the residual draining water. With continued drainage, this now contaminated water enters the saturated zone as an equivalent infiltration. A conservative estimate of this equivalent infiltration rate can be made using the following equation:

$$I_E = S_Y \frac{\Delta H}{\Delta t} \quad (3)$$

where  $I_E$  is the equivalent infiltration rate (inches / year)  
 $S_Y$  is the specific yield (volume water / area of aquifer / length of water table decline)  
 $\Delta H$  is the decrease in the water table elevation (inches)  
 $\Delta t$  is the time period during which the water table decrease occurred (years)

For example, a water table elevation decrease of 1 foot per year in an aquifer with a specific yield of 0.15 would have an equivalent infiltration rate of 1.8 inches per year. This equivalent infiltration rate is several times that of natural infiltration in both the Tucson and Phoenix basins.

Figure 1 shows the classical schematic representation of mechanical dispersion and diffusion processes on the pore scale. Molecular diffusion is a ubiquitous transport process in which the mass flux driving force is a gradient in chemical concentration. Solutes move from regions of high concentration to regions of low concentration. Aqueous-phase diffusive transport in porous media is generally described by a modified form of Fick's Law (Thomas, 1982):

$$J_D = -t f D_0 \frac{\partial C}{\partial z} \quad (4)$$

where  $J_D$  is the molecular diffusive flux (ug / cm<sup>2</sup> / sec)  
 $J$  is the tortuosity factor, which represents the ratio of the straight line distance a particle travels to its actual path length through the pores (dimensionless)  
 $f$  is the porosity (or saturated water content) (cm<sup>3</sup> pores / cm<sup>3</sup> bulk soil)  
 $D_0$  is the molecular aqueous diffusion coefficient in the porous medium (cm<sup>2</sup> / sec)  
 $z$  depth (cm)

Figure 3 shows that only vertically downward diffusive flux is considered in the model. Diffusive mass flux in the direction (x) of groundwater flow is minimal with respect to advection. Further, the model applies only to a vertical cross-section

through the contaminated site, parallel to the direction of groundwater flow, such that all mass flux perpendicular to the model cross section, including diffusion, is not considered.

Mechanical dispersion (Figure 1) causes spreading of dissolved constituents due to variations in the velocity profile across pore scale flow paths, and the larger scale direction and rate of water movement due to the tortuosity of flow paths within the soil<sup>1</sup>. Years of research have established that mechanical dispersion at small spatial scales is well described by a relationship similar to Fick's Law of diffusion (Bear, 1979):

$$J_M = -\overline{\mathbf{a}}_M \vec{v} \nabla C = -\overline{\mathbf{D}}_M \nabla C \quad (5)$$

where  $J_M$  is the mechanical dispersive flux (ug/cm<sup>2</sup>/sec)  
 $\overline{\mathbf{a}}_M$  is the mechanical dispersivity tensor (cm)  
 $\vec{v}$  is the vector of the absolute values of the groundwater pore velocity (cm/sec)  
 $\overline{\mathbf{D}}_M$  is the mechanical dispersion coefficient tensor (cm<sup>2</sup>/sec)  
 $\nabla$  is the gradient operator (1/cm)

Figure 3 shows the components of the dispersivity tensor, which consist of terms describing dispersion in the direction of advective flow ("xx) called the longitudinal dispersivity, and terms describing dispersion perpendicular to the direction of flow ("yx and "zx) called the horizontal and vertical transverse dispersivities, respectively. Equation (5) can result in a very complex relationship between dispersion and groundwater velocities. For the case of purely horizontal groundwater flow, mechanical dispersion will take place not only in the direction of flow (X) as described by:

$$J_{XX} = -\mathbf{a}_{XX} v_X \frac{\partial C}{\partial x} \quad (6)$$

but also horizontally perpendicular (Y) to the direction of flow:

$$J_{YX} = -\mathbf{a}_{YX} v_X \frac{\partial C}{\partial y} \quad (7)$$

and vertically perpendicular (Z) to the direction of flow:

$$J_{ZX} = -\mathbf{a}_{ZX} v_X \frac{\partial C}{\partial z} \quad (8)$$

where  $v_X$  is the magnitude of the groundwater velocity in the X-direction (cm/sec)

Because the model presented here considers only transport in a vertical plane parallel to the direction of groundwater flow (the X - Z plane), the horizontal transverse dispersion represented by (7) is not considered further. An additional dispersive flux will result from the vertical movement of infiltrating or draining water. This flux can be described by:

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<sup>1</sup> This process is not to be confused with macroscopic dispersion which results in "apparent" contaminant spreading when, for example, groundwater is sampled from wells that penetrate multiple lithologic units with varying contaminant concentrations. Contaminant spreading by macroscopic dispersion is not necessarily described by a simple linear relationship to groundwater velocity.

