



A nonsteady-state analytical model to predict gaseous emissions of volatile organic compounds from landfills

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Abstract

A general mathematical model is developed to predict emissions of volatile organic compounds (VOCs) from hazardous or sanitary landfills. The model is analytical in nature and includes important mechanisms occurring in unsaturated subsurface landfill environments: biogas flow, leachate flow, diffusion, adsorption, degradation, volatilization, and mass transfer limitations through the top cover. Two initial conditions simulating different environments are examined. The model is able to predict changes in subsurface concentrations and emission fluxes with time. The equations presented here can be extended to three dimensions to model VOC emissions from complex landfill sites.

1. Introduction

Many volatile organic compounds (VOCs) and toxic chemicals have been identified in the air downwind of landfills, even at those sites where only municipal waste is disposed [1, 2]. The chemicals emitted can be odorous, explosive, or even carcinogenic. Quantitative determination in the field of the airborne emission rate is time-consuming and costly. Because of this, air emission models are being increasingly used as an economical tool for predicting emission rates in the absence of field monitoring data [3, 4].

Most of the existing emission models can be termed as screening-level, because they primarily focus on the transport of contaminants through top soil cover under steady-state conditions. Several types of screening-level models proposed to estimate VOC emissions from landfill sites have been reviewed and summarized [5–7]. These models include pioneering work done by Mayer et al. [8], Farmer et al. [9], and Shen [10], which used simple diffusion equations based on either Fick's first or second law. Thibodeaux et al. [11–13] also proposed several emission models, including a

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two-film resistance model, a model modifying Fick's first law to include bulk gas motion, and one utilizing Darcy's law to account for pressure-induced gas flow.

The subsurface environment at landfill sites is heterogeneous, unsaturated, and complex. Yet, these models fail to address many of the complicated mechanisms that contribute to the movement and fate of VOCs within landfills. The assumptions in the screening-level models include, for example, a uniform and infinite contaminant supply, a steady and constant emission rate, and a single gas phase transport route [14]. These assumptions oversimplify the landfill environment and cause the emission rate to be overestimated since, in addition to the gas route, contaminants can also dissolve into leachate and be carried away. Furthermore, laboratory studies have shown that the emission rate is unsteady [15]. One major limitation of the screening-level models is that vapor pressure is required as an input parameter. To estimate the vapor pressure, one must first determine what equilibrium state exists under the soil cover. Typically, an equilibrium state is chosen from a table based on the composition and concentration of the waste material [13]. Depending on the equilibrium state, the equilibrium vapor pressure law (Brauner, Emmett, and Teller (BET), or Raoult's law, etc.) is then applied to estimate the vapor pressure. Despite the difficulty in determining this equilibrium state, these models are widely used. In fact, they are often combined with dispersion models in assessment studies to quantitatively evaluate human exposure to emissions from an area source such as a hazardous waste landfill or surface impoundment [16–18].

Jury et al., in a series of classical papers [19–22], introduced a behavior assessment model for categorizing pesticides into groups depending on their relative susceptibility to different loss pathways. They were interested in the chemical behavior in the liquid phase, so the possible migration of the vapor phase was neglected. The model was also not intended to simulate the liquid transport process, nor to predict the chemical's concentration distribution. Typographical errors in some of the mathematical equations found in Jury's published model make it difficult to use, even though it is more comprehensive than the screening-level models. Nevertheless, it has been used to estimate VOC emissions from landfarming operations [23]. Freeman and Schroy [24, 25] coupled continuity and energy equations to describe the vapor phase transport of low volatility organic chemicals in a soil column. In contrast to Jury's model, Freeman's model neglected liquid phase transport and did not include bulk gas motion. It also required numerical schemes for its solution. There are other numerical models existing for estimating emissions from landfills. Findikakis et al. [26–28] developed a mathematical model to simulate the movement and transport of gas mixtures (CH_4 , CO_2 , N_2) in sanitary landfills. While this model is able to predict gas production and compute vertical pressure profiles, it was not designed to model emissions of volatile organic compounds. A numerical VOC emission model proposed by Seigneur et al. [29] for landfill sites has been incorporated by Nair et al. [30] into a more comprehensive model that can predict contaminant source emissions, both into the atmosphere and via leachate, from the unsaturated zone.

Cernuschi and Giugliano [31] pointed out that due to the large number of mechanistic variables involved, a comprehensive emission model has yet to be proposed which can take into account the physical and chemical characteristics of wastes

and soils, the important mechanisms involved, and also incorporate meteorological influences. This paper applies a methodology similar to Jury's to move towards a more comprehensive analytical model by explicitly quantifying some of the most essential mechanisms affecting emissions from landfills. Significant modifications and extensions to Jury's model are proposed. Our goal is to present a method of modeling emissions of volatile organic compounds in the multiphase landfill environment that: removes the major assumptions in the screening-level models; maintains the mathematical equations in an analytically solvable form to provide a readily-accessible solution; yet still addresses most of the processes simulated in the numerical models.

2. Model development

The model proposed herein is a nonsteady-state analytical model that accounts for the following mechanisms occurring in a landfill: transport of the chemical of interest in the vapor phase as well as in the liquid phase, partitioning among phases (assuming linear equilibrium), degradation of the chemical into other compounds, and mass transfer limitations through the top soil cover.

2.1. Landfill chambers

Landfill sites are conceptualized as a one-dimensional, two-chamber system (Fig. 1): the lower compartment (of depth L) contains contaminants, and the upper compartment of compact cover (with depth d) separates the lower chamber from the atmosphere [13]. The soil in the landfill is assumed to be a homogeneous porous medium with uniform (time and space independent) properties such as the volumetric air content θ_G , volumetric water content θ_L , and bulk density ρ_B . The total porosity ϕ is equal to gas-filled porosity plus liquid-filled porosity:

$$\phi = \theta_G + \theta_L. \quad (1)$$

The loss of contaminants to the atmosphere is assumed to be limited by two layers: (i) the compact cover, which is less permeable than the soil underneath to restrict the infiltration of rainfall into the landfill and reduce the release of gas from the landfill; and (ii) the overlying air–soil boundary layer.

