Analytical solutions for the transport of volatile organic chemicals in unsaturated layered systems

S. R. Yates, S. K. Papiernik, F. Gao, and J. Gan

U.S. Salinity Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Riverside, California

Abstract. Several analytical solutions were developed that describe the transport of volatile organic chemicals or other gases in layered porous media. Solutions are presented for a one-dimensional system consisting of either two finite soil layers or a finite layer adjacent to an infinite soil layer. The proposed solutions may be useful for studying the movement of volatile chemicals or other gases in layered soils, as well as for gas movement from soils into passive flux chambers, which are commonly used for measuring the surface volatilization rate. The behavior of the solutions is illustrated by several examples showing the soil gas concentration and the flux density as a function of time. At early times it was found that the flux density into a chamber is relatively constant when the mass transfer coefficient h is small. However, the concentration at the soil-chamber interface changes rapidly. For large h the flux density at the interface changes rapidly, and the concentration is relatively constant.

1. Introduction

For decades, soil fumigants have played an important role in increasing crop production and quality. However, the increased use of fumigants over large agricultural areas has led to air pollution problems, has been shown to contaminate ground water, and can cause adverse health effects in people living near treated fields. Gas-phase transport and volatilization have been shown to be important processes affecting the environmental fate of volatile organic chemicals (VOC) [*Jury et al.*, 1983; *Taylor and Spencer*, 1990]. For many VOCs, such as methyl bromide, 1,3-dichloropropene (1,3-D), methyl isothiocyanate, and methyl iodide, volatilization is one of the most important processes governing movement during agricultural use [*Majewski et al.*, 1995; *van den Berg et al.*, 1992, 1993; *Jin and Jury*, 1996; *Gan et al.*, 1996], accounting for up to 70% of the applied mass [*Yates et al.*, 1996b]. Gas-phase transport is also very important in characterizing the production of climate-affecting gases such as CO_2, NO, and N_2O [*Suarez*, 1999; *Healy et al.*, 1996; *Jury et al.*, 1991].

There is currently a great deal of interest in increasing knowledge of the transport of agricultural fumigants under field conditions. This is due primarily to the anticipated phase-out of methyl bromide which will undoubtably cause an increased use of alternative chemicals, many of which are likely to cause further environmental contamination. Research is needed to determine the amount of chemical that enters the atmosphere or is transported to ground water and to develop methods that minimize contamination. The limited research, to date, directed at minimizing VOC emissions can be attributed to two factors. First, volatilization is not strictly regulated by environmental agencies. Second, because of the dynamic nature of the soil-atmosphere environment and the involvement of the gas, liquid, and solid phases, field studies for measuring volatilization are very complicated, expensive, and labor intensive. Continuous and extensive air sampling is essential for generating representative concentration profiles in the near-surface atmosphere which can be used to estimate the volatilization rate. Also, simultaneous measurements of many soil and/or ambient atmospheric conditions are required for calculating volatilization flux using methods such as the aerodynamic method, the theoretical profile shape, and integrated horizontal flux method [*Denmead et al.*, 1977; *Wilson et al.*, 1982; *Majewski et al.*, 1990; *Yates et al.*, 1996b]. The flux chamber method can be used as an alternative for estimating the surface flux and only requires measurement of fumigant concentration inside the chamber [*Hollingsworth*, 1980; *Clendening et al.*, 1990]. Direct and accurate measurement of flux through experimentation is essential when estimating the production of climate-affecting gases or for the testing of simulation models prior to their use in simulating VOC emissions [*Baker et al.*, 1996; *Wang et al.*, 1997].

The purpose of this paper is to report on the development of analytical solutions to the gas diffusion equation for layered soil systems. This research was motivated by a lack of analytical solutions which can be used to determine the effect of altering application methods on pesticide efficacy and total emissions into the atmosphere or transport to ground water. These solutions would provide a first approximation in describing VOC transport within a biologically active zone (e.g., root zone) and, subsequently, through the relatively unreactive porous media below (e.g., the vadose zone). Further, the solutions would be very useful for testing the accuracy of comprehensive numerical simulation models. In addition to layered soil systems the solutions can be used to study the performance of passive chambers used to measure the flux density from soil and may lead to new and more accurate approaches that utilize chambers to measure the surface emission rate.

2. Theory

The solutions are intended to describe the transport of a soil fumigant or other VOC in a one-dimensional system comprising two layers. This could be diffusion in a layered soil system or from soil into an enclosed passive chamber resting on top of the soil surface, with the chamber representing one of the

layers. It is further assumed that the water content of the soil is fairly low, so that water movement over relatively short time periods can be neglected, and that the diffusion coefficients for each layer and the mass transfer coefficient for a resistive barrier at the interface, if any, are spatially and temporally constant.

Two equations are necessary to describe vapor diffusion in a layered system [Bear, 1972] and must be coupled at the interface boundary. For the upper and lower layers, diffusion can be described by

$$R_a \frac{\partial C_a}{\partial t} = D_a^0 \frac{\partial^2 C_a}{\partial z^2} - \mu_a^0 C_a, \tag{1}$$

$$R_s \frac{\partial C_s}{\partial t} = D_s^0 \frac{\partial^2 C_s}{\partial z^2} - \mu_s^0 C_s, \tag{2}$$

respectively, where $C_i(z, t)$ is the gas-phase concentration $[M\, L^{-3}]$ in layer i ($i = a, s$), D_a^0 is a combined liquid and gas-phase diffusion coefficient in each layer $[L^2\, t^{-1}]$, $R_i = (\theta_i + \rho_{b,i} K_{d,i})/K_h + \varepsilon_i$ is the gas-phase retardation coefficient [Jury et al., 1983] for the ith layer, θ_i is the water content $[L^3\, L^{-3}]$, $\rho_{b,i}$ is the bulk density $[M\, L^{-3}]$, ε_i is the air content $[L^3\, L^{-3}]$, $K_{d,i}$ is the adsorption coefficient $[L^3\, M^{-1}]$, K_h is the dimensionless Henry's law constant, and μ_i^0 is a first-order degradation coefficient $[t^{-1}]$ defined as $\mu_i^0 = [(\mu_{\text{liq},i}\theta_i + \mu_{\text{sorb},i}\rho_{b,i}K_{d,i})/K_h + \mu_{\text{gas},i}\varepsilon_i]$, where $\mu_{\text{liq},i}$, $\mu_{\text{sorb},i}$, and $\mu_{\text{gas},i}$ are the first-order degradation coefficients in the liquid, sorbed, and gas phases, respectively, for the ith layer. Henceforth it is assumed that "a" layer is a chamber resting on the soil surface, and the soil layer will be denoted by "s." The effective diffusion coefficient can be estimated using the Millington-Quirk tortuosity model [Jury et al., 1983] where