$$J_{ZZ} = -\alpha_{ZZ} v_Z \frac{\partial C}{\partial z} \quad (9)$$

where  $v_Z$  is the magnitude of the velocity in the Z-direction (cm / sec)

Equation (8) implies that even in the absence of vertical groundwater flow, dispersion can transport contaminants from the capillary fringe deeper into the saturated zone (in the Z-direction), due solely to groundwater flow in the X-direction<sup>2</sup>. Processes that result in vertical movement of water, such as infiltration, seasonal changes in the water table elevation, and barometric pressure fluctuations, will further increase vertical mass transport from the vadose zone into the aquifer. While infiltration and declining water table drainage are explicitly included in the model, the remainder of these phenomena are implicitly represented by the dispersion terms.

The magnitude of vertical mass transport by mechanical dispersion of predominantly horizontal groundwater flow can vary greatly. McCarthy (1992) observed little or no mechanical dispersion between the saturated and unsaturated zones in laboratory sandbox experiments using trichloroethylene (TCE). Estimates of the vertical dispersivity based on field measurements have ranged from essentially zero up to a few centimeters (Engesgaard and others, 1996). Analysis of detailed field observations from a natural gradient tracer test at Cape Cod (Garabedian and others, 1991) indicated values of vertical transverse dispersivity due to horizontal groundwater flow ( $\alpha_{ZX}$ ) ranging from 0.1 cm to 0.4 cm. With respect to vertical dispersivity due to infiltration ( $\alpha_{ZZ}$ ), its magnitude is likely to be in the range from 1 to 100 cm, based on dispersivities estimated for a spatial scale of a few meters (Gelhar, et. al, 1992). Despite the greater magnitude of  $\alpha_{ZZ}$  relative to  $\alpha_{ZX}$ , the magnitude of the vertical dispersive flux (Equation 9) is generally insignificant because of the small magnitude of the vertical infiltration velocity.

### Transport Model

The model is used to calculate soil gas concentrations protective of groundwater, and was developed by conceptualizing the movement of a vertical column of groundwater under a contaminant source area in the vadose zone. The model is designed to compute both the vertical distribution of contaminant concentrations within the saturated zone and the vertically averaged concentration within a mixing zone (*b*). The mixing zone can be conceptualized as the water column within a downgradient point-of-compliance monitoring well, as illustrated in Figure 1. Note that the mixing zone includes the capillary fringe. This column of water is assumed to have an initial, vertically uniform background concentration ( $C_0$ ) before it enters the source area (at  $X = 0$ ). Groundwater flow is assumed to be primarily horizontal with a steady Darcian velocity ( $q_X$ ). The aqueous concentration ( $C_l$ ) at the top of the capillary fringe is assumed to be in equilibrium with the soil gas concentration (as determined from Henry's Law) and to be constant within the source area (Figure 1).

As the water column moves under the source area, mass is transported from the top of the capillary fringe into the water column by infiltration (advection), molecular diffusion, and mechanical dispersion. Neglecting longitudinal dispersion in the aquifer (Equation 6), only the vertical movement of contaminants in the water column needs to be accounted for. Concentration in the water column will increase as it moves horizontally under the source area, and will reach a maximum as the column passes the downgradient edge of the source area (at  $X = L$ , see Figure 1).

Given these assumptions, vertical contaminant transport in the moving water column is governed by the following differential equation<sup>3</sup>:

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<sup>2</sup> It is important to note that water within and slightly above the capillary fringe moves laterally, driven by the same hydraulic gradient as that of the groundwater, because the capillary fringe is roughly parallel to the top of the water table.

<sup>3</sup> The dispersion flux term in (10) is multiplied by porosity because  $C_{t,v}$  represents the mass-per-bulk volume of the aquifer, not the mass-per-unit volume of water. The diffusion flux term already accounts for this fact. Note also that (10) assumes the infiltration rate is a great deal less than the horizontal Darcian velocity, therefore the volume of water in the column does not change significantly as it passes under the source area, a reasonable assumption in arid environments.

$$\frac{\partial C_{T,V}}{\partial t} = -\frac{\partial J_D}{\partial z} - f \frac{\partial J_M}{\partial z} - q_z \frac{\partial C}{\partial z} \quad (10)$$

where  $C_{T,V}$  is the total concentration per volume of aquifer (ug VOC / L of bulk volume)  
 $q_z$  is the infiltration flux rate (cm / sec)

and all other parameters are as described above. The term  $C_{T,V}$  includes the mass of contaminant dissolved in water and the mass sorbed onto the aquifer solids so that:

$$C_{T,V} = fC + C_{S,V} \quad (11)$$

where  $C_{S,V}$  is the soil sorbed concentration (ug VOC / L bulk volume)

