

Vapor Phase Transport as a Groundwater Contamination Process at Arid Landfill Sites

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Abstract: The occurrence of halogenated volatile organic compounds (HVOCs) in groundwater beneath several municipal solid waste landfills in Tucson, Arizona in the absence of significant liquid phase movement has suggested that vapor phase transport may be the principal process transporting HVOCs from the vadose zone into the water table. The results of mathematical modeling of these transport processes were used to evaluate their relative importance under site specific conditions. The processes considered included molecular diffusion and mechanical dispersion through the capillary fringe and the effects of a falling water table on mass transport. Calibration of the mathematical model against soil gas and groundwater monitoring data indicated that mechanical dispersion due to natural groundwater flow is sufficient to result in groundwater plumes of HVOCs exceeding maximum contaminant levels. A falling water table further increases mass transport from the vadose zone to the water table through advective transport of dissolved HVOCs.

Keywords: Vapor Transport, Landfills

Introduction

This paper addresses the extent to which the presence of vapors of halogenated volatile organic compounds (HVOCs) in the vadose zone can result in groundwater concentrations exceeding maximum contaminant levels (MCLs).

Plumes of tetrachloroethene (PCE) and other HVOCs, such as freons, have been detected in groundwater beneath and downgradient of several closed landfills in the Tucson Basin. These landfills are unlined and typically were operated between the 1960s and early 1980s. The Tucson Basin receives approximately 12 inches per year of annual precipitation in the form of rain. The landfills are underlain by valley-fill sediments consisting of sand and silt with lenses of gravel and clay. The refuse in the landfills is relatively dry and no evidence of leachate generation has been detected, although the landfills do generate some landfill gas. Likewise, the soil beneath the landfills is also relatively dry with soil water content ranging from 5 to 20 % by weight.

At the landfill to be discussed later, the water table occurs at a depth of approximately 240 feet below land surface (ft bls). Although, PCE and other HVOCs were detected in gas samples collected from the refuse, their concentrations in the vadose zone beneath the landfill tended to be higher than in the refuse (Figure 1), with PCE ranging from approximately 4 to 570 $\mu\text{g/L}$. A plume of contaminated groundwater extends approximately 1,500 feet downgradient from the landfill with groundwater concentrations ranging for 5 $\mu\text{g/L}$ up to about 50 $\mu\text{g/L}$. Common indicators of aqueous phase transport

by leachate migration, such as elevated total dissolved solids and chloride concentrations, are absent. In addition, the only contaminants detected in the groundwater beneath the landfill were volatile organic compounds.

Transport Processes

The transport processes that can distribute HVOCs within the vadose zone include aqueous-phase advection in infiltrating soil water (including leachate, if present), vapor-phase advective transport due to LFG movement and barometric pumping, density driven flow of LFG during the early stages of LFG generation, and vapor-phase molecular diffusion. The absence of evidence for leachate migration, limited potential for infiltration of meteoric water into and through the landfills, and higher HVOC concentrations below the landfills than in the refuse prompted Ward and Smith (1998) and Murray and others (1998) to explain the distribution of HVOCs as being due to the expulsion of HVOC vapors from the refuse by LFG generation in the refuse. These processes are illustrated in Figure 2.

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). A schematic diagram of the distribution of the various contaminant phases in these three zones is presented in Figure 3.

Assuming mobile NAPL is not present, 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 capillary fringe. Assuming that the concentrations of VOCs in soil gas and pore water are in equilibrium, their can be described by Henry's Law:

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

where C_G is the concentration in the soil gas
 C is the aqueous concentration
 H_D is the dimensionless Henry's Coefficient
 H is the Henry's coefficient
 R is the universal gas constant
 T is the absolute temperature

Once dissolved in the soil water, the 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, or by drainage of soil water under falling water table conditions. Based on data from Scanlon and others (1997) for arid sites under natural land use, the median net infiltration rate is approximately 3% of annual precipitation, which for the Tucson basin would be about 0.4 inches per year.

Advective transport due to a falling or fluctuating water table has received little attention in the literature. 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:

$$I_E = S_Y \frac{\Delta H}{\Delta t} \quad (2)$$

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)
 ΔH is the decrease in the water table elevation (inches)
 Δt 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 the Tucson basin.