$$D_a = D_a^0/R_a = \frac{\varepsilon_a^{10/3}}{\eta_a^2} \frac{D_g^{\text{air}}}{R_a} + \frac{\theta_a^{10/3}}{\eta_a^2} \frac{D_l^{\text{water}}}{R_a K_h}, \tag{3}$$

where η_a is the porosity $[L^3\, L^{-3}]$. Since the diffusion coefficients are assumed to be constant, other methods for characterizing the soil tortuosity [Jin and Jury, 1995; Freijer, 1994] can be used in place of (3). Clearly, D_a is equivalent to the free-air diffusion coefficient if the chamber only has an air phase, since $\theta = 0$, $\varepsilon = \eta = 1$, and $R_a = 1$.

The solution to (1) and (2) is obtained by utilizing the Laplace transform method [Wylie and Barrett, 1982; Haberman, 1983], where $\overline{C_i}$ is the concentration in Laplace space and s is the complex Laplace transform variable. In the Laplace space the governing equations are

$$D_a \frac{d^2 \overline{C_a}(z, s)}{dz^2} - (s + \mu_a)\overline{C_a}(z, s) + C_a(z, 0) = 0, \tag{4}$$

$$D_s \frac{d^2 \overline{C_s}(z, s)}{dz^2} - (s + \mu_s)\overline{C_s}(z, s) + C_s(z, 0) = 0, \tag{5}$$

where $C_a(z, 0)$ and $C_s(z, 0)$ are functions describing the initial concentration of the pesticide gas in the chamber and soil, respectively, and $\mu_i = \mu_i^0/R_i$.

A general solution in the Laplace domain for a chamber with height F and positioned on top of a soil column of length d can be obtained by solving (4) and (5):

$$\overline{C_a}(z, s) = A_1 \cosh\left[\frac{\sqrt{s + \mu_a}}{\sqrt{D_a}}(F + z)\right]$$

$$+ B_1 \sinh\left[\frac{\sqrt{s + \mu_a}}{\sqrt{D_a}}(F + z)\right] + \overline{C}_{a,\text{part}}(z, 0), \tag{6}$$

$$\overline{C_s}(z, s) = A_2 \cosh\left[\frac{\sqrt{s + \mu_s}}{\sqrt{D_s}}(z - d)\right]$$

$$+ B_2 \sinh\left[\frac{\sqrt{s + \mu_s}}{\sqrt{D_s}}(z - d)\right] + \overline{C}_{s,\text{part}}(z, 0), \tag{7}$$

where $\overline{C}_{i,\text{part}}(z, 0)$ is the particular solution in the Laplace domain when $C_i(z, 0) \neq 0$. The motivation for this solution is transport in laboratory columns. A general solution for a semi-infinite soil domain with an arbitrary initial chemical distribution is [Haberman, 1983]

$$\overline{C_s}(z, s) = A_2 \exp\left[\frac{\sqrt{s + \mu_s}}{\sqrt{D_s}} z\right] + B_2 \exp -\left[\frac{\sqrt{s + \mu_s}}{\sqrt{D_s}} z\right]$$

$$+ \frac{1}{\sqrt{s + \mu_s}\sqrt{D_s}} \int_0^z f(u) \sinh\left[\frac{\sqrt{s + \mu_s}}{\sqrt{D_s}}(z - u)\right] du, \tag{8}$$

where in this case, $f(z) = C_s(z, 0)$ is a function describing the initial concentration of the volatile organic chemical of interest.

2.1. Boundary Conditions at the Interface

Two equations are needed to characterize transport across the boundary between the layers. To ensure that the mass of chemical leaving the lower layer (i.e., soil), by passing through the interface, is the same as the mass of fumigant entering the upper layer (i.e., chamber), the gas flux density at the interface must be identical. Therefore

$$D_s^0 \left.\frac{\partial \overline{C}_{s,\text{gas}}}{\partial z}\right|_{z=0} = D_a^0 \left.\frac{\partial \overline{C}_{a,\text{gas}}}{\partial z}\right|_{z=0}. \tag{9}$$

Another condition is needed which describes the behavior of the concentration across the boundary. To describe the presence of an interface resistance such as a surface crust, compaction or the presence of a resistive material such as polyethylene plastic (commonly used to cover fields treated with fumigants) requires the use of a mixed boundary condition

$$-D_s^0 \left.\frac{\partial \overline{C}_s}{\partial z}\right|_{z=0} = -H(\overline{C}_s - \overline{C}_a)|_{z=0} = -hR_s(\overline{C}_s - \overline{C}_a)|_{z=0}, \tag{10}$$

where H is the mass-transfer coefficient $[L\, T^{-1}]$ and $h = H/R_s$ is an effective mass-transfer coefficient. Since the gas flux density across the boundary is equal (i.e., (9)), the left-hand side of (10) could be also written in terms of C_a and would provide identical results. Also, when the mass-transport coefficient becomes large, (i.e., the limit as $h \to \infty$), dividing (10) by h and taking the limit results in an equal-concentration boundary condition (i.e., $C_a(0, t) = C_s(0, t)$). Therefore additional solutions with identical concentrations across the boundary are unnecessary.