Assuming linear, equilibrium sorption, the aqueous concentration is related to the soil sorbed concentration by:

$$C_{S,V} = r_b K_D C \quad (12)$$

where  $D_b$  is the dry bulk density (g solid / cm<sup>3</sup> bulk soil)  
 $K_D$  is the solid-water distribution coefficient (cm<sup>3</sup> / g)

The solid-water distribution coefficient can be calculated by:

$$K_D = K_{OC} f_{OC} = \frac{C_{S,M}}{C} \quad (13)$$

where  $C_{S,M}$  is the sorbed concentration per mass of soil solid (ug VOC / Kg solid)  
 $K_{OC}$  is the water-organic carbon distribution coefficient (cm<sup>3</sup> / g organic carbon)  
 $f_{OC}$  is the mass fraction of organic carbon in the soil

It is important to note that, strictly speaking, the “soil” concentration measured in a vadose zone soil, whether first preserved in the field with methanol or sub-sampled at an analytical laboratory, is the mass of VOC in both the ambient pore water and sorbed to the soil. However, for vadose zone soils of low water content, the measured soil concentration is approximately equal to  $C_{S,M}$ . This approximation seems warranted because the soil water content is rarely well known and highly variable.

Substituting (11) and (12) into (10) gives:

$$(f + r_b K_D) \frac{\partial C}{\partial t} = -\frac{\partial J_D}{\partial z} - f \frac{\partial J_M}{\partial z} - q_z \frac{\partial C}{\partial z} \quad (14)$$

The diffusive flux ( $J_D$ ) in (14) is given by (4). The dispersive flux ( $J_M$ ) can be accounted for by considering two components:

$$J_{ZX} = -a_{ZX} \frac{q_X}{f} \frac{\partial C}{\partial z} \quad (15)$$

which is just an expanded form of (8) representing the vertical transverse dispersive flux due to horizontal groundwater flow, and:

$$J_{ZZ} = -a_{ZZ} \frac{q_Z}{f} \frac{\partial C}{\partial z} \quad (16)$$

which is an expanded form of (9) for the vertical dispersive flux due to the downward movement of infiltrating water (Figure 3). Substituting (4), (15), and (16) into (14) gives (after dividing by  $\partial C / \partial z$ ):

$$\left(1 + \frac{r_b K_D}{f}\right) \frac{\partial C}{\partial t} = t D_0 \frac{\partial^2 C}{\partial z^2} + \left(a_{ZZ} \frac{q_Z}{f} + a_{ZX} \frac{q_X}{f}\right) \frac{\partial^2 C}{\partial z^2} - \frac{q_Z}{f} \frac{\partial C}{\partial z} \quad (17)$$

The coefficient on the left-hand side of (17) is the retardation coefficient:

$$R_D = 1 + \frac{r_b K_D}{f} \quad (18)$$

The first coefficient on the right-hand side of (17) is the effective molecular diffusion coefficient:

$$D_E = t D_0 \quad (19)$$

The second coefficient on the right-hand side of (17) is the effective vertical dispersion coefficient in the Z direction:

$$D_Z = \left(a_{ZZ} \frac{q_Z}{f} + a_{ZX} \frac{q_X}{f}\right) \quad (20)$$

The last coefficient on the right-hand side of (17) is the vertical pore velocity:

$$v_Z = \frac{q_Z}{f} \quad (21)$$

Substituting (18) through (21) into (17) and rearranging yields:

$$\frac{\partial C}{\partial t} = \frac{D_H}{R_D} \frac{\partial^2 C}{\partial z^2} - \frac{v_Z}{R_D} \frac{\partial C}{\partial z} \quad (22)$$

where  $D_H$  is the hydrodynamic dispersion coefficient ( $\text{cm}^2 / \text{sec}$ ), which equals  $D_E + D_Z$

The solution to (22) is subject to the aqueous concentration boundary condition at the top of the capillary fringe of:

$$C(0,t) = C_1 ; t > 0 \quad (23)$$

If the thickness of the aquifer is much greater than the depth of significant concentration changes, the water column can be treated as if it is infinitely thick so that the basal concentration boundary condition is:

$$C(\infty,t) = C_0 ; t > 0 \quad (24)$$

Finally, the background concentration in the water column as it enters the source area is:

$$C(z,0) = C_0 ; z \geq 0 \quad (25)$$

which is also the basal concentration. By letting the relative concentration be:

$$C^*(z,t) = \frac{C(z,t) - C_0}{C_1 - C_0} \quad (26)$$

(22) can be rewritten as:

$$\frac{\partial C^*}{\partial t} = \frac{D_H}{R_D} \frac{\partial^2 C^*}{\partial z^2} - \frac{v_Z}{R_D} \frac{\partial C^*}{\partial z} \quad (27)$$

subject to the relative concentration boundary and initial conditions:

$$C^*(0,t) = 1 ; t \geq 0 \quad (28)$$

$$C^*(\infty,t) = 0 ; t \geq 0 \quad (29)$$

$$C^*(z,0) = 0 ; z \geq 0 \quad (30)$$

Equation (26) reduces to the more familiar form of the relative concentration ( $C/C_1$ ) for  $C_0 = 0$ , in which case (22) applies.