Figure 3 shows the classical schematic representation of mechanical dispersion and diffusion processes on the pore scale. Molecular diffusion is an ubiquitous transport process in which the mass flux driving force is a gradient in chemical concentration. Aqueous-phase diffusive transport in porous media is generally described by a modified form of Fick's Law (Thomas, 1982):

$$J_D = -\tau \phi D_0 \frac{\partial C}{\partial z} \quad (3)$$

where J_D is the molecular diffusive flux (ug / cm² / sec)
 τ 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)
 ϕ is the porosity (or saturated water content) (cm³ pores / cm³ bulk soil)
 D_0 is the molecular aqueous diffusion coefficient in the porous medium (cm² / sec)
 z depth (cm)

Because molecular diffusion is a relatively weak process, its only significance for groundwater contamination may be through vertical diffusion across the capillary fringe.

Mechanical dispersion (Figure 3) 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. Mechanical dispersion at small spatial scales is well described by a relationship similar to Fick's Law of diffusion (Bear, 1979):

$$J_M = -\overline{\alpha}_M \overline{v} \nabla C = -\overline{D}_M \nabla C \quad (4)$$

where J_M is the mechanical dispersive flux
 $\overline{\alpha}_M$ is the mechanical dispersivity tensor
 \overline{v} is the vector of the absolute values of the groundwater pore velocity
 \overline{D}_M is the mechanical dispersion coefficient tensor
 ∇ is the gradient operator

The components of the dispersivity tensor consist of terms describing dispersion in the direction of advective flow (α_{XX}) called the longitudinal dispersivity, and terms describing dispersion perpendicular to the direction of flow (α_{YX} and α_{ZX}) called the horizontal and vertical transverse dispersivities, respectively. For the case of purely horizontal groundwater flow, mechanical dispersion will take place not only in the direction of flow, but also horizontally transverse to the direction of flow and vertically perpendicular (Z) to the direction of flow. An additional dispersive flux will result from the vertical movement of infiltrating or draining water. This flux can be described by:

$$J_{ZZ} = -\alpha_{ZZ} v_Z \frac{\partial C}{\partial z} \quad (5)$$

where v_Z is the magnitude of the velocity in the Z -direction

Equation (4) 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 -direction¹. 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.

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. 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 (α_{ZX}) ranging from 0.1 cm to 0.4 cm. With respect to vertical dispersivity due to infiltration (α_{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 α_{ZZ} relative to α_{ZX} , the magnitude of the vertical dispersive flux is generally insignificant because of the small magnitude of the vertical infiltration velocity.

Transport Model

The transport processes described were used to construct a simple, analytical model to test the hypothesis that vapor phase transport in the absence of significant advective soil water transport could explain the groundwater concentrations observed at the landfills. The model was developed by conceptualizing the movement of a vertical column of groundwater under a contaminant source area in the vadose zone as illustrated in Figure 3. The model was designed to compute the vertical distribution of contaminant concentrations within a column of water in the saturated zone. 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_I) 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 3).

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

¹ 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.

dispersion. Neglecting longitudinal dispersion in the aquifer, only the vertical movement of contaminants in the water column needs to be accounted for. The 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 3).

Given these assumptions, vertical contaminant transport in the moving water column is governed by the following differential equation:

$$\frac{\partial C_{T,V}}{\partial t} = - \frac{\partial J_D}{\partial z} - \phi \frac{\partial J_M}{\partial z} - q_z \frac{\partial C}{\partial z} \quad (6)$$

where $C_{T,V}$ is the total concentration per volume of aquifer
 q_z is the infiltration flux rate

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:

$$C_{T,V} = \phi C + C_{S,V} \quad (7)$$

where $C_{S,V}$ is the soil sorbed concentration

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

$$C_{S,V} = \rho_b K_D C \quad (8)$$

where ρ_b is the dry bulk density
 K_D is the solid-water distribution coefficient

After substituting the relationships described above along with the expressions for mechanical dispersion and after dividing by ϕ , (6) can be written as:

$$\left(1 + \frac{\rho_b K_D}{\phi}\right) \frac{\partial C}{\partial t} = \tau D_0 \frac{\partial^2 C}{\partial z^2} + \left(\alpha_{zz} \frac{q_z}{\phi} + \alpha_{zx} \frac{q_x}{\phi}\right) \frac{\partial^2 C}{\partial z^2} - \frac{q_z}{\phi} \frac{\partial C}{\partial z} \quad (9)$$

