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Estimating Persistent Mass Flux of Volatile Contaminants from the Vadose Zone to Ground Water

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Abstract

Contaminants may persist for long time periods within low permeability portions of the vadose zone where they cannot be effectively treated and are a potential continuing source of contamination to ground water. Setting appropriate vadose zone remediation goals typically requires evaluating these persistent sources in terms of their impact on meeting ground water remediation goals. Estimating the impact on ground water can be challenging at sites with low aqueous recharge rates where vapor-phase movement is the dominant transport process in the vadose zone. Existing one-dimensional approaches for simulating transport of volatile contaminants in the vadose zone are considered and compared to a new flux-continuity-based assessment of vapor-phase contaminant movement from the vadose zone to the ground water. The flux-continuity-based assessment demonstrates that the ability of the ground water to move contaminant away from the water table controls the vapor-phase mass flux from the vadose zone across the water table. Limitations of these approaches are then discussed with respect to the required assumptions and the need to incorporate three-dimensional processes when evaluating vapor-phase transport from the vadose zone to the ground water. The carbon tetrachloride plume at the U.S. Department of Energy Hanford Site is used as the example site where persistent vadose zone contamination needs to be considered in the context of ground water remediation.

Introduction

Estimating long-term contaminant mass flux to the ground water from persistent contaminant sources in the vadose zone may be necessary at some contaminated sites as a means to determine when active vadose zone remediation can be transitioned to passive remediation or to support remediation closure in the vadose zone. Soil vapor extraction (SVE) is a baseline remediation technology for volatile contaminants that can effectively treat transmissive zones in the vadose zone. Persistent contamination that cannot be readily removed by SVE may be present and result in a long-term, low-level extracted vapor concentration (compared to initial concentrations) in the SVE system. Diminishing returns in terms of the contaminant mass extracted per cost of the SVE system typically trigger a need for remedy assessment for continuing SVE operations, transitioning to a different approach for treating the persistent contamination, or for closure of the vadose zone remedy. Evaluating the impact of the vadose zone contamination on the ground water is an integral part of this assessment process. If the ground water is contaminated by sources within (e.g., immiscible-liquid or sorbed-phase contamination), the ground water concentration is not a direct indicator of the effect of the vadose zone source on ground water concentrations.

The USACE (2002) and EPA (2001) outline processes for assessing closure/transition of SVE systems using several types of analyses, including estimation of contaminant mass flux to ground water and the resultant ground water contamination concentration. Analysis of the contaminant mass flux to the ground water and resultant ground water concentration based on vadose zone conditions can provide input to setting a vapor-phase contaminant concentration remediation target. For a given ground water concentration target, the analysis can be conducted to determine the corresponding concentration in the vadose zone at the location of the persistent source as a means to set a remediation target in the vadose zone.

Numerical simulation and analytical solution techniques can be applied to estimate the mass flux to the ground water. For chlorinated organic contaminated sites, contamination may be present in four phases within the vadose zone: immiscible liquid, dissolved, sorbed, or vapor. Transport of chlorinated organics in the vadose zone is a dynamic process involving interaction of all four of these phases. Fate

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and transport assessment needs to consider these four phases and the physics of fluid flow in unsaturated porous media. Numerical simulation codes such as Subsurface Transport of Multiple Phases (STOMP) (White and Oostrom 2006) provide a platform for simulating contaminant fate and transport under these conditions in one, two, or three dimensions if appropriate information is available for the model configuration, including input for the initial and boundary conditions. As outlined by EPA (2001), analytical or simplified numerical modeling techniques may be advantageous to support decision making because they do not require extensive spatially dense data sets to describe the subsurface and contaminant fate and transport properties. Instead, the simplified techniques use a one-dimensional flow assumption with uniform hydraulic properties for the model configuration and diffusive transport in the gas phase. Initial and boundary conditions can be varied to bound the range of contaminant transport that is likely to occur at the site. However, the assumptions and simplified configuration of these techniques must be considered when interpreting the results.

The use of analysis techniques needs to be considered in the context of the dominant mode of contaminant transport within the vadose zone. Where aqueous transport dominates, contaminant transport in the vadose zone is primarily vertical (one-dimensional), the contact area of vadose zone contamination on the water table can be readily estimated, and transport across the water table can be represented simply. As vapor-phase transport becomes more important (e.g., for arid sites with low aqueous recharge), three-dimensional contaminant movement in the vadose zone may be more important, the contact area of vadose zone contamination on the water table is more difficult to estimate, and transport of contaminants across the water table includes a mass transfer resistance. Thus, when vapor-phase transport is significant, these issues should be considered in terms of computing contaminant flux to the ground water and the resultant ground water contaminant concentrations.