2.2. Phases

Contaminants in the subsurface can be present in a vapor, liquid, solid or adsorbed phase [19, 32]. The movement of a contaminant, other than molecular-scale gaseous and aqueous diffusion, is modeled as a one-dimensional countercurrent flow: gas is moving upward with interstitial velocity v_G , whereas leachate is moving downward with velocity v_L . Sorbed phase contaminants are considered to be immobile. The upward gas flow may result from the buildup of biogas (CO_2 and/or CH_4) generated by the decomposition of organic matter. Degradation is assumed to be first order with rate constants μ_G , μ_L , and μ_S in the gas, liquid, and solid phase, respectively. The

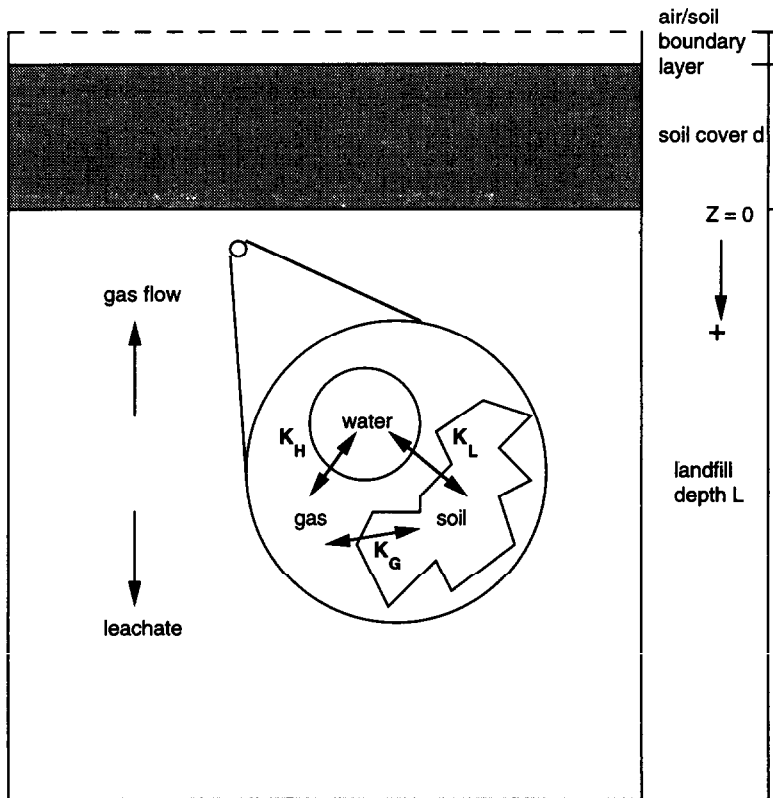


Fig. 1. Conceptualized landfill structure used in model.

continuity equations for each phase can therefore be written as follows (where z is positive downwards, and equals zero at the bottom of the soil cover):

$$\text{vapor phase: } \frac{\partial C_G}{\partial t} - v_G \frac{\partial C_G}{\partial z} = D_G \frac{\partial^2 C_G}{\partial z^2} - \mu_G C_G + \frac{\partial S_G}{\partial t}, \quad (2)$$

$$\text{liquid phase: } \frac{\partial C_L}{\partial t} + v_L \frac{\partial C_L}{\partial z} = D_L \frac{\partial^2 C_L}{\partial z^2} - \mu_L C_L + \frac{\partial S_L}{\partial t}, \quad (3)$$

$$\text{solid phase: } \frac{\partial q}{\partial t} = -\mu_S q + \frac{\partial S_S}{\partial t}. \quad (4)$$

D_G is the soil-gas molecular diffusion coefficient, and D_L is the soil-liquid molecular diffusion coefficient, both accounting for the tortuosity effect of the soil. C_G , C_L , and q are concentrations in the gas, liquid, and solid phases, respectively (with the units for q expressed as mass of contaminant sorbed per mass of dry soil, by convention). $\partial S/\partial t$ represents all the rate terms of interphase mass transfer [30, 33]. For example, $\partial S_G/\partial t$ includes four separate terms, two negative or loss terms for the rates of transfer from

(to) the vapor phase to (from) the liquid and the solid phases, and two positive or source terms for the reverse directions (indicated in the parentheses).

The total chemical concentration per unit volume of soil, C_T , is the sum of each contributing phase:

$$C_T = \theta_G C_G + \theta_L C_L + \rho_B q. \quad (5)$$

2.3. Partitioning

Mass transfer or partitioning occurs between two individual phases, namely liquid–soil, soil–vapor, or vapor–liquid. Partitioning to the soil, known as adsorption, influences the movement and fate of compounds via retardation. Adsorption can be from the gas phase, the liquid phase, or both. The extent of adsorption depends greatly on the moisture content of the soil: volatile compounds adsorb most strongly to soil under conditions where the moisture content is low [34]. Of particular importance here is that this process, while reducing the atmospheric emission rate, will also prolong the emission duration, even beyond closure of a landfill.

For mathematical simplicity, local equilibrium is assumed between phases. At equilibrium, the interphase mass transfers $\partial S/\partial t$ in Eqs. (2)–(4) disappear because the rate of the forward reaction is balanced by the rate of the backward reaction, and therefore the partitioning becomes linear [30]:

$$\text{liquid–soil: } q = K_L C_L, \quad (6)$$

$$\text{soil–vapor: } q = K_G C_G, \quad (7)$$

$$\text{vapor–liquid: } C_G = K_H C_L, \quad (8)$$

where K_L is the liquid–soil adsorption coefficient, K_G is the gas–soil adsorption coefficient, and K_H is Henry's law constant.

In order to reduce the dependent variables, the individual concentration in each phase (C_G , C_L , q) is expressed as a function of total concentration C_T , which has been chosen as the only dependent variable. Using the linear partitioning isotherms from Eqs. (6)–(8) to rewrite (5) in terms of one phase concentration alone leads to the *phase partitioning coefficients* (R_G , R_L , R_S), defined as the ratio of total concentration to the concentration of an individual phase [19]:

$$R_G = \frac{C_T}{C_G} = \theta_G + \frac{\theta_L}{K_H} + \rho_B \frac{K_L}{K_H} = \theta_G + \frac{\theta_L}{K_H} + \rho_B K_G, \quad (9)$$

$$R_L = \frac{C_T}{C_L} = \theta_G K_H + \theta_L + \rho_B K_L = \theta_G K_H + \theta_L + \rho_B K_G K_H, \quad (10)$$

$$R_S = \frac{C_T}{q} = \rho_B + \frac{\theta_L}{K_L} + \frac{\theta_G K_H}{K_L} = \rho_B + \frac{\theta_L}{K_G K_H} + \frac{\theta_G}{K_G}. \quad (11)$$

The local equilibrium assumption means that the system will adjust itself to any perturbation instantly and re-establish a new equilibrium. Therefore, the mass fraction distributed in each phase at any time t remains the same, and can be calculated

from the phase partitioning coefficients. Multiplying (9), (10), and (11) by $1/\theta_G$, $1/\theta_L$, and $1/\rho_B$, respectively, and taking the reciprocal of the results gives:

$$f_G = \frac{\theta_G}{R_G}; \quad f_L = \frac{\theta_L}{R_L}; \quad f_S = \frac{\rho_B}{R_S}, \quad (12)$$

where f_G , f_L , and f_S are mass fractions in the gas, liquid and solid phases, respectively.