2.2. Case 1: Chamber and Soil Have Finite Length

This solution is applicable to soil columns and closed passive chambers provided the VOC concentration in the chamber is initially zero and the concentration in the soil is C_0 everywhere. The initial and boundary conditions in the Laplace domain can be written as

$$\overline{C_a}(z, 0) = 0 \qquad \overline{C_s}(z, 0) = \frac{C_0}{s + \mu_s}. \tag{11}$$

Further, if the VOC cannot exit the top of the chamber or through the bottom of the soil column, the flux density at these locations must be zero. Therefore

$$\left.\frac{\partial \bar{C}_a}{\partial z}\right|_{z=-F} = \left.\frac{\partial \bar{C}_s}{\partial z}\right|_{z=d} = 0. \tag{12}$$

The remaining steps necessary to obtain a solution in terms of real variables are to incorporate (9) through (12) into (6) and (7) to obtain the coefficients A_1, A_2, B_1, and B_2 which is followed by a transformation to the real domain. For this case, B_1 and B_2 in (6) and (7) are set to zero so that the solution will satisfy the zero-gradient boundary conditions at $z = -F$ and $z = d$. The two remaining unknowns are found by applying (9) and (10). This gives

$$A_1 = \frac{C_0 h R_s \operatorname{csch}\left[\dfrac{\sqrt{s + \mu_a}}{\sqrt{D_a}}F\right]}{\sqrt{D_a}(s + \mu_s)\sqrt{s + \mu_a}R_a\bar{\Phi}(s)}, \qquad B_1 = 0, \tag{13}$$

$$A_2 = \frac{-C_0 h \operatorname{csch}\left[\dfrac{\sqrt{s + \mu_s}}{\sqrt{D_s}}d\right]}{\sqrt{D_s}(s + \mu_s)^{3/2}\bar{\Phi}(s)}, \qquad B_2 = 0, \tag{14}$$

where

$$\bar{\Phi}(s) = 1 + \frac{hR_s}{\sqrt{D_a}R_a\sqrt{s + \mu_a}}\coth\left[\frac{\sqrt{s + \mu_a}F}{\sqrt{D_s}}\right]$$

$$+ \frac{h}{\sqrt{D_s}\sqrt{s + \mu_s}}\coth\left[\frac{\sqrt{s + \mu_s}d}{\sqrt{D_s}}\right]. \tag{15}$$

A solution in terms of real variables can be obtained by finding the residues at the poles of $\bar{C}_s(z, s)$ and $\bar{C}_a(z, s)$. Combining (13) and (14) with (6) and (7), respectively, it can be shown that there are no branch points but an infinite number of simple poles which occur at the zeros of the denominators of (13) and (14). Two subcases are considered: (1) $\mu_s = \mu_a = \mu$ = constant, which may or may not be zero, and (2) $\mu_s \neq \mu_a$.

2.3. Case 1a: $\mu_s = \mu_a = \mu$ = Constant

When the degradation coefficients in the air, μ_a, and soil, μ_s, are the same, the solution to (6) and (7) is considerably simplified. When $\mu_s = \mu_a = \mu$, the inverse transform of (6) and (7) can be found using the shifting theorem, that is, $\mathscr{L}^{-1}\{\bar{C}(z, s + \mu)\} = e^{-\mu t}\mathscr{L}^{-1}\{\bar{C}(z, p)\}$. Once the shifting theorem has been applied, the residues at the zeros of the denominator must be obtained, namely, at $p = 0$ and $p = -k_n^2$, where the k_n are the roots of

$$\bar{\Phi}(p)|_{p \to \pm i k_n} = 0, \tag{16}$$

given in (15). In real space the k_n satisfy

$$\zeta_n^\infty = \sqrt{D_a D_s}k_n - \frac{\sqrt{D_s}hR_s}{R_a}\cot\left[\frac{k_n F}{\sqrt{D_a}}\right] - \sqrt{D_a}h\cot\left[\frac{k_n d}{\sqrt{D_s}}\right] = 0. \tag{17}$$

Obtaining the residues and simplifying, the solutions for the chamber and soil concentration as a function of distance and time are

$$\frac{C_a(z, t)e^{\mu t}}{C_0} = \frac{dR_s}{(FR_a + dR_s)}$$

$$- \frac{2hR_s}{D_a R_a}\sum_{n=1}^{\infty}\frac{\cos\left[\beta_n(F + z)\right]e^{-\beta_n^2 D_a t}}{\beta_n\sin\left[\beta_n F\right]\Phi_n}, \tag{18}$$

$$\frac{C_s(z, t)e^{\mu t}}{C_0} = \frac{dR_s}{(FR_a + dR_s)} + \frac{2h}{D_s}\sum_{n=1}^{\infty}\frac{\cos\left[\alpha_n(z - d)\right]e^{-\alpha_n^2 D_s t}}{\alpha_n\sin\left[\alpha_n d\right]\Phi_n}, \tag{19}$$

$$\Phi_n = 1 + \frac{dh}{D_s} + d\alpha_n\cot\left[\alpha_n d\right] - \frac{dhR_s\cot\left[\alpha_n d\right]\cot\left[\beta_n F\right]}{\sqrt{D_a}\sqrt{D_s}R_a}$$

$$+ \frac{FhR_s}{D_a R_a}\csc\left[\beta_n F\right]^2, \tag{20}$$

where $\alpha_n = k_n/\sqrt{D_s}$ and $\beta_n = k_n/\sqrt{D_a}$.

2.4. Case 1b: Degradation With $\mu_s > \mu_a$

When the degradation in the soil differs from that in the chamber, the solution is somewhat more difficult to obtain. This solution is more meaningful for laboratory and field studies with VOCs such as methyl bromide since degradation occurs primarily in the soil and water phases via hydrolysis and methylation [Gan et al., 1994]. These processes would not be significant in the chamber air space since methyl bromide degradation in air is negligible [Castro and Belser, 1981]. Therefore, given that μ_s is approximately constant and that degradation in air is negligible, the condition $\mu_s > \mu_a$ is satisfied.

The solution proceeds as in case 1a, except the shifting theorem is not used. Obtaining the residues at the zeros of the denominator of (6) and (7) requires obtaining a portion of the solution from two regions along the negative real axis, that is, between $-\mu_s < s < -\mu_a$ and from $-\infty < s < -\mu_s$. If the real part of $s > -\mu_a$, there are no zeros and thus no contribution to the solution. Obtaining the residues and simplifying, the solution for the chamber gas concentration as a function of distance and time is

$$\frac{C_a(z, t)}{C_0} = -\frac{2hR_s}{D_a R_a}\sum_{n=1}^{\infty}\frac{\cos\left[\beta_n(F + z)\right]e^{-k_n^2 t}}{\beta_n\sin\left(\beta_n F\right)\Psi_n}$$

$$+ \frac{2hR_s}{D_a R_a}\sum_{l=1}^{m}\frac{\cos\left[\xi_l(F + z)\right]e^{-\lambda_l^2 t}}{\xi_l\sin\left(\xi_l F\right)\phi_l}, \tag{21}$$

and the solution for the concentration in the soil is

$$\frac{C_s(z, t)}{C_0} = \frac{2h}{D_s}\sum_{n=1}^{\infty}\frac{\cos\left[\alpha_n(z - d)\right]e^{-k_n^2 t}}{\alpha_n\sin\left(\alpha_n d\right)\Psi_n}$$

$$+ \frac{2h}{D_s}\sum_{l=1}^{m}\frac{\cosh\left[\nu_l(z - d)\right]e^{-\lambda_l^2 t}}{\nu_l\sinh\left(\nu_l d\right)\phi_l}. \tag{22}$$