The solution to (27) for these boundary and initial conditions is (Bear, 1979)<sup>4</sup>:

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<sup>4</sup> Equation (31) is based on Bear's equation (7-135), with the exception of a typographical error. The minus sign in the last term of 7-135 should be a plus sign.

$$C^*(z,t) = \frac{1}{2} \cdot \left\{ \operatorname{erfc} \left[ \frac{z - \frac{v_z t}{R_D}}{2 \left( \frac{D_H t}{R_D} \right)^{1/2}} \right] + \exp \left[ \frac{v_z z}{D_H} \right] \cdot \operatorname{erfc} \left[ \frac{z + \frac{v_z t}{R_D}}{2 \left( \frac{D_H t}{R_D} \right)^{1/2}} \right] \right\} \quad (31)$$

Equation (31) describes the vertical relative concentration distribution as a function of time as the water column moves under the source. Because the center of the contaminant mass moves slower than the groundwater flow velocity, it is appropriate to use a retarded solute travel time. Time in (31) is related to lateral distance under the source by:

$$x = \frac{q_x t}{f R_D} \quad (32)$$

where  $x$  is the distance that the center of mass has moved after time (t) due to the horizontal groundwater velocity

The vertical concentration distribution of interest is that in a downgradient point-of-compliance monitoring well on the boundary of the source area (Figure 1) where  $X = L$ , the length of the source area. Substituting L into (32) and solving for the time required for this concentration distribution to evolve gives a retarded travel time of:

$$t_R = \frac{LR_D}{v_x} \quad (33)$$

Substituting  $t_R$  into (31) for (t) gives:

$$C^*(z,t) = \frac{1}{2} \cdot \left\{ \operatorname{erfc} \left[ \frac{z - \frac{v_z L}{v_x}}{2 \left( \frac{D_H L}{v_x} \right)^{1/2}} \right] + \exp \left[ \frac{v_z z}{D_H} \right] \cdot \operatorname{erfc} \left[ \frac{z + \frac{v_z L}{v_x}}{2 \left( \frac{D_H L}{v_x} \right)^{1/2}} \right] \right\} \quad (34)$$

Equation 34 gives the steady-state concentration distribution at the downgradient edge of the source area. If the mixing zone is within the screened interval of a downgradient point-of-compliance monitoring well, the vertically averaged concentration in the screened interval can be determined by numerically integrating the computed concentration distribution. Note that in (34) the relative concentration distribution is primarily a function of the length of the source area, the velocity of infiltration, the velocity of horizontal groundwater flow, and hydrodynamic dispersion. The only contaminant-specific dependency for the relative concentration is through the aqueous diffusion coefficient ( $D_o$ ), which for most VOCs is within 20% of  $1 \times 10^{-5}$  cm<sup>2</sup>/sec (U.S. EPA, 1996). As will be shown later, soil gas concentrations that are protective of groundwater are contaminant specific.

For a given set of site conditions (34) provides the basis for computing  $\overline{C^*}$ , the vertically averaged relative concentration in the mixing zone at the downgradient edge of the source area, which is assumed to equal that determined by purging the well of three wetted casing volumes and collecting a water quality sample. The soil gas concentration ( $C_{RAO}$ ) at the base of the vadose zone that will result in a vertically averaged groundwater concentration in the mixing zone equal to the Aquifer Water Quality Standard ( $C_{STD}$ ) can then be computed (assuming the background groundwater concentration of the contaminant is zero) by:

$$C_{RAO} = \overline{C^*} C_{STD} H_D \quad (35)$$



The corresponding total soil concentration ( $C_{S,T}$ ) can be computed from:

$$C_{S,T} = C_{RAO} \left\{ \frac{K_D}{H_D} + \frac{fS_W}{H_D r_b} + \frac{f(1-S_W)}{r_b} \right\} \quad (36)$$

where  $S_W$  is the water saturation in the vadose zone ( $\text{cm}^3$  water /  $\text{cm}^3$  pores)

Note that the first term on the right-hand side of (36) represents the soil sorbed concentration as given by (1) and (13), the second term represents the pore water concentration using (1), and the third term is the soil gas concentration.