Equation (9) can be rearranged as:

$$\frac{\partial C}{\partial t} = \frac{D_H}{R_D} \frac{\partial^2 C}{\partial z^2} - \frac{v_z}{R_D} \frac{\partial C}{\partial z} \quad (10)$$

where D_H is the hydrodynamic dispersion coefficient

The solution to (10) is subject to the aqueous concentration boundary condition at the top of the capillary fringe of:

$$C(0,t) = C_1 ; t > 0 \quad (11)$$

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:

$$C(\infty, t) = 0; t > 0 \quad (12)$$

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

$$C(z, 0) = 0; z \geq 0 \quad (13)$$

which is also the basal concentration.

The solution to (10) for these boundary and initial conditions is (Bear, 1979):

$$C(z, t) = \frac{1}{2} C_i \cdot \left\{ \operatorname{erfc} \left[\frac{z - \frac{v_z t}{R_d}}{2 \left(\frac{D_H t}{R_d} \right)^{1/2}} \right] + \exp \left[\frac{v_z z}{D_H} \right] \cdot \operatorname{erfc} \left[\frac{z + \frac{v_z t}{R_d}}{2 \left(\frac{D_H t}{R_d} \right)^{1/2}} \right] \right\} \quad (14)$$

Equation (14) describes the vertical 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 (14) is related to lateral distance under the source by:

$$x = \frac{q_X t}{\phi R_D} \quad (15)$$

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 3) where $X = L$, the length of the source area. Substituting L into (15) and solving for the time required for this concentration distribution to evolve gives a retarded travel time of:

$$t_R = \frac{LR_D}{v_X} \quad (16)$$

Substituting t_R into (14) for (t) gives:

$$C(z, t) = C_i \frac{1}{2} \cdot \left\{ \operatorname{erfc} \left[\frac{z - \frac{v_z L}{v_x}}{2 \left(\frac{D_H L}{v_x} \right)^{1/2}} \right] + \exp \left[\frac{v_z z}{D_H} \right] \cdot \operatorname{erfc} \left[\frac{z + \frac{v_z L}{v_x}}{2 \left(\frac{D_H L}{v_x} \right)^{1/2}} \right] \right\} \quad (17)$$

Equation 17 gives the steady-state concentration distribution at the downgradient edge of the source area. Note that in (17) the 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 dependencies are through the aqueous diffusion coefficient (D_0), which for most VOCs is within 20% of 1×10^{-5} cm²/sec (U.S. EPA, 1996) and the Henry's coefficient through C_1 .

Application

The transport model was applied to the landfill described previously by using the model to back calculate the values of certain transport parameters needed to reproduce the observed groundwater concentrations from the measured vadose zone soil gas concentrations. The length of the cross section passing under the landfill was 2,100 feet, which corresponds to the length of the source area (L) in the screening model. The calculations were performed assuming an average saturated water column of 21 feet representing water column sampled in downgradient monitoring wells. The effective infiltration rate was calculated to be 0.9 inches per year from the rate of decline of the water table of 6 inches per year and assuming a specific yield of 0.15. The calculations were performed for groundwater velocity of 50 ft/yr.

Given the fixed groundwater velocity and effective infiltration rate, the key parameter controlling the partitioning of the HVOCs between the vadose zone and the saturated zone is the transverse horizontal dispersivity. Experience with the model indicated that the calculations are not very sensitive to the vertical longitudinal dispersivity because the vertical infiltration velocity is very small with respect to the horizontal groundwater velocity (inches per year compared to feet per year). The model was calibrated by adjusting the value of the transverse dispersivity so as to best match the groundwater concentration of PCE computed from the measured soil gas concentration to the measured downgradient groundwater concentration. For consistency, the vertical longitudinal dispersivity was set equal to 10 times the horizontal transverse dispersivity. The calibrated value for the horizontal transverse dispersivity was determined to be 1.7×10^{-2} feet (0.6 cm). This calibrated value is within the experimental range discussed previously.