This article examines approaches for evaluating persistent vadose zone contamination in terms of its impact on the ground water under conditions where vapor-phase movement is the dominant transport process in the vadose zone. The VFLUX (DiGiulio et al. 1999; DiGiulio and Varadhan 2001; EPA 2001) and VLEACH (Varadhan and Johnson 1997) one-dimensional approaches for estimating vadose zone contaminant transport are considered and compared to a new flux-continuity-based assessment of contaminant movement from the vadose zone to the ground water. The key difference between the VFLUX/VLEACH approaches and the flux-continuity-based assessment is that the former impose a lower boundary condition to represent the water table whereas the latter includes interaction between the vadose zone and the ground water across the water table. This water table interaction is shown to be important in estimating the flux of vapor-phase contamination from the vadose zone to the ground water. Limitations of these approaches are discussed with respect to the required assumptions and the need to incorporate three-dimensional processes when evaluating vapor-phase transport from the vadose zone to the ground water. The carbon tetrachloride (CT) plume at the U.S. Department of Energy (DOE) Hanford Site is used as the example site where persistent vadose zone contamination needs to be considered in the context of ground water remediation.

Case Study Site

At the U.S. DOE Hanford Site, CT previously disposed at the surface resulted in CT distributed within an approximately 100-m-thick vadose zone and the underlying ground water (DOE 2007). Figure 1 shows a simplified

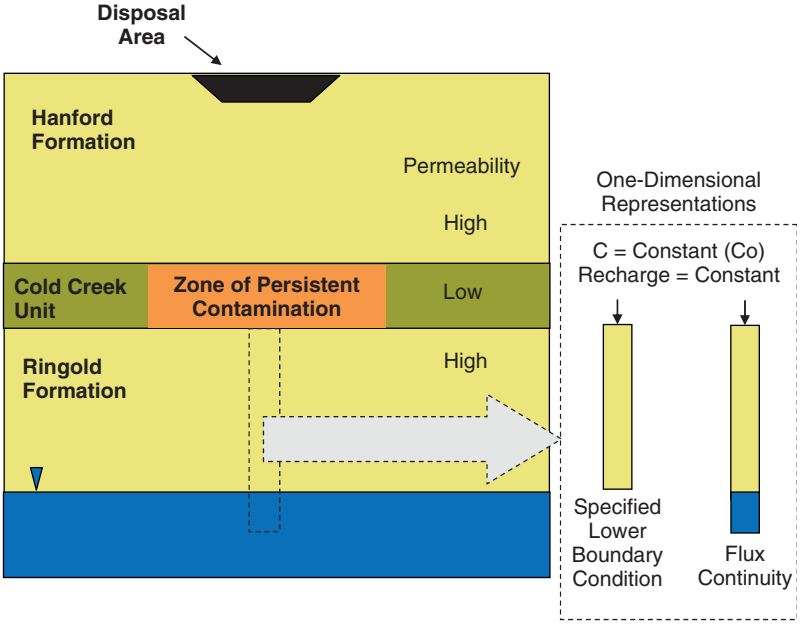

Figure 1. Conceptual depiction of the primary hydrogeologic units in the Hanford subsurface beneath former CT disposal sites. The figure also shows the relation of a one-dimensional vadose zone analysis to the site conceptual cross section using either a specified lower boundary condition or flux continuity at the water table.

cross section of the vadose zone beneath a CT disposal area at Hanford. SVE has been applied in the permeable Hanford and Ringold Formations. Likely zones of persistent CT contamination include the high silt content Cold Creek Unit (CCU) and smaller silt lenses within the dominant sand and gravel matrices of the Hanford and Ringold Formations. The extent of the CCU is much greater than the silt lenses within the Hanford and Ringold Formations. Therefore, the configuration of the case study example considers the CCU to be the only persistent vadose zone contamination source.

SVE has been applied as an interim remedial action in the vadose zone since 1992 (Rohay 2007). The current contaminant distribution in the vadose zone has been significantly affected through application of the SVE interim response action. The extracted vapor contaminant concentration data showed a dramatic decrease in concentrations within the first 2 years of operations. Subsequent periodic operation of the SVE system shows an initial short-lived rebound in concentrations followed by a resumption of low extracted vapor concentrations. These data suggest that SVE has been effective in the highly transmissive Hanford and Ringold Formations and that residual contamination in the CCU or potentially small silt lenses will be the primary contaminant source in the vadose zone over the long term. Numerical simulations also suggest that the water added to the vadose zone during waste disposal operations has substantially drained such that moisture conditions have reverted to near the initial conditions except for the high-silt portions of the vadose zone (Oostrom et al. 2007; White et al. 2008). Thus, future water movement in the vadose zone will be predominantly controlled by the natural recharge conditions. Numerical simulations have used an estimate of 0.5 cm/year for the recharge rate (Oostrom et al. 2007).

Methods

System Configuration and Parameter Determination

The evaluation of analysis methods in this article is specific to evaluating the impact of persistent vadose zone contamination on the ground water. The analyses assume that SVE has removed contamination from the transmissive zones of the vadose zone, the water flux to the ground water is controlled by the natural recharge rate, any immiscible liquid (or nonaqueous phase liquid, NAPL) phase is immobile, and the persistent contamination zone has a constant vapor concentration and corresponding equilibrium dissolved phase concentration in the pore water within the contaminated zone. If we further consider the condition where the persistent contamination in the vadose zone is present for a long duration compared to the transport time from the contaminated zone to the water table, then we can use a steady-state analysis as a bounding case for the impact of the vadose zone contamination on the ground water. The suitability of steady-state analysis would need to be considered based on the conceptual model for the specific site. For CT in the vadose zone at the Hanford case study site, transport is relatively rapid in the vapor phase and the residual mass of CT in the CCU may be quite large. Thus, use of a steady-state analysis may be a reasonable approach to estimate the long-term contaminant mass flux and resultant ground water concentrations beneath the CT disposal areas.