2.4. Governing equation

The equilibrium assumption and the phase partitioning coefficients enable us to combine Eqs. (2)–(4), representing the individual phases, into a single equation. Multiplying (2), (3), and (4) by θ_G , θ_L , and ρ_B , respectively, and adding them together, we obtain the following governing equation:

$$\frac{\partial C_T}{\partial t} + V_T \frac{\partial C_T}{\partial z} = D_T \frac{\partial^2 C_T}{\partial z^2} - \mu_T C_T, \quad (13)$$

where

$$V_T = -\frac{\theta_G v_G}{R_G} + \frac{\theta_L v_L}{R_L} = -\frac{v_G^B}{R_G} + \frac{v_L^B}{R_L}, \quad (14)$$

$$D_T = \frac{\theta_G D_G}{R_G} + \frac{\theta_L D_L}{R_L} = \frac{D_G^E}{R_G} + \frac{D_L^E}{R_L}, \quad (15)$$

$$\mu_T = \frac{\mu_G \theta_G}{R_G} + \frac{\mu_L \theta_L}{R_L} + \frac{\mu_S \rho_B}{R_S} = \mu_G f_G + \mu_L f_L + \mu_S f_S. \quad (16)$$

v_G^B and v_L^B are the bulk (apparent) gas and water velocities, D_G^E and D_L^E are the effective gaseous and aqueous diffusion coefficients in soil, and μ_T is the overall first order degradation rate. Note that the governing equation (13) takes the form of a conventional advection–diffusion equation, with the effects of adsorption and other parameters represented via the coefficients V_T and D_T . It holds even for the case where the barometric gradients result in a downward gas velocity (i.e., a negative v_G^B). In addition, if biodegradation is inhibited, such as in the toxic environments found at some hazardous landfill sites [10], v_G^B can be set to zero.

2.5. Flux

The flux of the gas or liquid phase at any cross section at a particular time is the sum of the advective and diffusive fluxes, multiplied by the corresponding void fraction:

$$J_G = \theta_G \left(-v_G C_G - D_G \frac{\partial C_G}{\partial z} \right), \quad (17)$$

$$J_L = \theta_L \left(v_L C_L - D_L \frac{\partial C_L}{\partial z} \right). \quad (18)$$

The overall flux of a contaminant J_T is the combination of these two fluxes. Adding together Eqs. (17) and (18), and substituting (14) and (15) into the result, lead to the overall flux equation, which will be used as the upper boundary condition:

$$J_T = J_G + J_L = V_T C_T - D_T \frac{\partial C_T}{\partial z}. \quad (19)$$

2.6. Boundary conditions

The gas flux through the landfill cover is limited by the presence of cover soil and the adjacent air–soil boundary layer. Thus, two-film resistance theory can be applied:

$$J_T(0, t) = -K_T [C_G(0, t) - C_a], \quad (20)$$

where

$$\frac{1}{K_T} = \frac{1}{D_G^{E_{cover}}/d} + \frac{1}{k}. \quad (21)$$

C_a is the ambient concentration in the atmosphere, $D_G^{E_{cover}}$ is the effective gaseous diffusion coefficient in the cover soil, k is the mass transfer coefficient in the air–soil boundary layer, and K_T is the overall mass transfer coefficient. Eq. (21) represents the overall resistance of chemical movement as the sum of the resistances due to cover soil characteristics and the air–soil interface.

The governing equation (13) requires two boundary conditions. The upper boundary condition is obtained by substituting Eq. (20) into (19), and assuming the background contaminant concentration in the atmosphere is negligible ($C_a = 0$):

$$V_T C_T - D_T \frac{\partial C_T}{\partial z} = -H_T C_T \quad \text{at } z = 0, \quad (22)$$

where

$$H_T = \frac{K_T}{R_G}, \quad (23)$$

The lower boundary condition assumes that the concentration drops to zero as z approaches infinity:

$$C_T(z, t) = 0 \quad \text{at } z = \infty. \quad (24)$$

This boundary condition is appropriate for the case where the water table is significantly below the contamination zone. Other types of boundary conditions can be assumed if deemed more appropriate than Eqs. (22) and (24).

2.7. Initial conditions

Two initial conditions will be explored. The first one simulates the environment where the chemical of interest is initially distributed from $z = 0$ to some depth L_D

(where $L_D \leq L$, the depth of the landfill). $f(z)$ is the concentration gradient within the landfill ($0 < z < L_D$), and can be any function of z . C_0 is an initial normalized or average concentration so that $f(z)$ becomes dimensionless. Since contaminants at landfills are usually measured in the gas or liquid phase rather than as a total concentration, transformation into C_T can be made through Eqs. (9)–(11):

$$C_T(z, 0) = C_0 f(z). \quad (25)$$

The second initial condition simulates an instantaneous release from a plane source located at $z = L_p$ below surface. This situation might approximate, for example, a contaminant layer of liquid solvent resting on an impermeable soil layer [35]. For this case, using δ to denote the Dirac delta function, M is the contaminant release strength:

$$C_T(z, 0) = M \delta(z - L_p). \quad (26)$$

2.8. Analytical solutions

The governing equation, with the two boundary conditions and each of the two initial conditions, was solved analytically using methods presented in Lindstrom and Boersma [36] and Lindstrom and Narasimham [37]. The outline of the solution technique is as follows: take the Laplace transform of the governing equation with respect to z and t successively; substitute the Laplace transform (with respect to t) of the initial condition at $t = 0$ and the Laplace transform (with respect to z) of the upper boundary condition at $z = 0$; solve $C_T(p, s)$ (p is z 's Laplace variable and s is t 's Laplace variable); separate the denominator into two parts, one with s , the other with p ; take the inverse transformation of $C_T(p, s)$ with respect to z to obtain $C_T(z, s)$; apply the Laplace transform (with respect to t) of the lower boundary condition at $z = \infty$; and finally invert $C_T(z, s)$ with respect to t to obtain $C_T(z, t)$.

2.8.1. Previously distributed chemicals

Eqs. (13), (22), (24), and (25) constitute the mathematical expressions for the case of previously distributed chemicals. The solution is:

$$\begin{aligned} C_T(z, t) = & \frac{C_0}{2D_T} \frac{\sqrt{D_T}}{\sqrt{\pi t}} \exp\left(-\mu_T t - \frac{V_T^2 t}{4D_T}\right) \int_0^\infty f(\xi) \exp\left[\frac{V_T(z - \xi)}{2D_T}\right] \\ & \times \left\{ \exp\left[-\frac{(z - \xi)^2}{4D_T t}\right] + \exp\left[-\frac{(z + \xi)^2}{4D_T t}\right] \right\} d\xi - \frac{C_0}{2D_T} (V_T + 2H_T) \\ & \times \exp\left[-\mu_T t + \frac{V_T + H_T}{D_T} (H_T t + z)\right] \\ & \times \int_0^\infty f(\xi) \exp\left(\frac{H_T \xi}{D_T}\right) \operatorname{erfc}\left(\frac{z + \xi + V_T t + 2H_T t}{2\sqrt{D_T t}}\right) d\xi, \end{aligned} \quad (27)$$

