

A GROUNDWATER MASS FLUX MODEL FOR GROUNDWATER-TO-INDOOR-AIR VAPOR INTRUSION

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ABSTRACT: A groundwater mass flux screening-level model has been developed to evaluate potential indoor air exposures associated with contaminant volatilization from affected groundwater underlying occupied structures. Prior screening-level models have characterized potential groundwater-to-indoor-air exposures based on contaminant volatilization from an assumed infinite contaminant source mass within the groundwater that is in equilibrium with the overlying soil vapor. For these models, steady-state mass transfer into the overlying building is controlled by the rate of vapor diffusion and advection through the unsaturated soil zone and the building foundation. However, for many sites, this prior method of analysis can provide overly conservative groundwater screening levels that are inconsistent with mass balance considerations. Specifically, the assumed mass transfer into the building air space can greatly exceed the maximum groundwater to soil-vapor release that could occur during migration of the affected groundwater plume beneath the building. As an alternative conceptual model, the groundwater mass flux approach presented in this paper calculates an upperbound contaminant mass transfer into the overlying structure as a function of the vertical contaminant mass flux within the affected groundwater flowing beneath the building. This model assumes no impedance of vapor transport by the unsaturated soil zone or the building foundation. For a given groundwater flow condition and building configuration, this conservative mass flux relationship can be used to back-calculate a screening limit concentration for groundwater that is protective of a specified indoor air exposure level.

INTRODUCTION

The potential for human exposure via volatilization of groundwater contaminants into indoor air has been a focus of increasing concern in recent years. At a small number of sites, elevated indoor vapor concentrations have been measured within buildings overlying shallow groundwater contaminated with chlorinated solvents, causing public concern over the potential for similar problems at other corrective action sites (Obmascik, 2002). In addition, use of the screening-level model developed by the USEPA for the groundwater-to-indoor-air exposure pathway has suggested that low microgram per liter (ug/L)-range concentrations of either chlorinated or non-chlorinated volatile organic compounds dissolved in groundwater could result in indoor vapor concentrations in excess of applicable risk-based exposure limits (U.S. EPA, 2000). This screening model is based on the Johnson and Ettinger (1991) unsaturated zone transport model and is modified for a dissolved groundwater source by assuming Henry's Law equilibrium between groundwater and soil gas, and is commonly referred to as the J&E spreadsheet model. To address the concerns with this exposure pathway, the USEPA has recently proposed groundwater screening levels for the groundwater-to-indoor-air exposure pathway as part of the "Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air

Pathway from Groundwater and Soils”, issued in November 2002. Under the proposed Vapor Intrusion (VI) Guidance, dissolved benzene concentrations in groundwater in excess of 5 ug/L are considered to pose possible unsafe indoor air exposures. Under this proposed benzene screening level, nearly all facilities where gasoline releases have occurred to groundwater would be identified as an indoor air exposure concern, representing a significant population of remediation sites. However, actual measurements of vapor profiles at affected groundwater sites show that the potential for indoor air impacts associated with volatilization from groundwater is quite limited, particularly for petroleum hydrocarbons such as benzene (Roggemans et al., 2001). These findings underscore the need for a simple, yet reliable, screening tool to identify those sites where groundwater conditions do not pose a potential concern with regard to indoor vapor exposures.

Unlike the USEPA VI Guidance screening levels or the J&E spreadsheet model, this groundwater mass flux approach considers the mass balance between the groundwater and vapor phases. Implicit in both the VI Guidance screening levels and J&E spreadsheet model is the assumption that the affected groundwater zone will act as a infinite source of contaminant mass release, producing an equilibrium soil gas concentration at the water table equal to the product of the contaminant concentration in groundwater times the Henry’s Law constant for that chemical. However, in many cases, the effective mass transfer associated with this assumed equilibrium water-vapor relationship can exceed the maximum theoretical volatile release that could occur from the affected groundwater plume as it passes beneath the building. Field measurements of groundwater and soil gas concentrations indicate that soil gas concentrations of volatile chemicals are typically a small fraction of that predicted by Henry’s Law (Fitzpatrick and Fitzgerald, 1996). In reality, the total mass flux from the groundwater to the vapor phase cannot exceed the total mass loss occurring from the affected groundwater plume due to vertical diffusion to the top of the groundwater table during the time required for the plume to travel beneath the length of the building. Ignoring this groundwater mass flux limitation can result in significant over-prediction of potential indoor vapor exposures, as well as calculation of groundwater screening levels that are significantly lower than necessary to prevent unsafe indoor air exposures. As an alternative screening tool, this paper presents a groundwater mass flux model which can be used to back-calculate a conservative groundwater screening limit based upon an allowable indoor air exposure concentration. The mass flux model is intended to serve as a highly conservative screening tool that over-predicts groundwater-to-indoor-air mass flux, yet still provides sufficient sensitivity to identify some sites for which the groundwater-to-indoor-air exposure pathway is not a concern.