The CCU is the dominant high-silt zone within the vadose zone. If we consider the CCU as the primary persistent contamination zone (e.g., where NAPL may be present and provide a very long-term contamination source) with constant vapor and related equilibrium pore water concentrations, we can ignore the impact of contamination in small silt lenses within the Hanford and Ringold Formations and ignore transport within the Hanford Formation with respect to impacts on the ground water. Under these conditions, a one-dimensional vadose zone analysis of the persistent contamination can be configured as shown in Figure 1. The top boundary condition for solute transport is a specified concentration based on the conditions in the CCU and the input water flux is based on the natural recharge rate. The bottom or water table boundary condition needs to be specified on the basis of the analysis technique. The analysis could be extended to two or three dimensions for a numerical simulation analysis with further assumptions about the boundary conditions and the real extent of the CCU persistent contamination zone.

The examples used for documenting the VLEACH (Varadhan and Johnson 1997) and VFLUX (DiGiulio et al. 1999; DiGiulio and Varadhan 2001; EPA 2001) analysis approaches are focused on sites where an initial soil concentration profile is imposed and the transient flux caused by this profile on the ground water is calculated. For sites with persistent contamination zones, such as the CCU for the Hanford case study site (Figure 1), estimating the mass distribution needed for the initial conditions in a transient analysis may be difficult. However, measurements of vapor concentrations may provide suitable input for the boundary conditions in a steady-state analysis. For such sites, a steady-state approximation for the analysis may be more appropriate using the contaminant concentration in the zone as a boundary condition. The steady-state analysis does not compute behavior based on an imposed initial condition and the associated contaminant mass in the system but is driven by the boundary conditions. Such an analysis also provides a bounding case to examine long-term contaminant flux to the ground water. Over time, the mass of contaminant will decline resulting in a lower flux to ground water than that estimated using the steady-state analysis. If the ground water flux and resultant ground water contamination estimated using the steady-state analysis is acceptable, the condition will only improve over time and a decision maker can use the steady-state analysis to justify transition or closure of the vadose zone remedy.

The one-dimensional VFLUX and VLEACH models and a new flux-continuity-based assessment of contaminant movement from the vadose zone to the ground water are discussed subsequently with respect to evaluating the long-term contaminant mass flux to the ground water and the resultant ground water concentrations for a specified vadose zone contaminant distribution. The flux-continuity approach results are then discussed in comparison to results of numerical simulations using the STOMP code (White

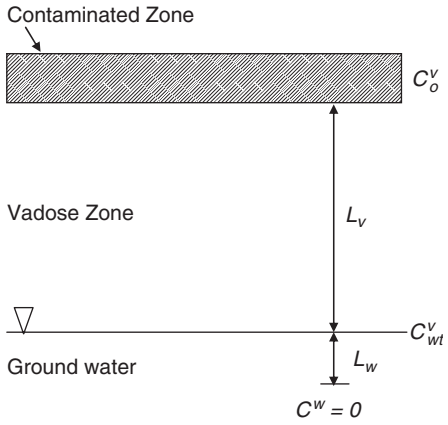

Figure 2. Configuration for the example mass flux analysis.

and Oostrom 2006). Based on the contamination scenario presented in Figure 1, the configuration for mass flux determination is defined by the scenario depicted in Figure 2.

For the example mass flux analysis in this article, the following assumptions and conditions were imposed. The analysis is for steady-state, one-dimensional, gaseous diffusive transport in the vadose zone with no sorption or reaction. The contaminated zone is considered to be a persistent contaminant source such that it maintains a constant, C_o^v, vapor concentration at a fixed distance, Lv, from the water table. The concentration C_{wt}^v shown in Figure 2 is the vapor concentration in the vadose zone at the water table. Other parameters from the case study site that must be specified for the analysis and the values used for the example calculations are shown in Table 1. An aqueous recharge rate of zero was used in the example to focus on vapor-phase transport comparisons. The impact of nonzero recharge is discussed later.

The values in Table 1 are specified on the basis of the contaminant and site properties and analysis configuration. The value of D_{as} in the unsaturated zone is calculated from the values of D_a, n, and θ_w based on Millington and Quirk (1961) using

$$D_{as} = D_a \frac{\left[n - \theta_w\right]^{\frac{10}{3}}}{n^2} \tag{1}$$

The value of D_{ws} in the saturated zone is calculated from the values of D_w and n using