The values for k_n are found from

$$\zeta_n^\infty = D_a D_s\alpha_n\beta_n - hD_a\beta_n\cot\left(\alpha_n d\right) - hR_s D_s\alpha_n\cot\left(\beta_n F\right)/R_a$$

$$= 0, \qquad n = 1, \ldots, \infty, \tag{23}$$

with $\alpha_n = \sqrt{(k_n^2 - \mu_s)/D_s}$ and $\beta_n = \sqrt{(k_n^2 - \mu_a)/D_a}$, and the values for λ_l are found by solving

$$\zeta_i^m = D_a D_s \nu_i \xi_i + h D_a \xi_i \coth (\nu_i d) - h D_s R_s \nu_i \cot (\xi_i F)/R_a$$

$$= 0, \qquad i = 1, \ldots, m, \qquad (24)$$

with $\xi_i = \sqrt{(\lambda_i^2 - \mu_a)/D_a}$ and $\nu_i = \sqrt{(\mu_s - \lambda_i^2)/D_s}$, and

$$\Psi_n = \frac{\alpha_n^2 D_s R_s h \cot (\beta_n F)}{D_a^2 R_a \beta_n^3} + \frac{h \cot (\alpha_n d)}{D_s \alpha_n} + \frac{hd}{D_s} \csc (\alpha_n d)^2$$

$$+ \frac{h F D_s R_s \alpha_n^2}{D_a^2 R_a \beta_n^2} \csc (\beta_n F)^2, \qquad (25)$$

$$\Phi_i = \frac{\nu_i^2 D_s R_s h \cot (\xi_i F)}{D_a^2 R_a \xi_i^3} + \frac{h \coth (\nu_i d)}{D_s \nu_i} + \frac{hd}{D_s} \operatorname{csch} (\nu_i d)^2$$

$$+ \frac{h F D_s R_s \nu_i^2}{D_a^2 R_a \xi_i^2} \csc (\xi_i F)^2. \qquad (26)$$

The limiting values for λ_i are μ_s and μ_a, and therefore the value of m depends on their magnitudes. The equation for the zeros, ζ_i^m, has singularities which occur at $\nu_i = 0$ and at values of $\xi_i = n\pi/F$. The singularities result in boundaries between which is contained a single zero. After rearranging, a simple relationship that gives the maximum possible m is

$$m \leq \text{integer} \left[\frac{F}{\pi} \frac{\sqrt{\mu_s - \mu_a}}{\sqrt{D_a}} \right] + 1. \qquad (27)$$

2.5. Case 2: Chamber on Top of a Soil Column of Infinite Length

Many soil fumigants are applied below the soil surface using nozzles located at the rear of shanks using high pressure. The soil fumigant is applied as a line source and moves from the injection point in two dimensions. When many of these nozzles are present or when a planar device such as a noble plow [*Yates et al.*, 1996a] is used to spread the initial pulse horizontally, a one-dimensional analog can be used to simulate the movement of a soil fumigant applied as a delta-function source. If this highly concentrated source is located in the soil at z_0, the initial spatial distribution of the VOC can be written

$$C_s(z, 0) = C_0 \delta(z - z_0) = \left. \frac{C_0 \exp \left[-\mu_s t - \frac{(z - z_0)^2}{4 D_s t} \right]}{2 \sqrt{\pi D_s t}} \right|_{t \to 0}. \qquad (28)$$

The solution in the Laplace domain can be obtained by incorporating the initial and boundary conditions (equations (9), (10), and (28)) into (6) and (8) and setting $A_2 = 0$, since $C_s(z, s)$ must remain finite as $z \to \infty$. For the chamber layer the solution in the Laplace domain is

$$\bar{C}_a(z, s) = \frac{C_0 h R_s \exp \left(-\sqrt{\dfrac{s + \mu_s}{D_s}} z_0 \right)}{\sqrt{D_s} \sqrt{s + \mu_s} R_a \bar{\Phi}(s)}$$

$$\cdot \cosh \left[\sqrt{\frac{s + \mu_a}{D_a}} (F + z) \right], \qquad (29)$$

and the solution for the soil is

$$\frac{\bar{C}_s(z, s)}{C_0} = A \exp \left[-\sqrt{\frac{s + \mu_s}{D_s}} (z + z_0) \right]$$

$$+ \frac{\exp \left(-\sqrt{\dfrac{s + \mu_s}{D_s}} |z - z_0| \right) + \exp \left[-\sqrt{\dfrac{s + \mu_s}{D_s}} (z + z_0) \right]}{2 \sqrt{D_s (s + \mu_s)}}, \qquad (30)$$

where

$$A = -\left[\frac{h \sqrt{D_a} \sqrt{s + \mu_a} \sinh (\text{arg}_F)}{D_s (s + \mu_s) \bar{\Phi}(s)} \right], \qquad (31)$$

$$\bar{\Phi}(s) = \frac{h R_s}{R_a} \cosh (\text{arg}_F)$$

$$+ \left[\frac{h \sqrt{D_a} \sqrt{s + \mu_a}}{\sqrt{D_s} \sqrt{s + \mu_s}} + \sqrt{D_a} \sqrt{s + \mu_a} \right] \sinh (\text{arg}_F), \qquad (32)$$

where $\text{arg}_F = F \sqrt{(s + \mu_a)/D_a}$.