where *erfc* is the complementary error function. The emission flux at the top of the lower chamber (i.e., the bottom of upper cover), $J_T(0, t)$, can be calculated by setting $z = 0$ in Eq. (27) and then substituting into (20) as shown below:

$$\begin{aligned}
 J_T(0, t) = -K_T C_G(0, t) = -H_T C_T(0, t) &= \frac{H_T C_0}{2D_T} (V_T + 2H_T) \\
 &\times \exp\left[-\mu_T t + \frac{(V_T + H_T)H_T t}{D_T}\right] \int_0^\infty f(\xi) \exp\left(\frac{H_T}{D_T} \xi\right) \\
 &\times \operatorname{erfc}\left(\frac{\xi + V_T t + 2H_T t}{2\sqrt{D_T t}}\right) d\xi - \frac{H_T C_0}{D_T} \frac{\sqrt{D_T}}{\sqrt{\pi t}} \exp\left(-\mu_T t - \frac{V_T^2 t}{4D_T}\right) \\
 &\times \int_0^\infty f(\xi) \exp\left(-\frac{V_T}{2D_T} \xi - \frac{1}{4D_T t} \xi^2\right) d\xi. \tag{28}
 \end{aligned}$$

Note that $f(z)$ appears in the integrals in (27) and (28). The model can thus estimate emission rates from landfills initially incorporated with any concentration gradient of chemical. However, if $f(z)$ is nonlinear or is a complicated function, the integrals may need to be evaluated numerically.

Example. For a chemical uniformly distributed to depth L_D ,

$$f(z) = \begin{cases} 1 & \text{if } 0 \leq z \leq L_D \\ 0 & \text{if } z > L_D \end{cases}.$$

The integrations in (27) and (28) can be carried out explicitly:

$$\begin{aligned}
 C_T(z, t) &= \frac{C_0}{2} \exp(-\mu_T t) \left[\operatorname{erfc}\left(\frac{z - L_D - V_T t}{2\sqrt{D_T t}}\right) - \operatorname{erfc}\left(\frac{z - V_T t}{2\sqrt{D_T t}}\right) \right] \\
 &+ \frac{C_0}{2} \left(1 + \frac{V_T}{H_T}\right) \exp\left(-\mu_T t + \frac{V_T z}{D_T}\right) \left[\operatorname{erfc}\left(\frac{z + L_D + V_T t}{2\sqrt{D_T t}}\right) \right. \\
 &\left. - \operatorname{erfc}\left(\frac{z + V_T t}{2\sqrt{D_T t}}\right) \right] + \frac{C_0}{2} \left(2 + \frac{V_T}{H_T}\right) \\
 &\times \exp\left[-\mu_T t + \frac{(V_T H_T + H_T^2)t + (V_T + H_T)z}{D_T}\right] \\
 &\times \left\{ \operatorname{erfc}\left[\frac{z + (V_T + 2H_T)t}{2\sqrt{D_T t}}\right] - \exp\left(\frac{H_T L_D}{D_T}\right) \right. \\
 &\left. \times \operatorname{erfc}\left[\frac{z + L_D + (V_T + 2H_T)t}{2\sqrt{D_T t}}\right] \right\}, \tag{29}
 \end{aligned}$$

$$\begin{aligned}
J_T(0, t) = & \frac{C_0}{2} V_T \exp(-\mu_T t) \left[\operatorname{erfc}\left(\frac{V_T t}{2\sqrt{D_T t}}\right) - \operatorname{erfc}\left(\frac{L_D + V_T t}{2\sqrt{D_T t}}\right) \right] \\
& + \frac{C_0}{2} (2H_T + V_T) \exp\left[-\mu_T t + \frac{(V_T H_T + H_T^2)t}{D_T}\right] \left\{ \exp\left(\frac{H_T L_D}{D_T}\right) \right. \\
& \times \operatorname{erfc}\left[\frac{L_D + (V_T + 2H_T)t}{2\sqrt{D_T t}}\right] - \operatorname{erfc}\left[\frac{(V_T + 2H_T)t}{2\sqrt{D_T t}}\right] \left. \right\}. \quad (30)
\end{aligned}$$

2.8.2. Instantaneous plane release

Eqs. (13), (22), (24), and (26) constitute the mathematical expressions for the case of an instantaneous release from a plane source located at $z = L_P$. The solution for $z < L_P$ is:

$$\begin{aligned}
C_T(z, t) = & \frac{M}{2} \exp[-\mu_T t + (D_T L_P^2 + V_T L_P)t] \\
& \times \left\{ \exp(-L_P z) \operatorname{erfc}\left[\frac{-z + (V_T + 2D_T L_P)t}{2\sqrt{D_T t}}\right] + \exp\left[\left(L_P + \frac{V_T}{D_T}\right)z\right] \right. \\
& \times \operatorname{erfc}\left[\frac{z + (V_T + 2D_T L_P)t}{2\sqrt{D_T t}}\right] \left. \right\} + \frac{M}{2} \frac{(V_T + 2H_T)}{(D_T L_P - H_T)} \\
& \times \exp\left[-\mu_T t + \frac{(V_T H_T + H_T^2)t + (V_T + H_T)z}{D_T}\right] \\
& \times \left\langle \exp\left\{\left(L_P - \frac{H_T}{D_T}\right)[z + (V_T + H_T + D_T L_P)t]\right\} \right. \\
& \times \operatorname{erfc}\left[\frac{z + (V_T + 2D_T L_P)t}{2\sqrt{D_T t}}\right] - \operatorname{erfc}\left[\frac{z + (V_T + 2H_T)t}{2\sqrt{D_T t}}\right] \left. \right\rangle, \quad (31)
\end{aligned}$$

$$\begin{aligned}
J_T(0, t) = & \frac{M}{2} \frac{(V_T + 2H_T)H_T}{(H_T - D_T L_P)} \exp\left[-\mu_T t + \frac{(V_T H_T + H_T^2)t}{D_T}\right] \\
& \times \left\{ \exp\left[\left(L_P - \frac{H_T}{D_T}\right)(V_T + H_T + D_T L_P)t\right] \operatorname{erfc}\left[\frac{(V_T + 2D_T L_P)t}{2\sqrt{D_T t}}\right] \right. \\
& - \operatorname{erfc}\left[\frac{(V_T + 2H_T)t}{2\sqrt{D_T t}}\right] \left. \right\} - MH_T \exp[-\mu_T t + (D_T L_P^2 + V_T L_P)t] \\
& \times \operatorname{erfc}\left[\frac{(V_T + 2D_T L_P)t}{2\sqrt{D_T t}}\right]. \quad (32)
\end{aligned}$$