The computed vertical distribution of PCE is shown in Figure 4. The calibration was then tested by using the model to compute the groundwater concentrations of the other contaminants of concern (COCs) (trichloroethene [TCE], 1,1-dichloroethene [DCE], vinyl chloride [VC] and dichloromethane [DCM]). The computed concentrations for the other COCs based on the calibrated value of transverse dispersivity are shown in Figure 5 along with the reported groundwater and soil gas concentrations. Reasonable agreement is seen between all of the COCs except DCM, for which the reported groundwater concentration is much less than would be computed from the soil gas concentration. The discrepancy for DCM is most likely due to biodegradation in the aquifer.

Conclusions

The fact that the observed groundwater concentration could be reasonably well reproduced from the soil gas concentration lends to support to the hypothesis even in the absence of significant vertical soil water movement, vapor concentrations near the water table can result in groundwater concentrations exceeding MCLs. Although strict quantification of the magnitude of various parameters controlling the transport processes is difficult, responsible parties and regulators should be aware of the potential for adverse groundwater impacts due to vapor transport and not focus

remedial actions solely on controlling the movement of liquid phase contaminants in the vadose zone. The model described above can also be used to develop soil remediation goals that are protective of groundwater quality.

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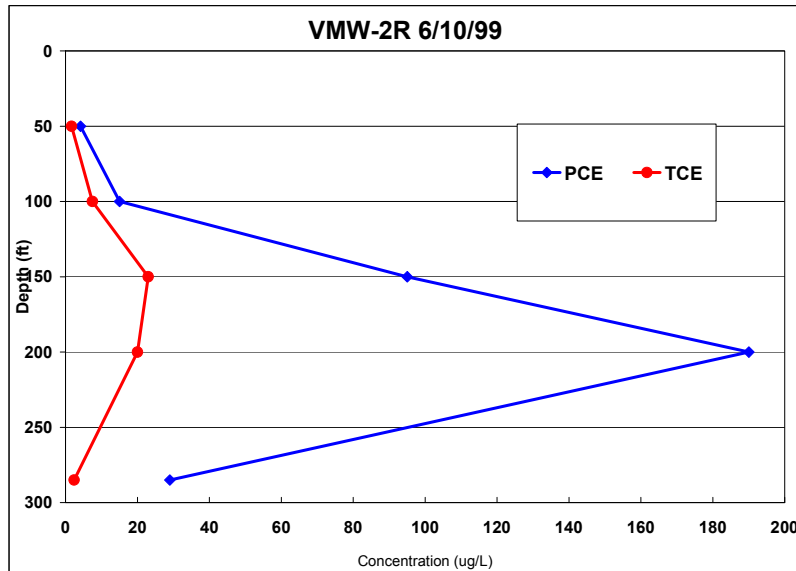


Figure 1: Vertical distribution of PCE and TCE gas concentrations.

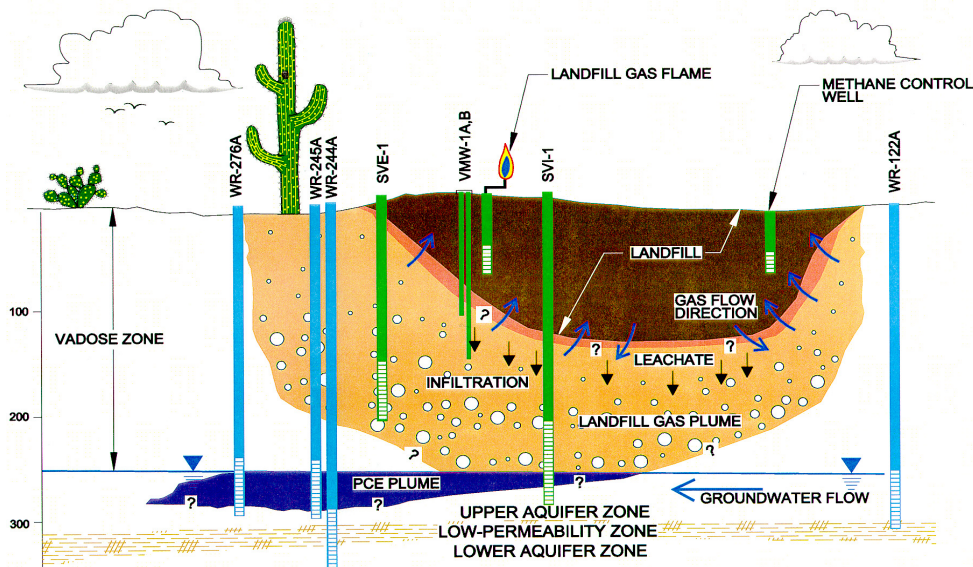


Figure 2: Schematic representation of HVOC transport processes in the vadose zone.