### Model Application

The model was used to compute the  $C_{RAO}$  that would result in a  $C_{STD} = 5$  ug/L of tetrachloroethene (PCE) at the downgradient edge of a hypothetical source area in the arid southwestern United States. The calculations were performed assuming a uniform gas concentration beneath the entire source area and a uniform average groundwater flow velocity. Table 1 (EPA, 1990) summarizes the parameters used as input to the model for this base simulation. Soil gas concentrations that are protective of groundwater are assumed to be less than or equal to  $C_{RAO}$ .

Figure 4 shows the PCE relative concentration distribution in the downgradient monitoring well, using the parameters in Table 1. Assuming a 30-foot mixing zone and a target vertically averaged concentration of  $C_{STD} = 5$  ug/L, the source concentration (corresponding to  $C^* = 1.0$ ) is approximately  $C_1 = 121$  ug/L. Using Henry's Law, the corresponding soil gas concentration required to generate this dissolved concentration at the water table is approximately  $C_{RAO} = 114$  ug/L. This close correspondence in concentration arises from the fact that  $H_D$  for PCE is close to unity. The corresponding total soil concentration at the water table calculated from (36) and using the parameters in Table 1 is  $C_{S,T} = 106.2$  ug/Kg.

To state these model results from a site investigation perspective, if a soil gas survey reveals a uniform vadose zone soil gas concentration beneath the site of 114 ug/L of PCE, the model would predict a PCE concentration at the water table surface (under the downgradient edge of the site) of approximately 121 ug/L, and a total soil PCE concentration at the water table of 106.2 ug/Kg. If the upper 30 feet of the water table under the downgradient edge of the site is sampled by pumping three wetted casing volumes, the sample concentration is predicted to be 5 ug/L.

Calculation of the concentration of PCE sorbed to the soil (the first term on the right hand side of (36) varies with both the  $K_{OC}$  and  $f_{OC}$  parameters (Equation 13). The Log  $K_{OC}$  used in the base simulation was 2.82 (Table 1), which results in a predicted soil sorbed concentration of 80 ug/Kg. Figure 5 shows that for an  $f_{OC}$  of 0.001, a range in Log  $K_{OC}$  from 2.780 to 2.875 (+/- 10%) results in a range of soil sorbed concentration from 73 to 91 ug/Kg (+/- 10%). The change in predicted soil sorbed concentration with Log  $K_{OC}$  is more significant for soils with a high  $f_{OC}$  than those with a low  $f_{OC}$ . Soils in the arid southwestern United States are thought to have an  $f_{OC}$  in the range from 0.001 to 0.0001. Figure 5 shows that as  $f_{OC}$  decreases, the effect of variation in Log  $K_{OC}$  on the estimate of soil sorbed concentration also decreases. The variations or uncertainty in  $f_{OC}$  and  $K_{OC}$  are only important, however, if the RAO is based on a soil concentration rather than a soil gas concentration.

### Model Sensitivity

For a given mixing zone thickness, the target soil gas concentrations based on (34) and (35) depend on the target groundwater concentration, the dimensionless Henry's Law coefficient of the specific contaminant, the source length, the tortuosity factor, the dispersivities ( $\alpha_{ZZ}$  and  $\alpha_{ZZ}$ ), and the groundwater velocity. A sensitivity analysis was performed to illustrate how variations or uncertainty in these parameters can affect the target soil gas concentrations. For a given set of site conditions, the target soil gas concentration is a linear function of the target groundwater concentration and the dimensionless Henry's Law

coefficient. Figure 6 shows model predictions for four common VOCs, based on  $C_{STD}$  equal to their maximum concentration limit (MCL):

- vinyl chloride (MCL = 2 ug/L)
- tetrachloroethene (PCE) (MCL = 5 ug/L)
- trichloroethene (TCE) (MCL = 5 ug/L)
- cis-1,2-dichloroethene (cis-1,2-DCE) (MCL = 70 ug/L)
- benzene (MCL = 5 ug/L)

The length of the source area (L) determines the length of contact time between the groundwater and the soil gas source, and therefore the resulting groundwater concentration. The resulting  $C_{RAO}$  is a nonlinear function of L. Figure 7 shows the variation in  $C_{RAO}$  for PCE with source lengths ranging from 30 to 300 feet based on the aquifer properties presented in Table 1, for three values of vertical transverse dispersivity (0.05, 0.10, and 0.15 cm).