2.6. Solution Where $\mu_s \geq \mu_a$

This solution proceeds by integrating along the negative real axis around the branch cut, $-\infty < s < -\mu_s$, and obtaining the residues at one or more simple poles in the region $-\mu_s < s < -\mu_a$. To do this, the image function is integrated along the negative real axis from $-\infty < s < -\mu_s$, where arg $[s] = e^{i\pi}$, is integrated around the branch point at $s = -\mu_s$, and is integrated along the negative real axis from $-\mu_s > s > -\infty$, where the arg $[s] = e^{-i\pi}$. As in case 1, the real part of $s > -\mu_a$ has no zeros and thus no contribution to the solution. A description of this procedure is given by *Carslaw and Jaeger* [1959]. Application of this approach for similar problems is given by *Tang and Babu* [1979] and *Yates* [1990, 1992]. Obtaining the residues and simplifying, the solution for the chamber and soil concentration as a function of distance and time is

$$\frac{C_a(z, t)}{C_0} = -\frac{2 h R_s}{\pi R_a}$$

$$\cdot \int_0^\infty \frac{x \cos [\beta_x(F + z)][Q \cos (\alpha_x z_0) - P \sin (\alpha_x z_0)] \, dx}{e^{x^2 t} (Q^2 + P^2)}$$

$$+ \frac{h R_s}{R_a} e^{-\mu_a t} \sum_{i=1}^m \frac{\exp (-D_a \beta_i^2 t - \alpha_i z_0) \cos [\beta_i (z + F)]}{[\gamma_1 \cos (\beta_i F) + \gamma_2 \sin (\beta_i F)]}, \qquad (33)$$

respectively, and the solution for the soil is

$$\frac{C_s(z, t)}{C_0}$$

$$= \frac{\exp \left[-\dfrac{(z - z_0)^2}{4 D_s t} - \mu_s t \right] + \exp \left[-\dfrac{(z + z_0)^2}{4 D_s t} - \mu_s t \right]}{2 \sqrt{\pi D_s t}} + \frac{2 h D_a}{\pi D_s}$$

$$\cdot \int_0^\infty \frac{\beta_x \sin (\beta_x F)\{P \cos [\alpha_x(z + z_0)] + Q \sin [\alpha_x(z + z_0)]\} x \, dx}{\alpha_x e^{x^2 t} (Q^2 + P^2)}$$

$$+ \frac{h D_a e^{-\mu_a t}}{D_s} \sum_{i=1}^m \frac{\beta_i \exp [-D_a \beta_i^2 t - \alpha_i(z + z_0)] \sin (\beta_i F)}{\alpha_i [\gamma_1 \cos (\beta_i F) + \gamma_2 \sin (\beta_i F)]}, \qquad (34)$$

where

$$P = -D_a h \beta_x \sin (\beta_x F),$$

$$Q = \alpha_x D_s \left[D_a \beta_x \sin (\beta_x F) - \frac{h R_s}{R_a} \cos (\beta_x F) \right]$$

$$\alpha_x = \frac{\sqrt{x^2 - \mu_s}}{\sqrt{D_s}}; \qquad \beta_x = \frac{\sqrt{x^2 - \mu_a}}{\sqrt{D_a}};$$

$$\gamma_1 = \frac{F}{2} [h + \alpha_t D_s],$$

$$\gamma_2 = \frac{1}{2\beta_t} \left[h + \alpha_t D_s + \frac{D_a h \beta_t^2}{D_s \alpha_t^2} + \frac{F h D_s \alpha_t R_s}{D_a R_a} \right]$$

$$\alpha_t = \frac{\sqrt{\mu_s - K_t^2}}{\sqrt{D_s}}, \qquad \beta_t = \frac{\sqrt{K_t^2 - \mu_a}}{\sqrt{D_a}}$$

and the K_t are found by solving

$$\alpha_t D_s h R_s \cos (\beta_t F) - D_a \beta_t R_a [\alpha_t D_s + h] \sin (\beta_t F) = 0. \quad (37)$$

2.7. Case 3: Soil Column of Infinite Length With Initial Square Pulse and $\mu_s \geq \mu_a$

The solution for this case follows the same procedures described in case 2. The initial concentration in the soil is assumed to be zero in the chamber and everywhere in the soil zone except between depths $z_t < z < z_b$, where the concentration is C_0. Therefore

$$C_s(z, 0) = C_0 \{u(z - z_t) - u(z - z_b)\}, \quad (38)$$

where $u(x)$ is a Heaviside step function [Haberman, 1983, p. 297].

Incorporating (38) into (7), the VOC movement in the chamber with $B_1 = 0$, gives

$$\frac{\bar{C}_a(z, s)}{C_0}$$

$$= \frac{\sqrt{D_s} h R_s \left[\exp\left(-\sqrt{\frac{s + \mu_s}{D_s}} z_t \right) - \exp\left(-\sqrt{\frac{s + \mu_s}{D_s}} z_b \right) \right]}{\Phi(s)}$$

$$\cdot \cosh \left[\sqrt{\frac{s + \mu_a}{D_a}} (F + z) \right] \quad (39)$$

for the chamber and

$$\frac{\bar{C}_s(z, s)}{C_0} = B_2 \exp\left(-\sqrt{\frac{s + \mu}{D_s}} z \right)$$

$$+ \frac{\left(\cosh \left[\sqrt{\frac{s + \mu}{D_s}} (z - z_t) \right] - \cosh \left[\sqrt{\frac{s + \mu}{D_s}} (z - z_b) \right] \right)}{(s + \mu)} \quad (40)$$

for the soil, where B_2, is

$$B_2 = \frac{h R_a \sqrt{s + \mu_a} \left[\exp\left(-\sqrt{\frac{s + \mu_s}{D_s}} z_b \right) - \exp\left(-\sqrt{\frac{s + \mu_s}{D_s}} z_t \right) \right]}{\sqrt{s + \mu_s} \Phi(s) \operatorname{csch} \left[\sqrt{\frac{s + \mu_a}{D_a}} F \right]}$$

$$+ \frac{\sinh \left[\sqrt{\frac{s + \mu}{D_s}} z_b \right] - \sinh \left[\sqrt{\frac{s + \mu}{D_s}} z_t \right]}{(s + \mu)} \quad (41)$$

$$\Phi(s) = \sqrt{D_s} h R_s(\mu_s + s) \cosh \left[\sqrt{\frac{s + \mu}{D_a}} F \right]$$

$$+ D_a R_a \sqrt{\mu_a + s} \{ h \sqrt{\mu_s + s}$$

$$+ \sqrt{D_s}(\mu_s + s) \} \sinh \left[\sqrt{\frac{s + \mu}{D_a}} F \right]. \quad (42)$$