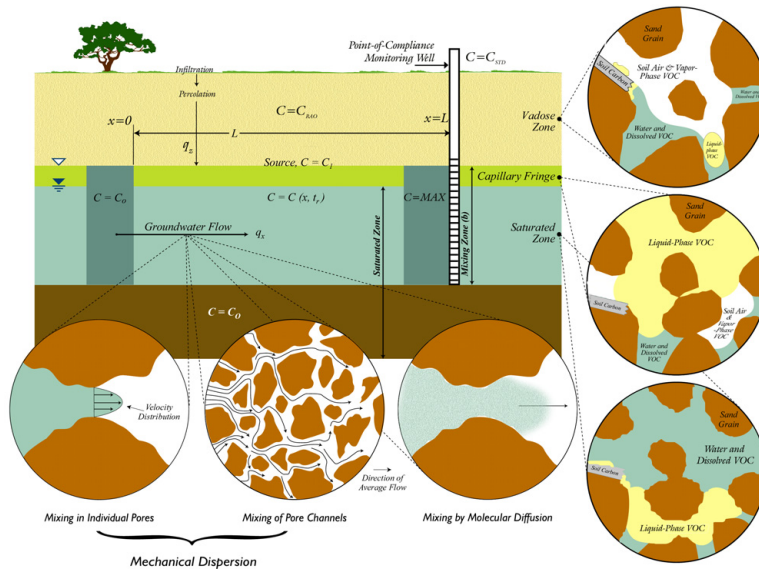


Figure 3: Schematic representation of transport processes from vadose zone to saturated zone.

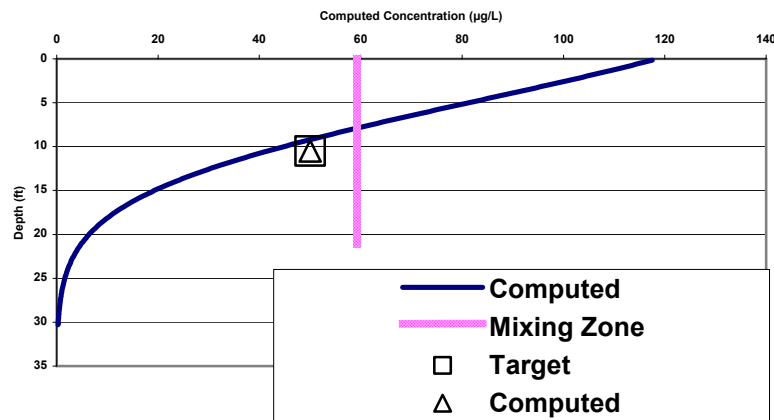


Figure 4: Computed vertical distribution of PCE

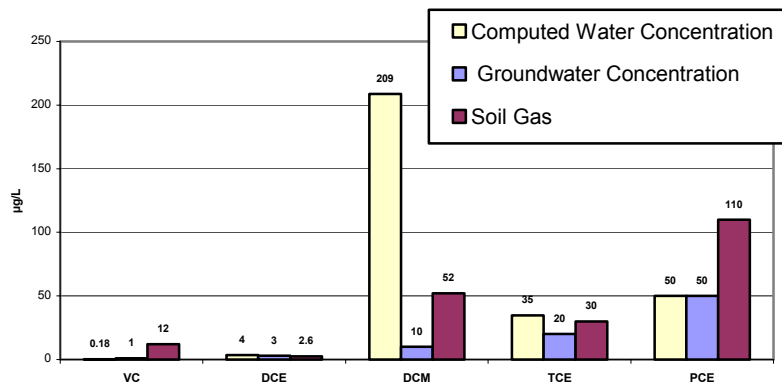


Figure 5: Comparison of computed to observed groundwater concentrations.