$$D_{ws} = D_w \; n^{4/3} \tag{2}$$

Table 1
Example Analysis Input Parameters

Parameter	Symbol	Value	Unit
Vapor concentration of persistent contamination at upper boundary of the analysis	C_o^v	1[1]	mg/L
Distance from vadose zone source to water table	L_v	30.5	m
Aqueous recharge rate	q_r	0	cm/year
Gas diffusion coefficient of CT in air	D_a	0.715	m^2/d
Gas diffusion coefficient of CT in sediment	D_{as}	0.118	m^2/d
Water diffusion coefficient of CT in water (flux continuity only)	D_w	8.25e–5	m^2/d
Water diffusion coefficient of CT in sediment (flux continuity only)	D_{ws}	1.64e–5	m^2/d
Dimensionless Henry's law coefficient for CT	H	0.813	—
Darcy velocity of ground water (flux continuity only)	q	0.03, 0.3, 3	m/d
Porosity	n	0.3	—
Volumetric moisture content	θ_w	0.0175	—
Bulk density (VFLUX and VLEACH only)	ρ_b	1.75	kg/L
Vapor concentration in the vadose zone at the water table (specified for VFLUX and VLEACH only)	C_{wt}^v	0	mg/L
Fraction of organic carbon (VFLUX and VLEACH only)	f_{oc}	0.001	—
Linear partitioning coefficient for sorption (VFLUX and VLEACH only)	K_d	0	mL/g
Solubility of CT in water (VFLUX and VLEACH only)	—	800	mg/L
Simulation time (VLEACH only)	—	200	years
Time step (VLEACH only)	—	1	year
Cell size (VLEACH only)	—	1	feet
Number of cells (VLEACH only)	—	100	—

[1]Approximately 145 ppmv.

Summary of VLEACH and VFLUX Approaches

The VLEACH model (Varadhan and Johnson 1997) is a one-dimensional, finite difference numerical simulation technique for estimating contaminant profiles in the vadose zone over time and the mass flux of contaminant to the ground water. The initial conditions include the contaminant concentration as a function of location (e.g., z coordinate), an upper vadose zone specified–concentration boundary condition, and lower ground water specified–concentration boundary condition.

The VFLUX model (DiGiulio et al. 1999; DiGiulio and Varadhan 2001; EPA 2001) is a one-dimensional analytical solution technique for estimating contaminant profiles in the vadose zone over time and the mass flux of contaminant to the ground water. The initial conditions include the contaminant concentration as a function of location (e.g., z coordinate), an upper vadose zone specified–concentration (time variant) boundary condition, and a lower ground water boundary condition with either a specified-concentration (time variant) or a specified-gradient of dC/dz = 0.

Results and Discussion

Boundary Condition Assessment of VFLUX and VLEACH under Steady-State Conditions

For a one-dimensional analysis of vadose zone transport, there are several options for establishing the boundary conditions. The VLEACH and VFLUX analyses can use a specified concentration boundary condition at the water table. VFLUX can also use a specified zero-gradient boundary condition. These boundary conditions have limitations for evaluating the interaction of vadose zone contamination with the ground water because they do not consider the coupled nature of transport in the vadose zone and the ground water. To demonstrate the importance of considering these coupled transport processes, a flux-continuity-based assessment of contaminant movement from the vadose zone to the ground water is presented after the discussion of the specified concentration and specified zero-flux boundary conditions.

Specified-Concentration Boundary Condition

With a specified-concentration boundary condition, the lower boundary concentration (C^v_{wt}) is fixed. Under these conditions, the steady-state contaminant mass flux to the ground water computed by VFLUX or VLEACH would be J = D_{as}(dC/dz) for a one-dimensional solution with no degradation and assuming that vapor diffusion dominates transport. For the example purposes, aqueous recharge is set to zero. Aqueous recharge is discussed in more detail later. The maximum contaminant mass flux to the ground water is bounded by the condition when the lower boundary concentration (C^v_{wt}) is set to zero. This condition assumes instantaneous mixing and removal of contaminant from the entry point in the ground water. For the example where the top boundary is the only source of contaminant (e.g., the initial concentration elsewhere in the vadose zone is zero), the calculated contaminant flux to the ground water using J = D_{as}(dC/dz), a diffusion distance of L_v, and the C^v_o, C^v_{wt}, and D_{as} values presented in Table 1, is 0.00387 g/(d–m^2) with the lower boundary condition set to zero. The VLEACH model simulation result using the input parameters listed in Table 1 was 0.00382 g/(dm^2), consistent with the simple linear calculation above. The resultant downgradient ground water concentration could be calculated on the basis of the estimated contaminant mass flux and a mixing volume approach for a specified mixing volume. The value of the lower boundary condition can also be set to greater than zero if a long-term ground water source is present. Under this scenario, the component of the resultant downgradient ground water concentration could also be calculated on the basis of the estimated contaminant mass flux and a mixing volume approach for a specified mixing volume.

Imposing a specified concentration at the lower boundary can bound the steady-state analysis for determining flux to the ground water; however, determining an appropriate value for this concentration may be difficult. Consider a contaminant that is not very water soluble but is volatile, that is, a compound with a high Henry's law coefficient. One would expect vapors to diffuse down to the ground water, but that the ground water concentration would remain relatively low. Using a specified lower boundary concentration of zero as a maximum flux condition may not be realistic because this condition would assume that the ground water is highly efficient at removing contamination from the water table interface and ignores the partitioning relationship at the water table. VFLUX and VLEACH do not explicitly model the water table partitioning process. Imposing a specified-concentration lower boundary condition larger than zero is feasible, but should also consider the partitioning behavior at the water table in terms of estimating the concentration that is the driving force for the diffusive flux in the vadose zone. Setting the lower boundary condition based on the current or expected ground water concentration can provide a means to incorporate known and expected ground water conditions, but constrains the analysis by imposing a ground water concentration rather than having the vadose zone contaminant flux and partitioning at the water table determine the ground water concentration.