The model was found to have little sensitivity to the vertical dispersivity due to infiltration ( $\alpha_{ZZ}$ ), but to be relatively sensitive to the vertical transverse dispersivity of horizontal flow ( $\alpha_{ZX}$ ). This sensitivity is illustrated in Figure 8 for PCE for a plausible range of  $\alpha_{ZX}$  (for the site conditions in Table 1) and net infiltration rates of 0, 1, and 2 inches per year. Figure 8 illustrates that  $C_{RAO}$  is more sensitive to  $\alpha_{ZX}$  at lower infiltration rates. It also illustrates that the values of  $C_{RAO}$  converge as  $\alpha_{ZX}$  increases.

Finally, Figure 9 illustrates the model sensitivity to groundwater velocity, for the site conditions in Table 1. The figure shows that the predicted  $C_{RAO}$  are more sensitive to  $\alpha_{ZX}$  at higher groundwater flow rates.

## Conclusions

The modeling approach described above is the basis for developing soil cleanup concentrations for VOCs that are protective of groundwater quality. The approach considers mass transport processes in addition to infiltration that may result in groundwater contamination at sites with little or no infiltration. The methodology provides soil gas concentrations at the base of the vadose zone that are protective of groundwater quality, although equivalent soil concentration can also be computed. Basing soil cleanup standards on soil gas rather than on soil concentrations provides a reliable and convenient way of tracking remedial progress. This is partly due to the fact that permanent soil gas monitoring probes can be installed, whereas soil sampling requires mobilization of a drill rig. But more importantly, the soil gas phase is mobile, and can sample a much larger volume of potentially contaminated soil than soil sampling can. At many sites it has been our experience that soil gas surveys indicate a threat to groundwater while soil sampling is inconclusive or suggests no threat to groundwater.

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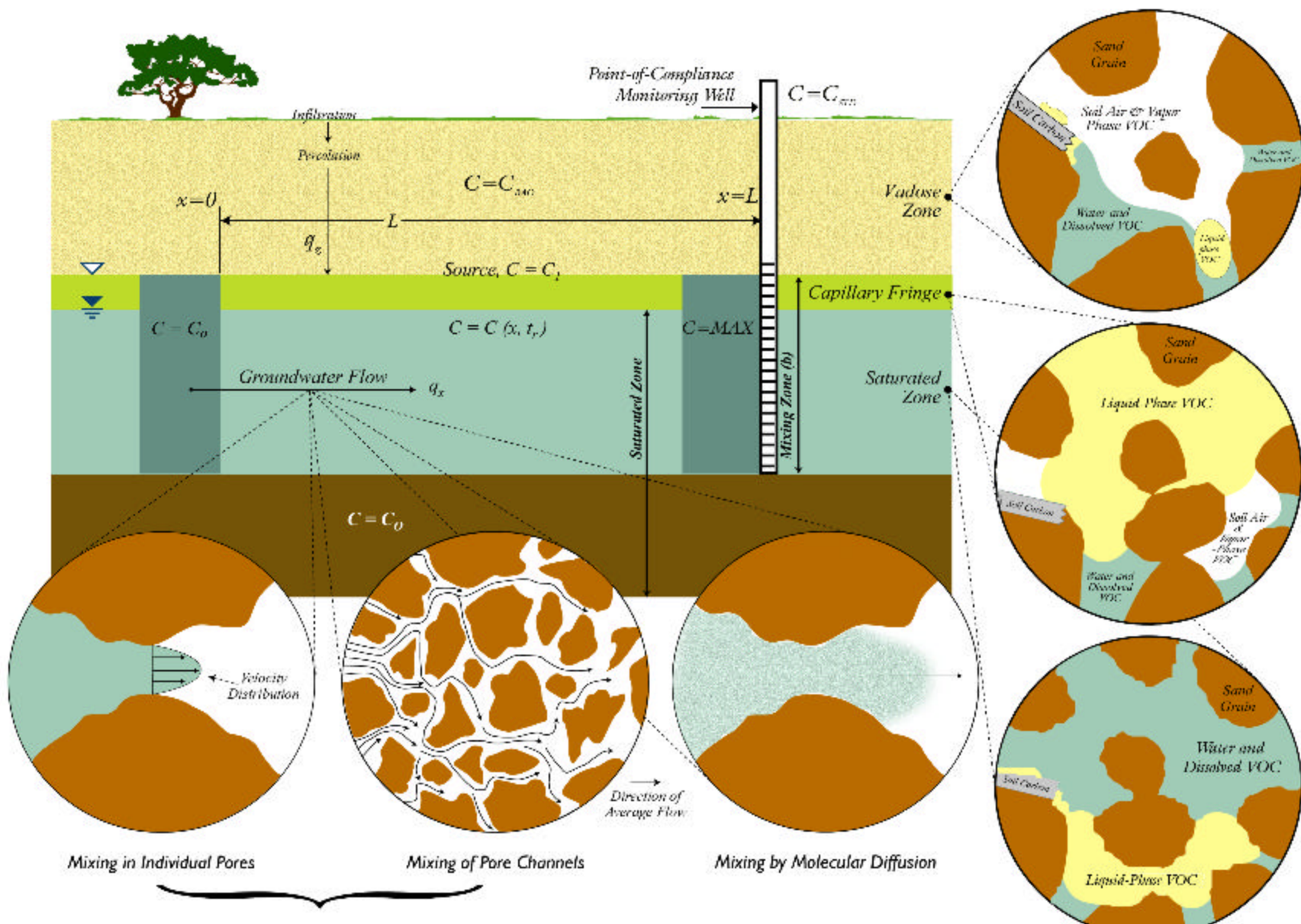
## TABLES