3. Input parameters

The input parameters required by this model can be divided into three categories: landfill characteristics, chemical properties, and field measurements, which are summarized in Table 1. Parameters in the first and third categories can be obtained from daily operational records and/or by conducting simple field measurements. The greatest difficulty in input requirements is accurately determining the chemical properties of the compounds of interest. Although properties such as the Henry's law constant have been experimentally measured and have extensive data available, others such as adsorption coefficients and effective diffusivities are more difficult to estimate accurately. In particular, since past efforts in adsorption research have almost exclusively focused on organic behavior under saturated (wet) conditions, the adsorption coefficients within multiphase (dry) systems have only recently begun to become available. For hydrophobic solute in water-saturated soil, it is now generally

Table 1
Input parameters

Category/input data	Symbol (units)
Landfill characteristics	
Landfill cover depth	d (m)
Bulk density of soil	ρ_B (kg/m ³)
Volumetric air content	θ_G (-)
Volumetric water content	θ_L (-)
Chemical properties	
Effective gaseous diffusivity in soil	D_G^E (m ² /day)
Effective aqueous diffusivity in soil	D_L^E (m ² /day)
Effective gaseous diffusivity in cover	D_G^{Ecover} (m ² /day)
Overall first order degradation rate	μ_T (day ⁻¹)
Gas/solid adsorption coefficient	K_G (m ³ /kg)
Liquid/solid adsorption coefficient	K_L (m ³ /kg)
Henry's Law constant	K_H (-)
Field measurements	
Bulk gas velocity	v_G^B (m/day)
Bulk leachate velocity	v_L^B (m/day)
Mass transfer coefficient	k (m/day)
(A) Previously distributed chemicals	
(a) Case of concentration gradient	
Initial concentration	C_0 (kg/m ³)
Concentration gradient function	$f(z)$ (-)
(b) Case of uniform concentration	
Vertical depth of contamination	L_D (m)
(B) Instantaneous plane release	
Plane source strength	M (kg/m ²)
Distance of the source plane beneath the surface	L_P (m)

acknowledged that the liquid–soil partition coefficient K_L is dependent on the organic fraction of soil f_{OC} , and the octanol–water partition coefficient K_{OW} [38, 39]:

$$K_L(\text{m}^3/\text{kg}) = 6.3 \times 10^{-4} f_{OC} K_{OW} = f_{OC} K_{OC}. \quad (33)$$

For estimating the effective diffusivities in soil D_G^E and D_L^E , the Millington–Quirk formulas [40, 41], which relate effective diffusivities to the molecular diffusion coefficients in pure phase and the soil porosity, are most widely used:

$$D_G^E = \frac{\theta_G^{10/3}}{\phi^2} D_G^{\text{air}}, \quad (34)$$

$$D_L^E = \frac{\theta_L^{10/3}}{\phi^2} D_L^{\text{water}}. \quad (35)$$

D_G^{air} is the molecular diffusion coefficient in air, and D_L^{water} is the molecular diffusion coefficient in water. The effective gaseous diffusivity in the cover soil D_G^{cover} in Eq. (21) can also be estimated by Eq. (34) with corresponding θ_G and ϕ .

Another difficulty in input requirements relates to the uncertainty of some chemical properties. For example, published data for the degradation rate constant of the same compound can vary by several orders of magnitude. If a compound's half-life $T_{1/2}$ is measured, the degradation rate constant can be estimated by:

$$\mu_T(1/\text{day}) = \frac{0.693}{T_{1/2}}. \quad (36)$$

4. Numerical simulation

Eqs. (27)–(32) involve mixed multiplications between exponential and complementary error functions. Due to the limited number of significant digits that even today's computers can store, if the power term in the exponential function is high, overflow often occurs during multiplications. Cadena [42] proposed an approach to overcome this problem. The technique is to approximate the complementary error function in terms of another exponential function with a negative power term, thereby greatly reducing the high power raised by the original exponential function that causes overflow. As an example, suppose W is the multiplication that needs to be evaluated:

$$W = e^y \times \text{erfc}(x). \quad (37)$$

The numerical approximation of W using the formula for an error function in Abramowitz and Stegun is [43]:

$$W = (a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5) \times e^{y-x^2}, \quad t = \frac{1.0}{1.0 + px}, \quad \text{if } x \geq 0, \quad (38)$$

where

$$a_1 = 0.254829592, \quad a_2 = -0.284496736,$$

$$a_3 = 1.42141741, \quad a_4 = -1.453152027,$$

$$a_5 = 1.061405429, \quad p = 0.3275911.$$

The above approximation is only applicable for a complementary error function with a positive argument x . If the argument is negative, the following scheme is derived:

$$W = 2e^y - (a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5) \times e^{y-|x|^2}, \quad t = \frac{1.0}{1.0 + p|x|},$$

if $x < 0$. (39)

5. Strengths and weaknesses of the model

As was noted several years ago [44], the strengths and weaknesses of currently available models still directly result from the present level of understanding regarding the fundamental processes that control the transport and fate of contaminants. Unfortunately, the research on multiphase systems in unsaturated porous media has only recently begun [45], so our understanding of complicated processes in the subsurface is limited. Although the model proposed in this paper is able to predict concentration profiles and shows how the emission flux varies with time, an improvement over previous models, some limitations exist. First, linear equilibrium partitioning (saturation in vapor–liquid phase, local equilibrium adsorption in soil grain, etc.) is assumed, while in reality adsorption appears to be nonlinear and equilibrium may not be reached. In other words, adsorption, volatilization and transport processes may be controlled by mass transfer limitations [46]. The potential effects of temporal and spatial variations in moisture and temperature on chemical volatilization are also ignored [33].

The model presented here, though a one-dimensional approach, can be extended into three dimensions for a point source release, providing a kernel for sources of any geometrical shape and thereby forming the basis for a more comprehensive analytical VOC emission model. Three-dimensional models for solute transport in saturated porous media and the solution techniques can be found in Carnahan and Remer [47] or Goltz and Roberts [48]. The effects of soil properties and moisture on the sorption of vapor within a three phase system can be found in Ong and Lion [49].

6. Model predictions

Three compounds were chosen to illustrate model performance. Vinyl chloride and benzene are common airborne pollutants near landfill sites, whereas lindane is

Table 2
Chemical properties of three selected compounds

Parameters	VC	Benzene	Lindane
D_G^{air} (m ² /day)	9.24×10^{-1a}	7.52×10^{-1b}	5.01×10^{-1b}
D_G^{water} (m ² /day)	1.08×10^{-4a}	8.81×10^{-5b}	4.75×10^{-5b}
μ_T (day ⁻¹) ^c	0.0	0.0	2.605×10^{-3d}
K_G (m ³ /kg)	—	—	—
K_{OC} (m ³ /kg) ^e	4.0×10^{-1}	8.3×10^{-2}	1.3
K_L (m ³ /kg) ^e	5.0×10^{-3}	1.038×10^{-3}	1.625×10^{-2}
K_H (-) ^e	9.7×10^1	2.2×10^{-1}	1.3×10^{-4}

^a Yeh and Kastenbergl [50].