DERIVATION OF MASS FLUX MODEL

Conceptual Model. The conceptual model for evaluation of the groundwater-to-indoor-air exposure pathway based on consideration of groundwater mass flux is illustrated in Figure 1. Under this approach, as groundwater passes beneath the building, the contaminant mass migrates to the vapor phase of the overlying soil zone via diffusion and subsequently moves upward into an overlying structure. During the time period of plume migration beneath the building, the vertical mass flux from the groundwater plume to the

unsaturated soil zone is assumed to be limited by only vertical diffusion and dispersion of contaminants through the groundwater-bearing unit. The groundwater seepage velocity influences the vertical mass flux by establishing the residence time for the plume under the building. The model assumes that vertical mass flux through groundwater under the building is the sole factor limiting the transport of volatile chemical from groundwater to indoor air. Because the unsaturated soil zone is assumed to provide no impedance to vapor migration from groundwater to indoor air, the groundwater-to-soil-gas mass flux (F_{sg}) is equal to the soil-to-indoor-air mass flux (F_{ia1}), and the unsaturated soil attenuation factor is conservatively assumed to be 1. A steady-state indoor air concentration is then determined assuming complete mixing of the influent vapor flux with the clean air exchange within the building. Affected vapors entering the building are assumed to mix with indoor air in the same manner as idealized in the J&E spreadsheet model (i.e., mixing and dilution with the standard outdoor air exchange occurring within the building).

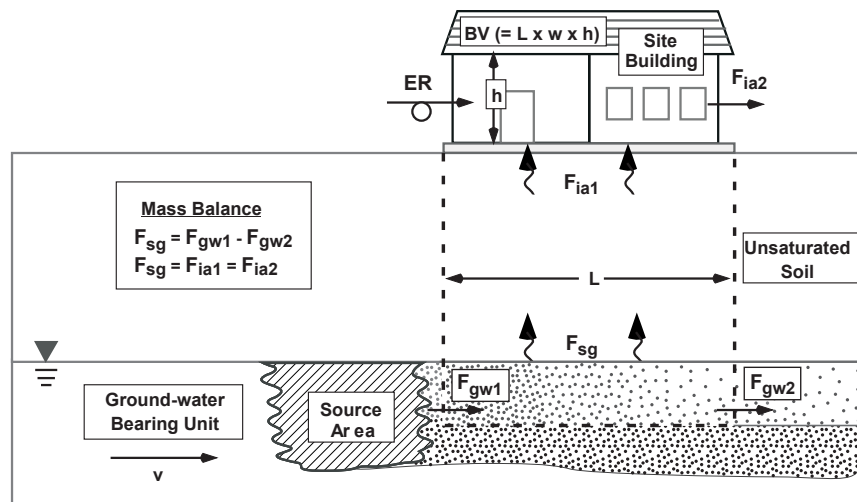


FIGURE 1. Conceptual model for groundwater-to-indoor-air mass flux analysis.
 F_{gw1} = mass flux through groundwater at upgradient edge of building, F_{gw2} = mass flux through groundwater at downgradient edge of building, F_{sg} = mass flux from groundwater to soil gas under building, F_{ia1} = mass flux from soil gas to building, F_{ia2} = mass flux from building to outdoor air.