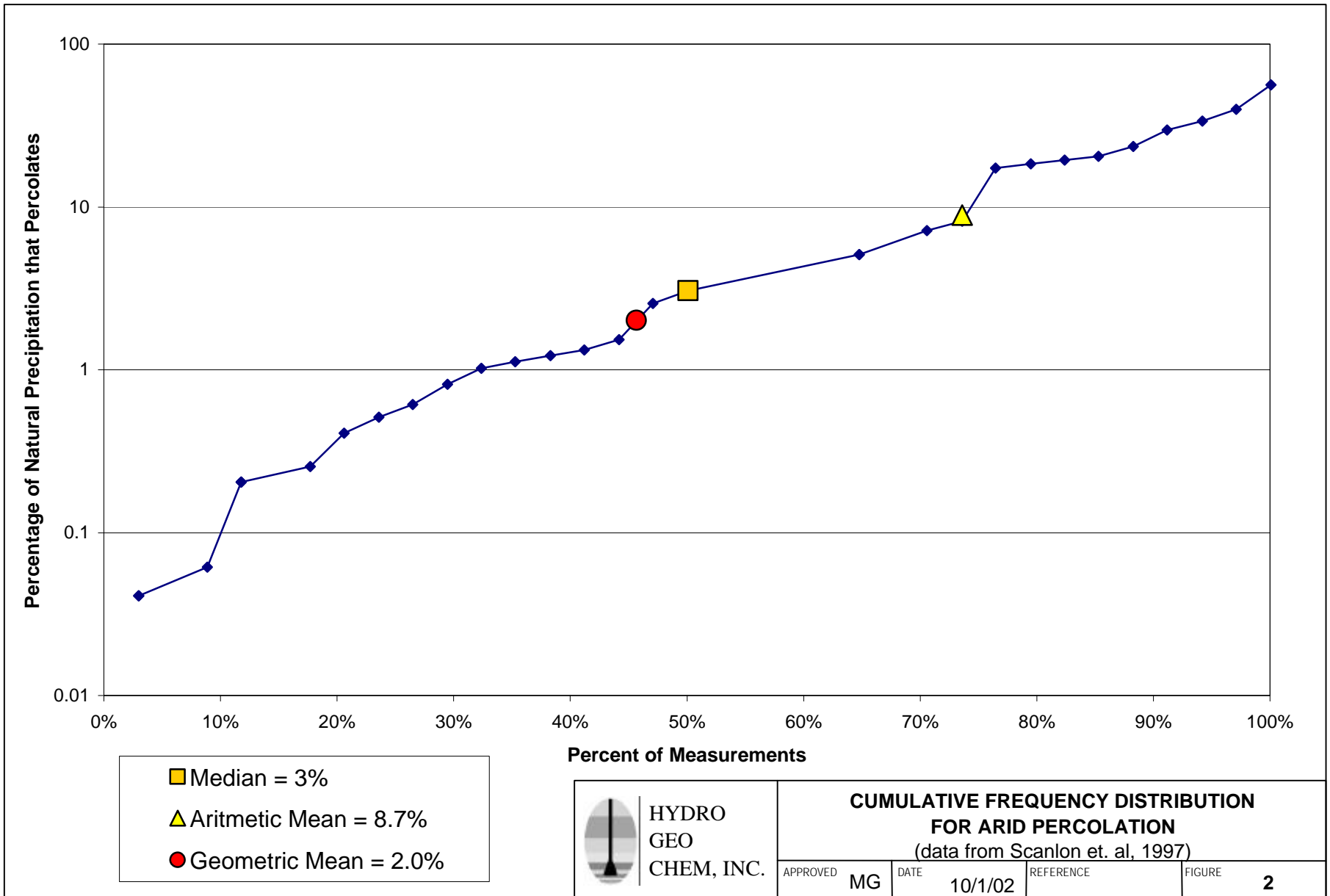
**TABLE 1**  
**Input Parameters for Base Simulation**