^b Cohen and Ryan [33].

^c Jury et al. [21].

^d Assumes that $\mu_T \approx \mu_s$, since > 98% of lindane partitions into the solid phase.

^e $K_L = f_{OC} \times K_{OC}$.

a widely-present soil contaminant. Table 2 lists the chemical properties required for model input. The adsorption coefficient, K_L , is estimated from Eq. (33), and the effective diffusivities in soil D_G^E and D_L^E are from the Millington–Quirk formulas. The landfill is assumed to be an “open dump” (no cover, $d = 0$) and initially incorporated with uniform contaminants in the uppermost one meter (so that $L_D = 1$ m in Eq. (29)). Thus the only barrier for gas movement is the surface boundary layer immediately above the landfill (i.e., $K_T = k$). The mass transfer coefficient, k , is assumed to be 90.5 m/day, which corresponds to a boundary layer thickness of about 0.5 cm [19]. Bulk gas velocity v_G^B and leachate velocity v_L^B values used in the examples are indicated in the figures. (It should be noted that much higher velocities have been reported in the literature for some sites.) Other input data are $f_{OC} = 0.0125$, $\rho_B = 1350$ kg/m³, $\theta_G = 0.2$, and $\theta_L = 0.3$, all chosen as representative of “typical” conditions.

The time-invariant mass fraction of the chemical distributed in each phase is calculated from Eq. (12). The results for three compounds are shown in Table 3. For vinyl chloride, the majority of mass (73.4%) is in gas phase; for benzene and lindane, the majority (80.3% and 98.7%) is adsorbed onto solid. These distributions have a great impact on how the chemicals behave and are transported in the subsurface landfill environment.

Fig. 2 shows a typical concentration evolution in a landfill for benzene. Velocities for gas and leachate are set to be equal (0.05 m/day) in this case. The contaminant front moves downwards with peak concentration gradually reducing with time due to spreading via dispersion and loss via volatilization (loss via degradation is negligible since $\mu_T = 0$). It is interesting to evaluate how important of a removal pathway volatilization is for the compound of interest. This can be done by estimating the mass remaining in the underground plume at time t :

$$m \text{ (kg/m}^2\text{)} = \int_0^z C_T(z, t) dz \approx C_0 L_D - \int_0^t J_T(0, t) dt \quad (\text{for } \mu_T = 0). \quad (40)$$

Table 3
Distributions among phases

Phase	Mass fraction		
	VC	Benzene	Lindane
Gas f_G	0.734	0.025	< 0.001
Liquid f_L	0.011	0.172	0.013
Solid f_S	0.255	0.803	0.987

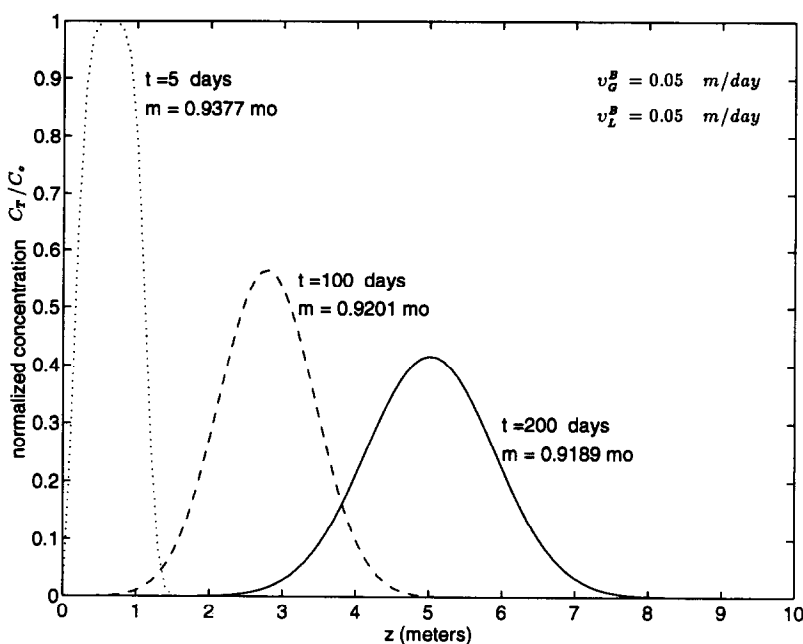


Fig. 2. Evolution of the subsurface concentration profile for benzene as function of time.

Numerical integration schemes (such as Simpson's rule or Trapezoidal rule) can be applied to evaluate the above integral. For benzene, even though 80.3% of the mass exists in the solid (sorbed) phase (see Table 3), migration with leachate is noticeable. However, this migration is slow due to the retardation caused by the adsorption: it takes about 100 days for the centerline to travel 2.5 m downwards, despite the fact that the leachate is moving 5 m/100 days. In addition, over 90% of the mass remains in the landfill after 200 days, implying that volatilization is not a significant loss pathway under these conditions.

As a comparison, the concentration profiles for vinyl chloride, a highly volatile compound, are plotted in Fig. 3. Despite a leachate flow of 0.15 m/day (three times as

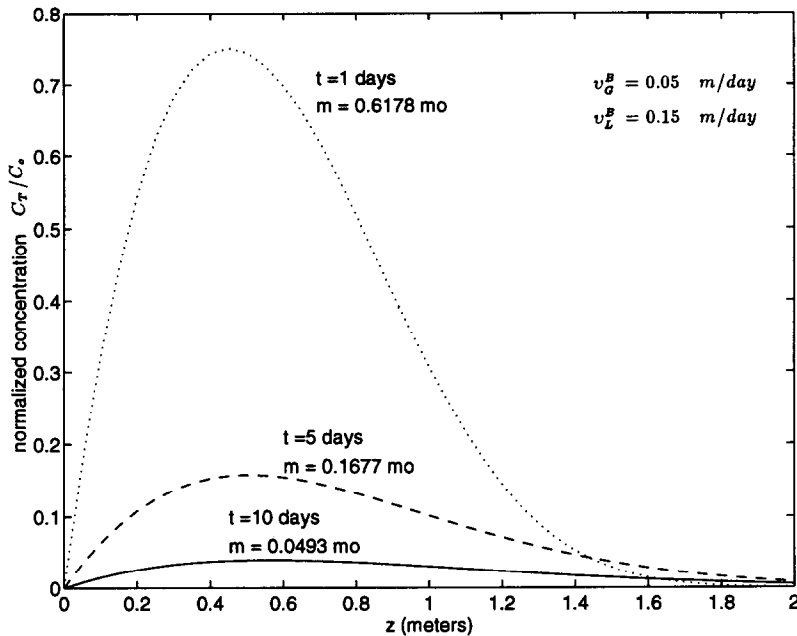


Fig. 3. Evolution of the subsurface concentration profile for vinyl chloride as function of time.

high as the gas flow) acting as a downward “drag force”, the mass remaining in the landfill decreases to almost zero ($m \simeq 5\% m_0$) within ten days as a result of volatilization losses. Thus, despite the relatively high leachate flowrate, a significant portion of the mass is released to the atmosphere before the contaminant has a chance to migrate with the leachate. The high volatility of vinyl chloride prevents it from migrating downward in substantial quantities, so the majority of the remaining mass stays immobile (within the initial one meter of contaminated depth), whereas the less volatile nature of benzene allows it to eventually infiltrate deep into the landfill (Fig. 2).