Model Development. During transport of an affected groundwater plume beneath an overlying building, the mass flux occurring from groundwater to soil vapor via volatilization can be determined using Fick's Second Law:

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial z^2} \quad (1)$$

where C is the concentration of chemical in groundwater, t is time, D_a is the apparent diffusion coefficient, and z is the vertical distance below the top of the groundwater-bearing unit. Analytical solutions to Fick's Second Law are available for a variety of boundary conditions (Crank, 1975). Under steady-state conditions, volatile chemical concentration in groundwater can be expressed as a function of distance downgradient

from the upgradient edge of the building by using the substitution $t=x/v$ where x is the downgradient distance from the upgradient edge of the building and v is the groundwater seepage velocity, yielding:

$$\frac{\partial C}{\partial x} = \frac{D_a}{v} \frac{\partial^2 C}{\partial z^2} \quad (2)$$

For the conservative scenario where the affected groundwater source is located directly upgradient of the structure and the groundwater plume extends deep into the groundwater-bearing unit, the groundwater-to-soil-vapor mass flux model is solved with the boundary conditions shown in Figure 2, where C_{gw} is the groundwater concentration at the upgradient edge of the building. In other words, we assume that: (1) the chemical concentration in the groundwater at the upgradient edge of the building is constant with depth; (2) the chemical concentration in groundwater at the top of the groundwater-bearing unit is zero; and (3) the groundwater plume has sufficient vertical thickness so that mass flux to the soil vapor is not limited by depletion of the plume mass at the base of the plume. In reality, the chemical concentration at the top of the groundwater-bearing unit is some value greater than zero, however, the assumption of zero concentration serves to provide a conservative (over)estimation of mass flux by maximizing the vertical diffusion gradient.

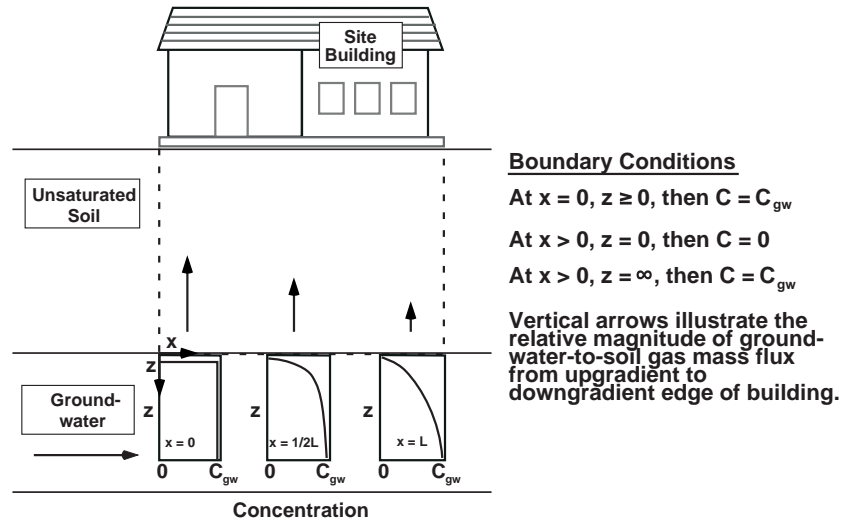


FIGURE 2. Illustration of boundary conditions used for groundwater-to-soil-gas mass flux. x = lateral distance downgradient from upgradient edge of building, z = vertical distance below top of water-bearing unit, C = constituent concentration in groundwater, C_{gw} = constituent concentration in groundwater at the upgradient edge of the building, L = length of the building in the direction of groundwater flow.

For these boundary conditions, a general solution for the groundwater concentration as a function of x and z is:

$$\frac{C_{x,z}}{C_{gw}} = 1 - \operatorname{erf} \left[\frac{z}{2\sqrt{(D_a/\nu)x}} \right] \quad (3)$$

In this expression, contaminant retardation in the groundwater-bearing unit, associated with mass sorption to the saturated soil matrix, need not be addressed, as sorbed mass is not included in the groundwater concentration measurement C_{gw} and does not migrate either vertically or laterally in the groundwater.

The boundary conditions provided above also yield the following relationship for steady-state contaminant mass flux from the groundwater to the soil vapor phase within the overlying unsaturated soil zone beneath the building:

$$F_{sg} = 2 C_{gw} n L w \sqrt{\frac{D_a}{\pi t_r}} \quad (4)$$

where L is building length parallel to groundwater flow; w is the width of the building perpendicular to groundwater flow; n is the porosity of the saturated soil; t_r is the residence time of the groundwater under the building (equal to L/ν); and the other terms are as previously defined. Equation 4 provides the average mass flux under the length of the building. The mass flux is highest at the upgradient edge of the building and decreases downgradient (see Figure 2).