Specified Zero Gradient Boundary Condition

A specified zero-gradient lower boundary condition can also be imposed for VFLUX (DiGiulio and Varadhan 2001). At steady state, this solution converges to a ground water concentration in direct equilibrium with the imposed steady-state vadose zone concentration. This result for a persistent vadose zone contaminant sources has limited applicability and is only appropriate for static ground water that can come to equilibrium with the vadose zone within the time frame of the persistent vadose zone source.

Flux-Continuity-Based Assessment

The flux-continuity-based assessment uses one-dimensional (downward) transport in the vadose zone coupled to lateral ground water movement. The assessment considers vertical, but not lateral, concentration gradients in the ground water. The approach uses a control volume

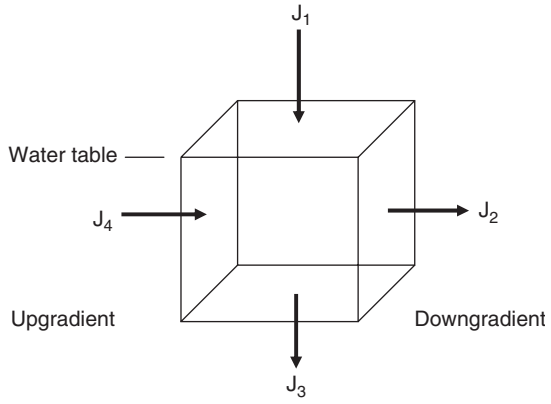

Figure 3. Control volume for flux continuity at the water table where J_1 is the mass flux from the vadose zone to the ground water, J_2 and J_4 are the mass flux in the direction of ground water flow for the downgradient and upgradient locations, respectively, and J_3 is the downward mass flux in the ground water at the bottom of the control volume.

assessment at the water table to link the flux from the vadose zone to the flux in the ground water. Consider the control volume shown in Figure 3 where J_n is the mass flux in each of the directions shown. The approach considers J_1 to be the flux from the entire vadose zone source. This control volume considers ground water flow from left to right and that the flux into and out of the page perpendicular to ground water flow is zero.

If the upgradient water is clean, then J_4 is zero. With finite vertical movement of contaminant in the ground water, J_3 is zero at the depth, L_w, where the concentration in the ground water is zero. Under these conditions and for flux continuity at steady-state, J_1 equals J_2. Using a steady-state diffusion transport solution in the vadose zone, neglecting dispersion in the ground water, and considering a constant ground water Darcy velocity, q, Equation 3 defines the flux continuity for J_1 and J_2.

$$J_1 = D_{as}\frac{\left(C_o^v - C_{wt}^v\right)}{L_v} = qC_2^w = J_2 \tag{3}$$

In Equation 3, C_2^w is the average concentration of contaminant in the ground water at the right side of the control volume, averaged over the full unit depth. Assuming L_w is less than unit depth, specified here as U (m), and using a linear approximation for the concentration profile, concentration C_2^w can be described in relation to C_{wt}^v with Equation 4.

$$C_2^w = \frac{C_{wt}^v \; L_w}{2HU} \tag{4}$$

In this equation, a simple average, division by 2, is applied due to the assumption of a linear concentration profile between the water table concentration and a concentration of zero at depth, L_w. The Henry's law coefficient, H, is used to convert the vadose zone concentration to a concentration in the ground water at the water table with the assumption of equilibrium conditions at the water table.

Flux continuity can also be defined within the ground water considering the balance of downward diffusive flux ($J_{1,gw}$) and the advective flux as shown in Equation 5 using Equation 2 to define J_2 in terms of C_{wt}^v.

$$J_{1,gw} = D_{ws}\frac{\left(\frac{C_{wt}^v}{H} - 0\right)}{L_w} = \frac{q \; C_{wt}^v \; L_w}{2HU} = J_2 \tag{5}$$

With ground water flow, L_w increases along the flow path as depicted in Figure 4. In Equation 5, the flux-continuity analysis uses a single value for L_w as an approximation. Equation 6 can be derived from Equation 5 to define L_w as a function of the known diffusion coefficient in water-saturated sediment, D_{ws}, and the specified ground water Darcy velocity, q.

$$L_w = \left(\frac{2UD_{ws}}{q}\right)^{0.5} \tag{6}$$

Combining Equations 3, 4, and 6, solving for C_{wt}^v, and simplifying yields Equation 7.

$$C_{wt}^v = \frac{C_o^v}{\left[1 + \frac{L_v}{HUD_{as}}\left(\frac{qUD_{ws}}{2}\right)^{0.5}\right]} \tag{7}$$

Once C_{wt}^v has been calculated, the vadose zone flux, J_1, can be calculated from the left hand portion of Equation 3. The average concentration over unit depth in the ground water, C_2^w, can be calculated from Equation 4.