Completing the Laplace inversion gives the solution in the chamber as

$$\frac{C_a(z, t)}{C_0} = \frac{-4 h R_s}{\pi}$$

$$\cdot \int_0^\infty \frac{x \cos [\beta_x(F + z)] \{P \cos (\alpha_x w_0) + Q \sin (\alpha_x w_0)\} \, dx}{e^{x^2 t} \alpha_x \csc \left[\frac{\alpha_x}{2} (z_b - z_t) \right] (Q^2 + P^2)}$$

$$+ D_s h R_s e^{-\mu_a t} \sum_{t=1}^m \frac{\alpha_t e^{-D_a \beta_t^2 t} \cos [\beta_t(z + F)](e^{-z_t \alpha_t} - e^{-z_b \alpha_t})}{\gamma_1 \cos (\beta_t F) + \gamma_2 \sin (\beta_t F)},$$

$$(43)$$

where α_t, β_t, and K_t are defined in (36) and (37). In the soil zone the concentration is

$$C_s(z, t) = C_0 \{C_{s,1}(z, t) + C_{s,2}(z, t) + C_{s,3}(z, t)\}, \quad (44)$$

where

$$C_{s,1}(z, t) = \frac{e^{-\mu_s t}}{2} \left[\operatorname{erfc} \left(\frac{z_t - z}{2 \sqrt{D_s t}} \right) + \operatorname{erfc} \left(\frac{z + z_t}{2 \sqrt{D_s t}} \right) \right.$$

$$\left. - \operatorname{erfc} \left(\frac{z_b - z}{2 \sqrt{D_s t}} \right) - \operatorname{erfc} \left(\frac{z + z_b}{2 \sqrt{D_s t}} \right) \right], \quad (45)$$

$$C_{s,2}(z, t) = - \frac{4 h R_a D_a}{\pi D_s}$$

$$\cdot \int_0^\infty \frac{x \beta_x \sin (\beta_x F) \sin [\alpha_x(z_b - z_t)/2][Q \cos (\alpha_x w) - P \sin (\alpha_x w)]}{e^{x^2 t} \alpha_x^2 (Q^2 + P^2)} dx,$$

$$(46)$$

$$C_{s,3}(z, t) = 2 D_a h R_a e^{-\mu_a t}$$

$$\cdot \sum_{t=1}^m \frac{\beta_t e^{-D_a \beta_t^2 t} \sinh [\alpha_t(z_b - z_t)/2][\cosh (\alpha_t w) - \sinh (\alpha_t w)]}{\gamma_1 \cot (\beta_t F) + \gamma_2},$$

$$(47)$$

$$P = D_s \alpha_x [D_a R_a \beta_x \sin (\beta_x F) - h R_s \cos (\beta_x F)],$$

$$Q = D_a h R_a \beta_x \sin (\beta_x F), \quad (48)$$

$$\gamma_1 = \frac{D_s F R_a \alpha_t^2}{2} \left[h + \alpha_t D_s + \frac{D_s h R_s \alpha_t}{D_a F R_a \beta_t^2} \right],$$

$$\gamma_2 = \frac{D_s^2 F h R_s \alpha_t^3}{2 D_a \beta_t} + \frac{D_a h R_a \beta_t}{2}, \quad (49)$$

$$w = \frac{1}{2}(2z + z_b + z_t), \qquad w_0 = \frac{1}{2}(z_b + z_t). \quad (50)$$

2.8. Solution Verification

The solutions described above have been checked using the symbolic mathematics program Mathematica® (Wolfram Research, Inc., Champaign, Illinois). It is not difficult to show that each solution satisfies the differential equation and boundary

Table 1. Soil and Chemical Parameters

Parameter	Example I	Example II	Dimensions
Soil retardation coefficient R_s	2.40	2.40	
Chamber retardation coefficient R_a	1.0	7.70	
Soil dispersion D_s	0.00527	0.00527	$m^2\,d^{-1}$
Chamber dispersion D_a	0.432	0.00105	$m^2\,d^{-1}$
Soil degradation μ_s	0.05	0.05	d^{-1}
Chamber degradation μ_a	0.0	0.05	d^{-1}
Mass transfer coefficient h	0.01	10	$m\,d^{-1}$
Soil column length d	1.0	1.0	m
Chamber height F	0.25	1.0	m

conditions with the exception of the interface boundary condition in (10). For example, substituting (33) and (34) into (10) and simplifying produces, after considerable manipulation, a relationship that does not evaluate directly to zero [*Gradshteyn and Ryzhik*, 1980, equation 3.896.4];

$$-\frac{\exp\left(-\mu t - z_0^2/4D_s t\right)}{\sqrt{D_s t\,\pi}} + \frac{2}{\sqrt{D_s \pi}} \int_0^\infty \cos\left(\frac{x z_0}{\sqrt{D_s}}\right) e^{-x^2 t - \mu t}\,dx$$

$$= 0. \tag{51}$$

However, completing the integral demonstrates that the above relationship is true and that the boundary condition is satisfied. This procedure is also required for the solution in case 3.

3. Examples

To illustrate the behavior of the analytical solutions, several hypothetical examples were prepared. The values used for the soil and chemical parameters are shown in Table 1. The first

example uses the solution for case 1 to describe the behavior of the concentration and flux density for situations where a 25 cm passive chamber is located on the surface of a 1 m thick soil block. The diffusion coefficient in the soil and chamber, 0.00527 and 0.432 $m^2\,d^{-1}$, respectively, are shown in Table 1. Since $\mu_s > \mu_a$, the first step in obtaining the concentrations for this example is to find the roots to (23) and (24). Equation (27) is used to determine the number of roots between $\mu_a < \lambda_t < \mu_s$ and yields a value for the maximum number of roots, $m = 1$, (e.g., $m = $ integer (0.027) + 1). A search in this region is conducted for the zero, $\lambda_1 = 0.184$, using (24). For illustrative purposes the behavior of the function $\zeta_t^m(\lambda)$ is shown in Figure 1a as the solid line. When the value of μ_s is larger, additional zeros may exist in this range. This can be seen in Figure 1b, where μ_s in increased to 100 d^{-1}. For this value of μ_s, two zeros occur at $\lambda_1 = 0.307$ and $\lambda_2 = 8.27$. In most cases an unreasonably large value of μ_s is required to yield more than one zero in this portion of the solution. Next, a search is conducted in the region $K_n > \sqrt{\mu_s}$ using (23). The function $\zeta_n^\infty(\lambda)$ in the region from $\sqrt{\mu_s}$ to 1 is shown as dashed lines in Figure 1a. For the examples provided below, a total of 2000 zeros were used to evaluate the series solution in (21) and (22) which far exceeds the number necessary to provide concentrations accurate to three decimal places for the stated example.