Parameter Name	Symbol	Value	Units
<b>System and Aquifer Parameters</b>			
Longitudinal Dispersivity of Infiltration Flux	$\alpha_{ZZ}$	<b>0.10</b>	(cm)
Tortuosity Factor	$\tau$	<b>0.20</b>	
Porosity	$\theta$	<b>0.35</b>	
Horizontal Groundwater Flow Velocity	$v_x$	<b>0.50</b>	(ft/day)
Transverse Dispersivity of Horizontal Groundwater Flow	$\alpha_{ZX}$	<b>0.10</b>	(cm)
Infiltration Flux	$q_z$	<b>1.0</b>	(in/year)
Source Length	$L$	<b>245</b>	(ft)
Soil Bulk Density	$r_b$	<b>1.60</b>	(g/cm <sup>3</sup> )
Mixing Zone Thickness	$b$	<b>30</b>	(ft)
Fraction of Organic Carbon	$f_{OC}$	<b>0.001</b>	
Temperature	$T$	<b>293.15</b>	(K)
<b>Contaminant Parameters</b>			
Contaminant Aqueous Molecular Diffusion Coefficient	$D_0$	<b>1.01 E-05</b>	(cm <sup>2</sup> /sec)
Vinyl Chloride Henry's Law Coefficient	$H$	<b>0.695</b>	(atm-m <sup>3</sup> /mol)
Dimensionless Henry's Law Coefficient for Vinyl Chloride	$H_D$	<b>28.9</b>	(at 20 °C)
Log Vinyl Chloride Water-Organic Carbon Partitioning Coefficient	Log $K_{OC}$	<b>0.91</b>	(cm <sup>3</sup> / g <sub>oc</sub> )
PCE Henry's Law Coefficient	$H$	<b>0.02270</b>	(atm-m <sup>3</sup> /mol)
Dimensionless Henry's Law Coefficient for PCE	$H_D$	<b>0.944</b>	(at 20 °C)
Log PCE Water-Organic Carbon Partitioning Coefficient	Log $K_{OC}$	<b>2.82</b>	(cm <sup>3</sup> / g <sub>oc</sub> )
TCE Henry's Law Coefficient	$H$	<b>0.00892</b>	(atm-m <sup>3</sup> /mol)
Dimensionless Henry's Law Coefficient for TCE	$H_D$	<b>0.371</b>	(at 20 °C)
Log TCE Water-Organic Carbon Partitioning Coefficient	Log $K_{OC}$	<b>2.10</b>	(cm <sup>3</sup> / g <sub>oc</sub> )
cis-1,2-DCE Henry's Law Coefficient	$H$	<b>0.00750</b>	(atm-m <sup>3</sup> /mol)
Dimensionless Henry's Law Coefficient for cis-1,2-DCE	$H_D$	<b>0.312</b>	(at 20 °C)
Log cis-1,2-DCE Water-Organic Carbon Partitioning Coefficient	Log $K_{OC}$	<b>1.50</b>	(cm <sup>3</sup> / g <sub>oc</sub> )
Benzene Henry's Law Coefficient	$H$	<b>0.00543</b>	(atm-m <sup>3</sup> /mol)
Dimensionless Henry's Law Coefficient for Benzene	$H_D$	<b>0.226</b>	(at 20 °C)
Log Benzene Water-Organic Carbon Partitioning Coefficient	Log $K_{OC}$	<b>1.81</b>	(cm <sup>3</sup> / g <sub>oc</sub> )

(contaminant data from USEPA. 1990. Subsurface Contamination Reference Guide. EPA / 540 / 2-90 / 011.

## FIGURES







$$J_{XX} = -a_{XX} v_X \frac{\partial C}{\partial x}$$

(Eqn. 6: Dispersive flux in the direction of groundwater flow)

(Eqn.7: Horizontal transverse dispersive flux due to horizontal groundwater flow)

$$J_{YX} = -a_{YX} v_X \frac{\partial C}{\partial y}$$



$$J_{ZX} = -a_{ZX} v_X \frac{\partial C}{\partial z}$$

(Eqn. 8: Vertical transverse dispersive flux due to horizontal groundwater flow)

$$J_D = -tfD_0 \frac{\partial C}{\partial z}$$

(Eqn. 4: Vertical diffusive flux due to concentration gradient)

$$J_{ZZ} = -a_{ZZ} \frac{q_z}{f} \frac{\partial C}{\partial z}$$

(Eqn. 16: Vertical dispersive flux due to vertical infiltration)



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**SCHEMATIC DIAGRAM OF DIFFUSIVE AND DISPERSIVE FLUXES**

Approved

MG

Date

10/1/02

Reference

H:/0865/NEW-GPL/Fig-3.srf

Figure

3