Calculation results for the example using the flux-continuity-based assessment are presented in Table 2. As expected, the mass flux across the water table, J_1, increases and the concentration at the downgradient edge of the unit volume, C_2^w, decreases with increasing Darcy velocity

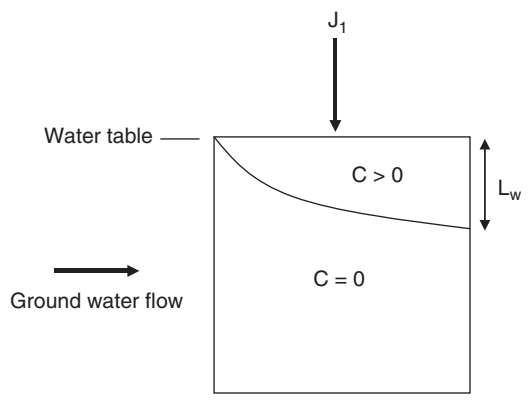

Figure 4. Conceptual depiction of how L_w changes in the direction of ground water flow. J_1 is the contaminant mass flux from the vadose zone (see Figure 3) and C is the concentration of contaminant in the ground water. This figure is based on the assumption that the upgradient ground water is clean.

Table 2
Calculation Results for the Example Using the Flux-Continuity Approach as a Function of Specified Ground Water Darcy Velocity (q). The Mass Flux 3w Computed Using the STOMP Simulator And VLEACH Are Presented for Comparison. Input Parameters Are Defined in Table 1.

	Flux-Continuity Approach				STOMP Simulation		VLEACH
q (Specified) (m/d)	C^v_{wt} (g/m³) Equation 7	L_w (cm) Equation 6	C^w_2 (ppb) Equation 4	J_1 [g/(d-m²)] Equation 3	C^v_{wt} (g/m³)	J_1 [g/(d-m²)]	J_1 [g/(d-m²)]
0.03	0.863	3.32	17.6	5.0E–04	0.881	4.2E–04	3.8E–03
0.3	0.665	1.05	4.3	1.3E–03	0.508	1.7E–03	3.8E–03
3	0.386	0.33	0.8	2.4E–03	0.240	2.7E–03	3.8E–03

(Table 2). Note that the magnitude of the mass flux, J_1, is lower than the mass flux calculated by VFLUX or VLEACH with the lower boundary set to zero even for the relatively high ground water Darcy velocity of 3 m/d because the flux-continuity approach computes a ground water concentration greater than zero. As the Darcy velocity approaches infinity, C^v_{wt} approaches zero in Equation 7 and the flux-continuity approach converges to provide the same result as for the VFLUX/VLEACH linear diffusion analysis with a lower boundary concentration of zero. Using a flux-continuity approach demonstrates that the ability of the ground water to move the contaminant away from the water table controls the vapor-phase mass flux from the vadose zone across the water table. The mass flux calculated from VFLUX and VLEACH simulations is dependent on the lower boundary condition, which is input by the user rather than being calculated as a function of ground water conditions. A VFLUX and VLEACH lower boundary condition of zero represents a condition that can only be obtained at very high ground water specific flux values where the ground water is able to maintain near zero concentrations at the water table.

Numerical Simulation Assessment of the Flux-Continuity Approach

The water–air operational mode of the STOMP simulator (White and Oostrom 2006) was used to compute mass flux and concentrations profiles for Darcy velocities of 0.03, 0.3, and 3 m/d using a configuration that mimicked the one-dimensional vadose zone transport configuration that was used for the flux-continuity-based assessment. The numerical configuration parameters of the model were selected for comparison to the simplified cases presented above and do not include sorption, density-driven advection, or barometric pressure effects that could be included in a numerical simulation. The model domain is 31.5 m high and 1 m wide. The water table is located at 30.5 m from the upper boundary. The imposed Van Genuchten (1980) saturation–pressure relationship parameters (α of 1000 m and pore geometry factor of 5) were such that the transition zone from fully saturated to irreducible water saturation conditions was less than 1 cm. Solute transport was simulated using a total-variation diminishing scheme. Longitudinal dispersivity, α_L, was 1.0E–3 m and transverse dispersivity, α_T, was 1.0E–4 m. The x-direction was uniformly discretized into 100 nodes. The z-direction was also discretized into 100 nodes, but additional refinement was applied in the unsaturated and saturated areas near the water table, while a coarser discretization was used in the vadose zone. Simulations use no-flow aqueous and gas boundary conditions on the vertical boundaries in the vadose zone to enable comparison to the one-dimensional assessments. A constant gas concentration of 1 mg/L (Table 1) was imposed at the top and a third-type outflow boundary condition was used at the east side of the saturated zone.