Shown in Figure 2 are the chamber concentrations for a 25 cm tall chamber located at the soil surface (i.e., between $-0.25 < z < 0$ m) along with the concentration in the soil from $0 < z < 1$ m and at times 0.0, 1, 5, 14, 30, and 60 days. It is evident from Figure 2 that for the first 14 days the VOC is moving from the soil into the chamber. By day 30, however, the direction of movement has reversed with the chamber supplying VOC to the soil. This occurs because there is no degradation in the chamber, so when gradients permit, the VOC will diffuse back into the soil zone where it is degraded.
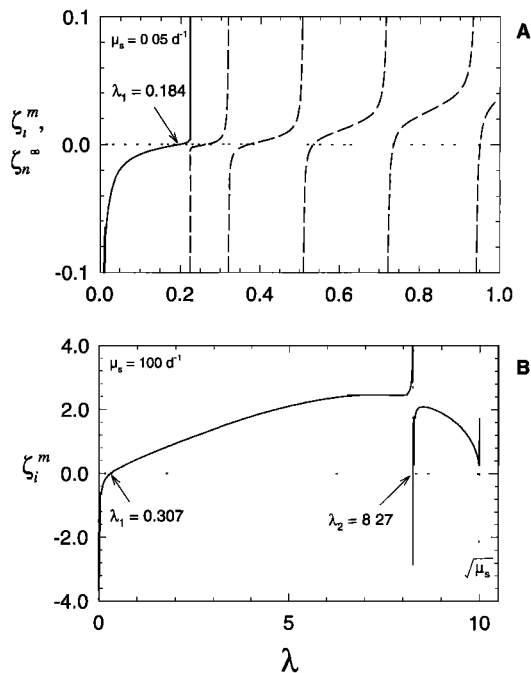

Figure 1. (a) Plots of the function $\zeta_t^m(\lambda)$ and $\zeta_n^\infty(K_n)$ from equation (23) (solid line) and equation (24) (dashed lines). The zeros are required to obtain the concentrations in equations (21) and (22). (b) When μ_s is large, more than one zero may occur for $\zeta_t^m(\lambda)$. For this case, there are two zeros when μ_s is 100 d^{-1}.
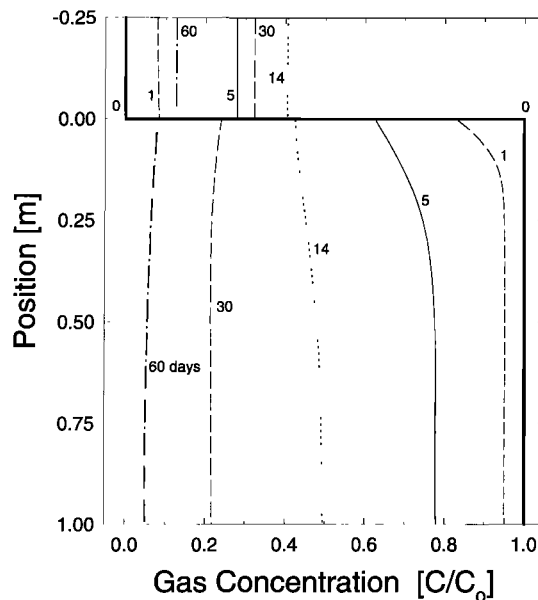

Figure 2. The gas concentration in a finite soil column and a chamber resting on the soil surface. The soil zone extends from $0 < z < 1.0$ m and the chamber from $-0.25 < z < 0$ m. A mixed boundary condition occurs at $z = 0$ with a mass-transfer coefficient of 0.01 m d^{-1}. The numbers on the concentration profiles indicate days.

Also, when the mass transfer coefficient at the chamber-soil boundary is low, the concentration profiles in the soil remain relatively straight compared to the profiles that are produced when an equal-concentration (e.g., $C_a(0, t) = C_s(0, t)$) boundary condition is used (or equivalently, when $h \to \infty$).

Figure 3 shows the early-time flux density (Figures 3a and 3b) and concentration (Figures 3c and 3d) profiles inside a chamber resting on a finite soil column of length 1m and a constant initial concentration of 5000 mg m^{-3} for two values of the mass-transfer coefficient, $h = 0.01$ m d^{-1} (Figures 3a and 3c) and $h = 10$ m d^{-1} (Figures 3b and 3d). The time intervals shown in Figure 3 are 5, 10, 20, 40, and 60 min. The early-time behavior of the flux density into the chamber depends strongly on the mass transfer coefficient. For low values of h a nearly constant flux density occurs during the time period from 5 to 60 min after the chamber is placed on the soil surface and represents less than a 3% change during this time interval. This suggests that a constant flux assumption may be appropriate for describing early-time behavior under these conditions. For large values of h, however, the flux density changes considerably from approximately 6500 mg m^{-2} d^{-1} at 5 min to 1900 mg m^{-2} d^{-1} at 60 min, a 71% change. Also, the flux density profile in the chamber is initially highly curvilinear and becomes much more linear by 60 min.