To demonstrate the effect of the moving flows on pollutant transport, a situation where no apparent moving flows occur ($v_G^B = v_L^B = 0$) is plotted in Fig. 4 for benzene. The concentration profiles for this diffusion-only case are very different from those in Fig. 2, because the plume is no longer migrating away from the surface. The loss via gas diffusive flux accounts for 58% of the initial mass after 200 days, compared to only 8% for advective and diffusive fluxes combined. Therefore, the impact of moving flows on concentration profiles can be significant.

The emission fluxes for the three compounds are plotted versus time in Fig. 5(a) and (b). Vinyl chloride, with a high Henry’s law constant, volatilizes strongly and dominates in the early stage of emissions, but also dies down quickly due to the limited amount of the mass available for emissions. In contrast, the flux for lindane is relatively small, because of its low Henry’s law constant and the high percentage of

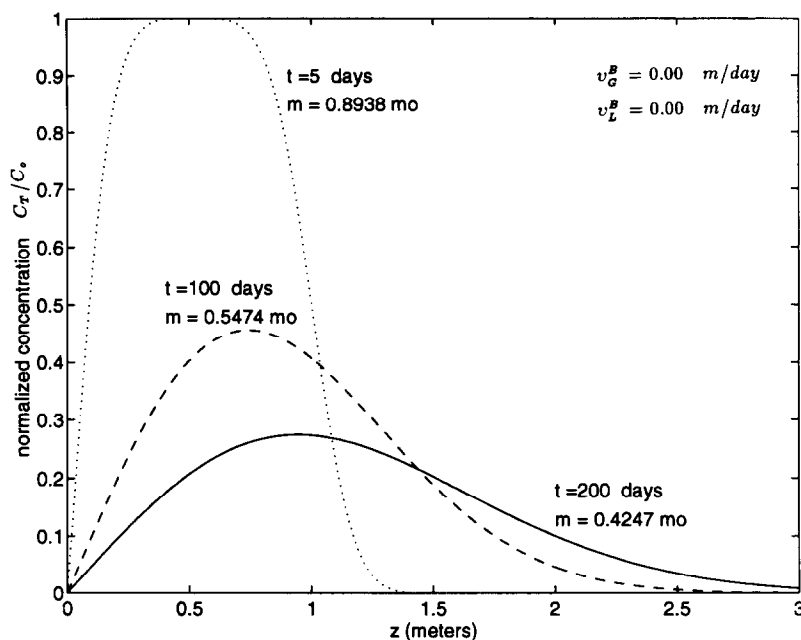


Fig. 4. Evolution of the subsurface concentration profile for benzene as function of time, with diffusion only.

mass bound as solid. Nevertheless, lindane emissions persist over a long time period, despite having a nonzero degradation rate, and eventually become dominant when benzene has decreased, as can be seen in Fig. 5(b). It should be noted that the fluxes are normalized with initial concentration; hence, the actual emission rate may not be negligible even though the emission curves asymptotically approach zero.

To briefly examine how the moving flows affect benzene emissions, emission fluxes are plotted with varying bulk gas flow and leachate flow. A higher gas flow sweeps out more contaminants, resulting in higher emission rates for benzene early on (Fig. 6). However, the effect on lindane is minimal (Fig. 7) because virtually all the mass resides in the solid phase and the very low Henry's law constant is unfavorable for volatilization. Fig. 8 shows the influence of leachate flowrate on benzene emissions. The more contaminants are carried with the leachate, the less volatilization occurs early on. Later, the amount of initial mass remaining in the landfill becomes important.

Finally, to assess the maximum possible magnitude of prediction differences between the current model and other screening-level models, a worst case emission scenario is plotted in Fig. 9. The worst case scenario shown – negligible adsorption ($K_G = K_L = 0$), single gas transport route ($v_L^B = 0$), and recalcitrant contaminant ($\mu_T = 0$) – is generally assumed in screening-level models. Overestimation by at least one order of magnitude early on can be expected in this worst case scenario.