The computed values for the vapor concentration at the water table in the vadose zone, C^v_{wt}, and the contaminant flux across the water table, J_1, are shown in Table 2 and are comparable to the approximations from the flux-continuity-based assessment. Figure 5 shows the simulated concentration profiles in the ground water for the three specified ground water Darcy velocity values. These figures also show the value of L_w from the flux-continuity-based assessment for comparison. In contrast to the constant L_w approximation from the flux-continuity-based assessment, the simulation results show the expected progression of the concentration profile along the ground water flow direction. Some differences between the L_w approximation and the numerical result are expected because the L_w approximation does not specifically account for ground water flow processes.

Because the vadose zone and ground water transport processes are coupled, the mass flux across the water table and the ground water concentration profile will vary along the flow path. Considering the pseudo one-dimensional configuration example where the vadose zone source is constant across the imposed cross-sectional width of the numerical modeling domain, the mass flux across the water table decreases along the ground water flow path. In the example with a Darcy velocity of 0.3 m/d, the mass flux simulated for the most upgradient 10 cm of the numerical model cross section (left-hand side of Figure 5b) is 2.90×10^{-4} g/d-m² (~16% of total flux), compared to 1.21×10^{-4} g/d-m² (~6% of total flux) for the most downgradient 10 cm of the numerical model cross section (right-hand side of Figure 5b).

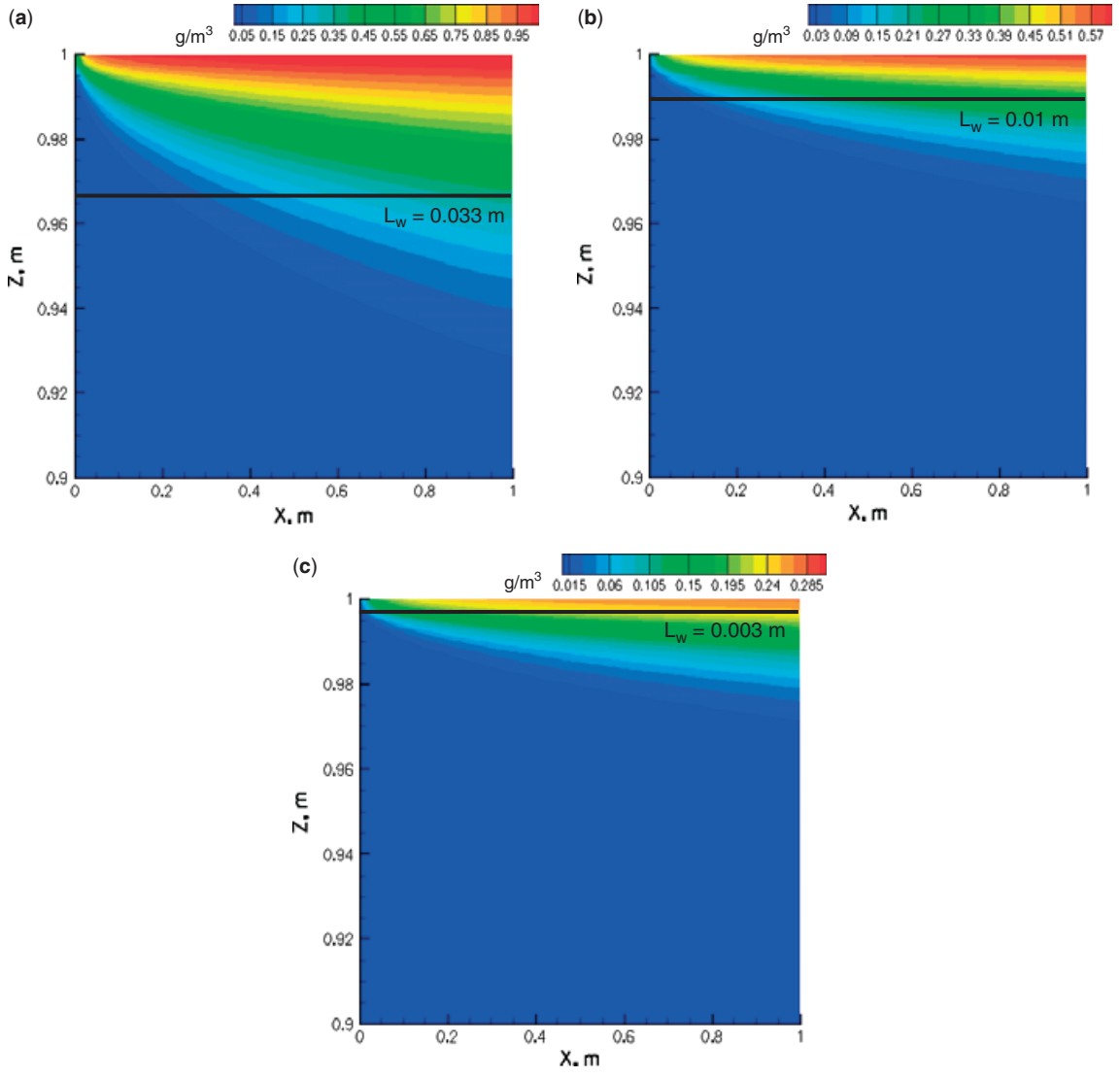

Figure 5. Numerical simulation results showing the contaminant concentration in ground water for ground water Darcy flux values of 0.03 (a), 0.3 (b), and 3 (c) m/d. The values of L_w from the flux-continuity-based assessment are shown for comparison.