The apparent vertical diffusion coefficient in groundwater can be estimated accounting for both vertical diffusion and vertical dispersion in groundwater as:

$$D_a = (\alpha_z \nu) + (n^{1/3} D_m) \quad (5)$$

where α_z is the vertical dispersivity in groundwater, D_m is the molecular diffusion coefficient in groundwater for the volatile chemical, and $n^{1/3}$ is an estimate of tortuosity in the saturated aquifer (Millington and Quirk, 1961).

As a conservative and simplifying measure, we can assume that the mass flux into the building is equal to the mass flux from groundwater to the soil vapor phase. This assumption neglects mass loss in the unsaturated soil zone and vapor transport around, rather than into the overlying building, resulting in an overprediction of mass flux into the building. Based on this assumption, the indoor air concentration (C_{ia}) can be calculated based on the mixing and dilution of influent soil vapor flux (F_{sg}) with the standard exchange of clean outdoor air within the building as follows:

$$C_{ia} = \frac{F_{sg}}{Q_{building}} \quad (6)$$

where $Q_{building}$ is the building ventilation rate in volume/time (commonly expressed as $BV \times ER$, where BV is the indoor air volume and ER is the building air exchange rate with units of time^{-1}).

Calculating Upperbound Indoor Air Concentration for a Given Groundwater Concentration. Substituting Equation 4 into Equation 6 and substituting L/v for t_r yields:

$$C_{ia} = \frac{2C_{gw}nw\sqrt{\frac{D_aLv}{\pi}}}{BVER} \quad (7)$$

which predicts an upperbound indoor air concentration (C_{ia}) based on the dissolved contaminant concentration in the underlying groundwater (C_{gw}), applicable building factors (L , w , BV , ER), groundwater parameters (v , α_z , and n), and the molecular diffusivity of the dissolved chemical in the groundwater (D_m).

Calculating Groundwater Screening Limit Protective of a Given Indoor Air Concentration. As an alternative use of the mass flux relationship, risk-based screening levels in groundwater can be calculated by rearranging Equation 7 to yield:

$$C_{gw} = \frac{1}{2} \frac{C_{ia}BVER}{wn\sqrt{\frac{D_aLv}{\pi}}} \quad (8)$$

In this expression, the calculated concentration in groundwater (C_{gw}) is protective for a specified indoor air concentration limit (C_{ia}) for any chemical of concern, based upon the applicable building factors (EV , ER , L , w), groundwater parameters (v , α_z , and n), and the molecular diffusivity of the dissolved chemical in groundwater (D_a).

TABLE 1A. Site-dependent input parameters and values used for calculation of groundwater screening concentrations (from U.S. EPA, 2000).

Parameter	Symbol	Value	Units
Building air exchange rate	ER	10.8	day ⁻¹
Building volume	BV	451	m ³
Building width perpendicular to GW flow	w	9.61	m
Building length parallel to GW flow	L	9.61	m
Porosity of saturated aquifer	n	0.43	dim
Vertical dispersivity of saturated aquifer	α_z	0.000625 x L	m
Groundwater seepage velocity (1)	v	0.01 to 0.1	m/day

Note: (1) Values used to calculate range of groundwater screening limits in Tables 2A and B.

Selection of Model Input Parameters. Model input values for all building parameters (BV , ER , w , and L) are commonly estimated based on typical values for a residential or commercial building; however, they may be measured to evaluate potential impacts to a specific building. Groundwater parameters (n and v) can be measured or can be estimated based on site characteristics such as aquifer soil type. Vertical dispersivity (α_z) is not easily measured on a site-specific basis, but is typically estimated based on flow distance or length in the direction of groundwater flow (i.e., building length for this application). Estimates of vertical dispersivity reported in the literature range from 0 to 1% of building length (U.S. EPA, 1996). Finally, model input values for molecular diffusion (D_m) can

be matched to published properties for the volatile chemical being evaluated. Model input parameters are defined in Tables 1A and 1B.

TABLE 1B. Chemical-dependent input parameters and values used for calculation of groundwater screening concentrations (from U.S. EPA, 2002).