The concentration profiles within the chamber behave in an opposite manner to the flux density. For small values of h the concentration at the boundary surface changes rapidly with time. For large values of h the concentration at the boundary remains nearly constant, increasing by approximately 5% during the 5 to 60 min time interval. In both cases the concentration profiles have similar shape except that the slopes near the
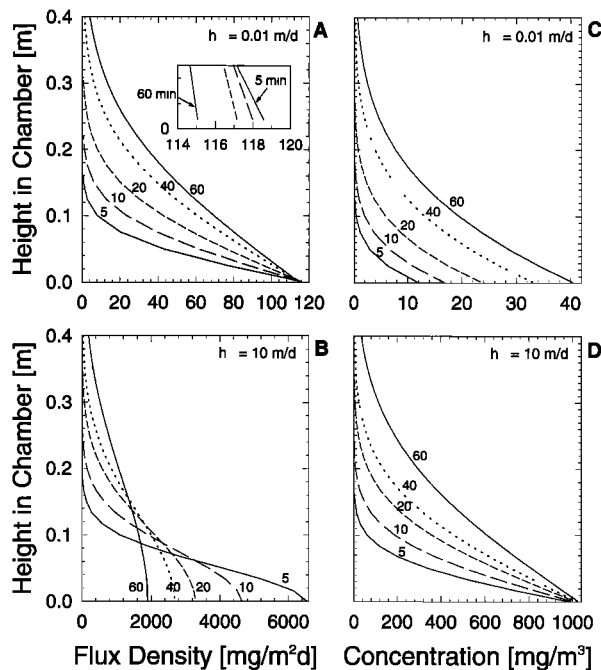

Figure 4. (a) The gas concentration in the soil and chamber when a delta-function pulse is added to the soil at a depth of 0.25 m. Equations (33) and (34) were used to obtain the concentration. (b) The flux density at the interface, where negative values indicate diffusion into the chamber and positive values indicate diffusion into the soil.

boundary are approximately parallel for small h, consistent with the observed nearly constant flux density in Figure 1a.

Figure 4 is an example of the concentration distribution when a delta-function source is located 0.25 m deep in the soil. At early times the concentration curve resembles a Gaussian distribution, and the concentration in the chamber remains zero until the VOC plume has had sufficient time to diffuse to the soil surface. The behavior of the system after the VOC enters the chamber is similar to the constant-concentration case, in that the flux density vectors are directed toward the chamber at early times and toward the soil after about 15 days. This is shown in Figure 4b where a negative flux density indicates movement into the chamber.

An example of a step concentration pulse located between 0.25 and 0.5 m from the soil surface and subsequent diffusion into an overlying soil layer is shown in Figure 5. The soil and chemical properties for this example are different than the prior cases and are listed in Table 1 in example II. For this case a large value for h was used to demonstrate that this produces a equal-concentration boundary condition at the interface. In addition, the large value for the retardation coefficient in the upper layer, R_a, produces a more nonlinear concentration curve in this layer (see inset). This is due to the smaller diffusion coefficient together with a nonzero degradation coefficient. In addition, since the degradation coefficients are equal, the flux density vectors are directed into the upper layer for all times. It can be shown that reversals in the flux density vector only occur for solutions where $\mu_s > \mu_a$.

4. Summary and Conclusions

Analytical solutions were developed to simulate one-dimensional transport of volatile organic chemicals or other

Figure 3. (a and b) The flux density and (c and d) concentration within the chamber shortly after being placed on the soil surface. The mass-transfer coefficient is 0.01 m d^{-1} in Figures 3a and 3c and 10 m d^{-1} in Figures 3b and 3d. The number on each curve indicates the time in minutes. The initial concentration in the soil is assumed to be 5000 mg m^{-3}.
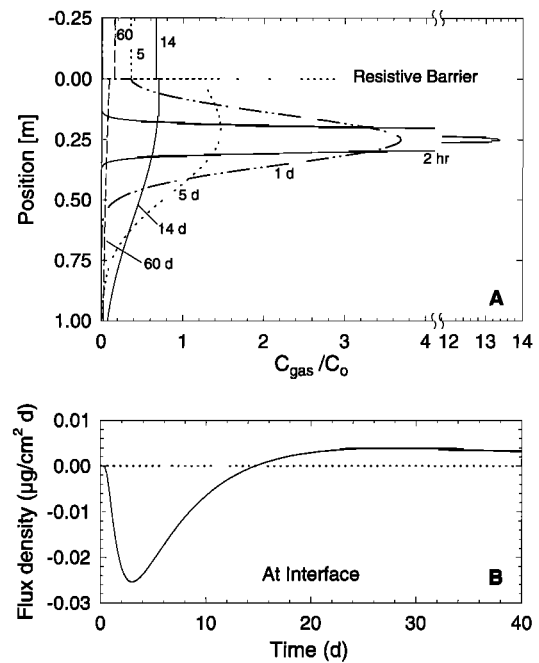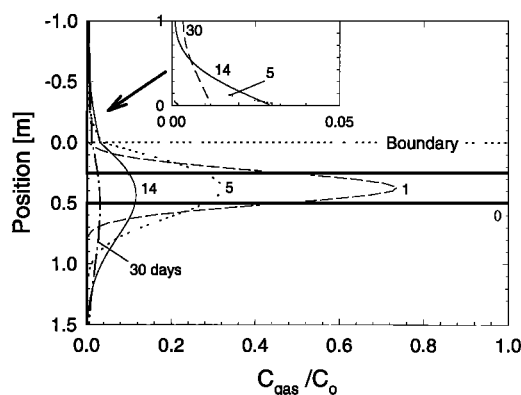
Figure 5. The gas concentration in the soil and an overlying soil layer for a step-pulse initial condition between 0.25 and 0.5 m in the soil. The soil and chemical parameters from example II in Table 1 were used to obtain the concentration from equations (43) and (44).

gases in layered porous media. One solution considers a system consisting of two finite soil layers with a constant initial concentration in one layer. Two additional solutions are developed for situations where a finite layer is adjacent to an infinite soil layer and the initial concentration in the infinite layer is represented by a (1) delta function at position z_0, or (2) a square pulse between depths z_t and z_b. Two partial differential equations are used to describe the gas transport. At the interface boundary an equal flux density and a mass-transfer boundary condition are used to couple the partial differential equations. The solutions were obtained using Fourier series and Laplace transform methods and result in either series or integral equations. A unique feature of the solutions is the need for additional terms when the degradation coefficients in each layer differ.

Several examples are provided that show the soil gas concentration and the flux density as a function of time for gas movement from a soil into passive flux chambers. The analytical solutions provide an efficient method for exploring the early times behavior of the soil gas concentration and flux density into the chamber. This allows a test of the assumptions implicit when estimating the flux density using passive chambers. For example, the flux density into a chamber is relatively constant when the mass transfer coefficient h is small, offering the possibility of using a constant-flux solution for estimating chamber flux under this condition. However, for large h the flux density at the interface changes rapidly, and a constant-flux solution would be inappropriate.

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J. Gan, F. Gao, S. K. Papiernik, and S. R. Yates, U.S. Salinity Laboratory, ARS, USDA, 450 W. Big Springs Road, Riverside, CA 92507-4617. (syates@ussl.ars.usda.gov)