In the subsurface, lateral vapor movement causes a decrease in vapor concentrations away from the footprint of the vadose zone source zone and mass flux to the ground water at these distal locations also decreases. In some cases, the relative vadose zone/ground water concentrations at locations away from the source zone footprint may induce mass flux from the ground water to the vadose zone. Thus, depending on the scale of the site and distance of the vadose zone source from the ground water, an estimate for the impact of a persistent vadose zone contaminant source may need to consider the ground water flow rate and dimensions of the source area and compute a total mass flux and associated ground water contaminant concentration profile.

Limitations of the Flux-Continuity Approach

Several phenomena that can affect contaminant transport in the vadose zone are not included in this assessment. First, the flux-continuity-based assessment assumes only diffusive transport of vapors in the vadose zone. At steady state, the vapor and aqueous contaminant concentrations are at equilibrium and the aqueous-phase flux across the water table, J_r, for a constant recharge rate can be estimated from Equation 8.

$$J_r = \frac{q_r \; C^v_{wt}}{H} \tag{8}$$

Table 3 shows the aqueous-phase flux computed as a function of C^v_{wt} and the recharge rate. This type of analysis can be used to determine the relative magnitude of the aqueous- and vapor-phase fluxes based on the site conditions. For the example with a recharge rate of 0.5 cm/year, vapor flux is significantly greater than the aqueous flux. However, at higher recharge rates, the impact of vertical water flow on concentration gradients may need to be considered when applying the flux-continuity approach.

Additionally, sorption and reaction processes are not included in the flux-continuity approach. Neglecting sorption in the analysis for steady-state conditions with a persistent contaminant source is reasonable because the system is at an equilibrium condition. Sorption would need to be

Table 3
Aqueous-Phase Mass Flux across the Water Table as a Function of C^v_{wt} and Recharge Rate

q (Specified) (m/d)	C^v_{wt} (g/m^3)	q_r (cm/year)	J_r [g/(d-m^2)]	J_1 [g/(d-m^2)] Equation 3
0.03	0.863	0.5	1.45E–05	5E–04
0.03	0.863	5	1.45E–04	5E–04
0.03	0.863	50	1.45E–03	5E–04
0.3	0.665	0.5	1.12E–05	1.3E–03
0.3	0.665	5	1.12E–04	1.3E–03
0.3	0.665	50	1.12E–03	1.3E–03
3	0.386	0.5	6.50E–06	2.4E–03
3	0.386	5	6.50E–05	2.4E–03
3	0.386	50	6.50E–04	2.4E–03

Values for J_1 are from Table 2.

included in the analysis as part of a transient analysis, and both VFLUX and VLEACH allow consideration of this process. Reaction processes may need to be considered for some contaminants and under some site conditions. In many cases for chlorinated solvents, reaction processes in the vadose zone may be very slow compared to the rate of vapor phase transport, and neglecting the reaction processes would be a suitable assumption.

Use of a steady-state analysis with coupled mass transfer processes at the water table provides a useful perspective for evaluating the impact of a persistent vadose zone contaminant source. The flux-continuity approach is useful for demonstrating the coupled transport processes that need to be considered. However, the coupled transport processes are by nature multidimensional. At a minimum, except under static conditions, the downward flux in the vadose zone must be coupled to a lateral and vertical flux in the ground water. The ground water transport processes including advection, dispersion, diffusion, sorption, and reaction (if appropriate) impact the vertically downward concentration gradient from the water table and, thereby, can affect the mass flux into the ground water from the vadose zone. Flux continuity across the water table is maintained under these conditions so that changes in the flux of contaminants away from the water table in the ground water will affect the flux of contaminant to the ground water in the vadose zone.

Advective vapor transport may also be important to include in the assessment. At some sites under natural conditions, pressure gradients induced by barometric pressure variation may need to be considered and, if important, would require a transient approach for inclusion in a mass flux analysis. For chlorinated solvents, vapor density at high contaminant concentrations can be significantly greater than air and lead to density-driven flow, which would alter the vapor concentration profile in the vadose zone and, thereby, alter the mass flux to ground water. Advective gradients further accentuate the dependence of vapor concentrations on three-dimensional flow in the vadose zone and the need to use numerical methods to estimate the flux to the ground water. A three-dimensional analysis would enable estimating a total mass flow from the vadose zone to the ground water over the footprint of the vapor plume and accounting for the vapor concentration gradients in the vadose zone.

As noted previously, the steady-state approach provides no analysis of the temporal dynamics of the mass flux. If estimated mass fluxes are such that vadose zone clean-up objectives are not met, information regarding the time frame over which this condition would be expected to persist is of obvious use to site managers. One approach for characterizing temporal dynamics of mass flux is to use advanced numerical modeling. Another approach is to analyze historical SVE operations data. For example, one such analysis is based on extrapolation of temporal extraction-concentration profiles (i.e., elution tails). Such information can be used to estimate the time scale over which mass flux may persist from the zone influenced by the SVE system. This information can in turn be used to constrain the steady state analysis of mass flux.

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