Chemical	Target Indoor Air Limit (C_{ia} , mg/m ³)	Molecular Diff. in Water (D_m , m ² /day)
Benzene	1.30E-03	8.47E-05
MTBE	3.00E+00	8.13E-04
1,1 Dichloroethene	2.00E-04	8.99E-05
Trichloroethene	5.90E-03	7.86E-05
Tetrachloroethene	1.70E-02	7.08E-05

USE OF MASS FLUX MODEL FOR GROUNDWATER SCREENING

Tables 2A and B presents groundwater concentration screening levels that are protective of chronic air exposure limits for various volatile organic compounds, calculated for a range of groundwater seepage velocities and the default building parameters specified in USEPA guidance (U.S. EPA, 2002). To illustrate the significance of the assumed vertical groundwater dispersivity (α_z) to the model results, groundwater concentrations levels are presented for two alternative assumptions: i) no vertical dispersion (i.e., $\alpha_z = 0$), whereby volatilization is controlled by diffusion only, and ii) vertical dispersion estimated per USEPA guidance (Charbeneau, 2000) as $\alpha_z = 0.0625\%$ of the building length, corresponding to volatilization driven by both diffusion and dispersion effects. Consideration of vertical dispersion ($\alpha_z > 0$) increases volatilization and therefore decreases the resulting groundwater screening concentrations. As shown in Table 2A, for the diffusion-only case, groundwater screening concentrations are proportional to $1/v^{1/2}$. With both diffusion and vertical dispersion (Table 2B), the screening concentrations are proportional to $1/v$ at higher groundwater velocities (due to the effects of dispersion) and $1/v^{1/2}$ at lower velocities (when dispersion is negligible). The results of this analysis indicate that the potential for groundwater-to-indoor-air vapor impacts is dependent on groundwater flow velocity, a factor not currently considered in U.S. EPA guidance or common vapor intrusion models.

TABLE 2A. Groundwater screening concentration values for groundwater-to-indoor-air exposures derived from mass flux model: diffusion-only ($\alpha_z = 0$).

Chemical Dissolved in Groundwater	USEPA Target Indoor Air Limit (mg/m ³)	Model-Predicted Groundwater Screening Limits (mg/L) for Various Groundwater Seepage Velocities (m/day)			Proposed USEPA VI Screening Limits (mg/L) ¹	Ratio of GW Limits: Mass Flux Value/ VI Value (range)
		$v=0.1$	$v=0.03$	$v=0.01$		
Benzene	3.1E-04	4.1E-02	7.5E-02	1.3E-01	5.0E-03	8.2 to 26x
MTBE	3.0E+00	1.3E+02	2.4E+02	4.1E+02	1.2E+02	1.1 to 3.4x
1,1-Dichloroethene	2.0E-01	2.6E+01	4.7E+01	8.2E+01	1.9E-01	140 to 430x
Trichloroethene	2.2E-05	3.0E-03	5.6E-03	9.2E-03	5.0E-03	0.6 to 1.8x
Tetrachloroethene	8.1E-04	1.2E-01	2.2E-01	3.7E-01	5.0E-03	24 to 74x

TABLE 2B. Groundwater screening concentration values for groundwater-to-indoor-air exposures derived from mass flux model: diffusion plus dispersion ($\alpha_z = Lx 0.000625 = 0.006m$).

Chemical Dissolved in Groundwater	Target Indoor Air Limit (mg/m ³)	Model-Predicted Groundwater Screening Limits (mg/L) for Groundwater Seepage Velocities (m/day)			Proposed USEPA VI Screening Limits (mg/L) ¹	Ratio of GW Limits: Mass Flux Value/ VI Values (range)
		v=0.1	v=0.03	v=0.01		
Benzene	3.1E-04	1.3E-02	3.9E-02	9.4E-02	5.0E-03	2.6 to 19x
MTBE	3.0E+00	9.2E+01	2.1E+02	3.9E+02	1.2E+02	0.8 to 3.2x
1,1-Dichloroethene	2.0E-01	8.2E+00	2.5E+01	6.0E+1	1.9E-01	43 to 310x
Trichloroethene	2.2E-05	9.1E-04	2.8E-03	6.9E-03	5.0E-03	0.2 to 1.4x
Tetrachloroethene	8.1E-04	3.4E-02	1.0E-01	2.6E-01	5.0E-03	6.8 to 52x

Note: Values are generic screening values from Question 4 of U.S. EPA 2002, higher screening values may be used later in the evaluation process in some cases based on site-specific considerations.

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