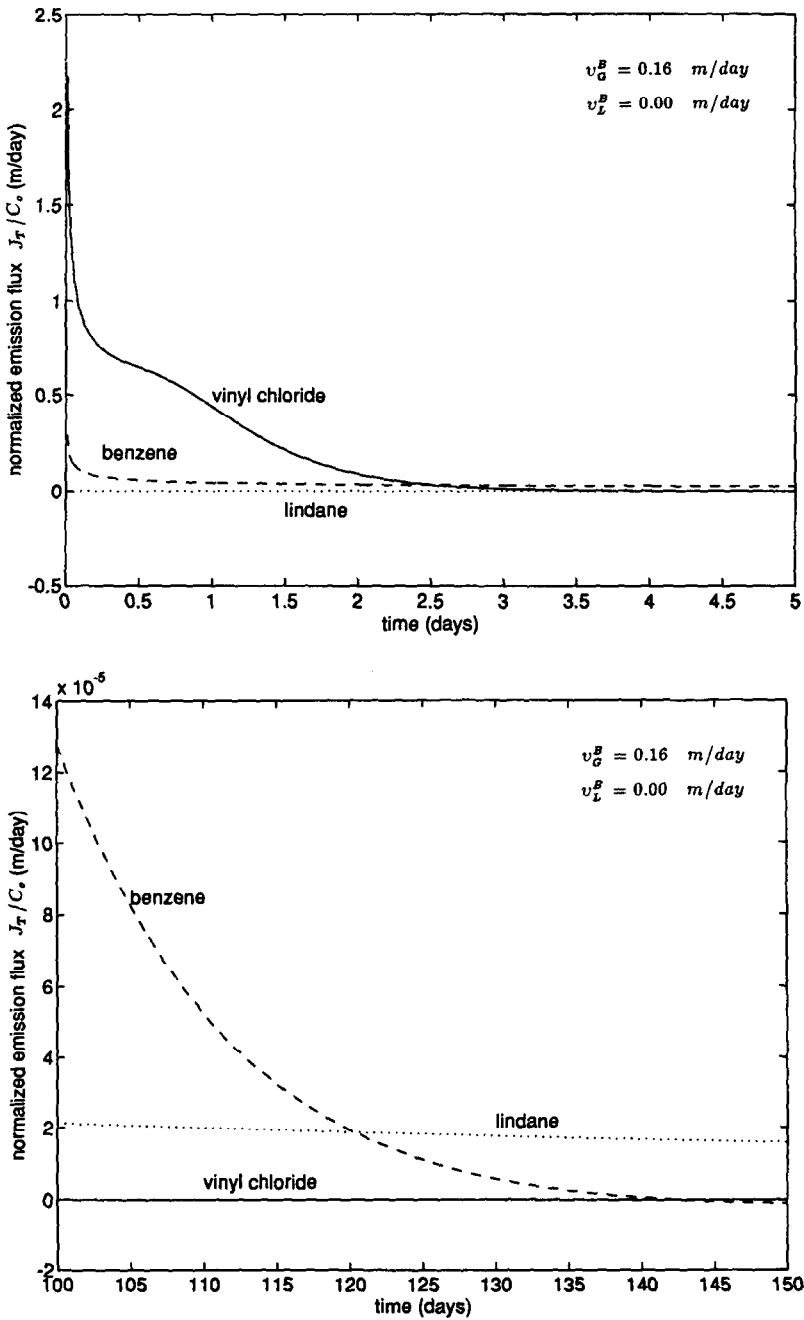


Fig. 5. The normalized atmospheric emission rate of vinyl chloride, benzene, and lindane from a landfill: (a) the early stage (0-5 days); (b) the later stage (100-150 days).

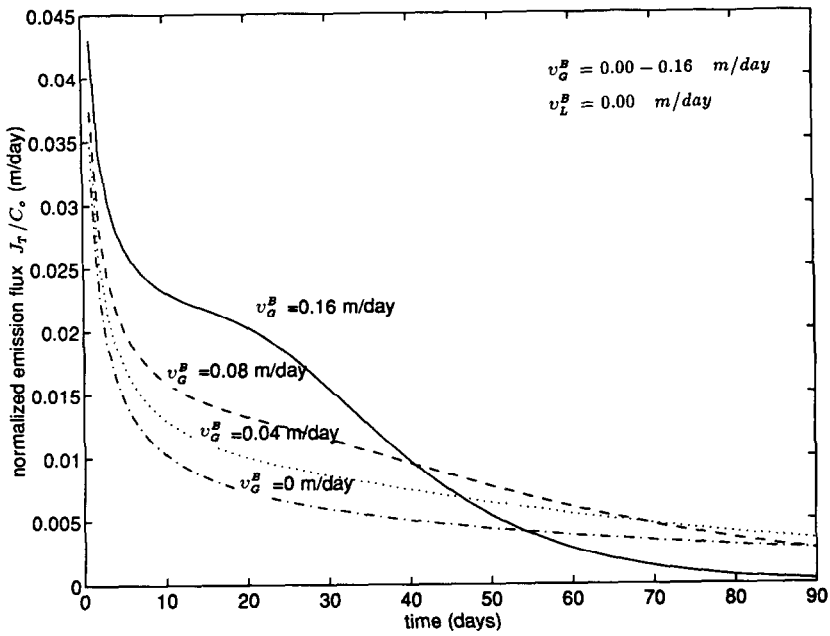


Fig. 6. The normalized atmospheric emission rate of benzene versus time, as function of the bulk gas flowrate.

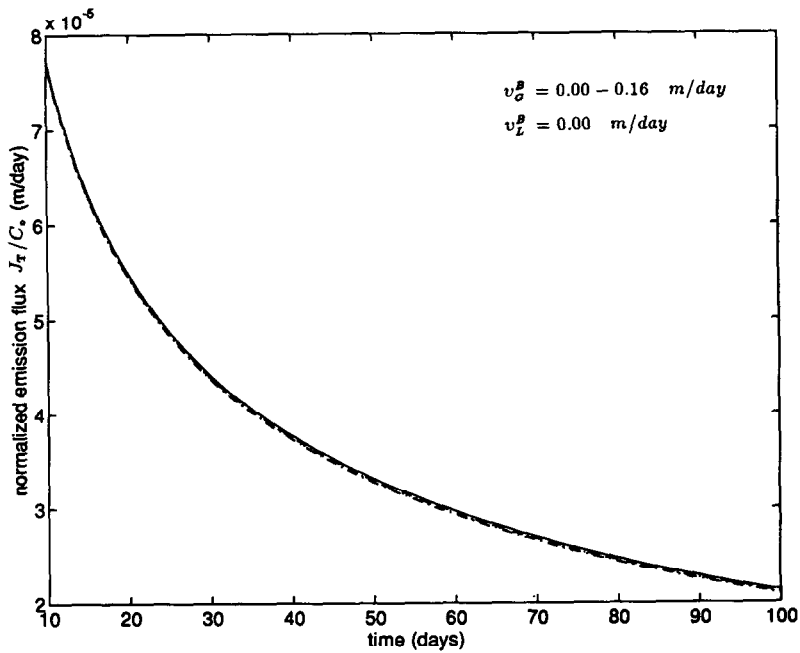


Fig. 7. The normalized atmospheric emission rate of lindane versus time, as function of the bulk gas flowrate.

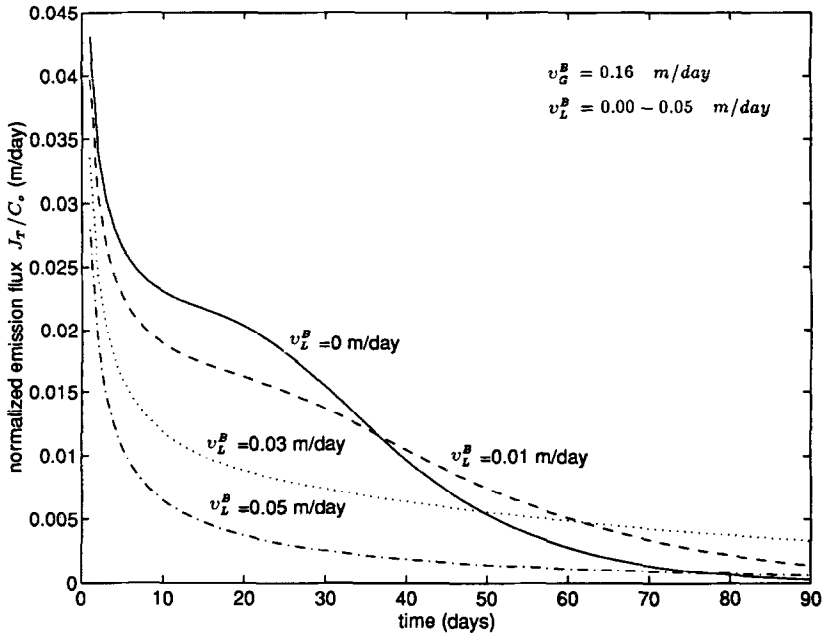


Fig. 8. The normalized atmospheric emission rate of benzene versus time, as function of the leachate flowrate.

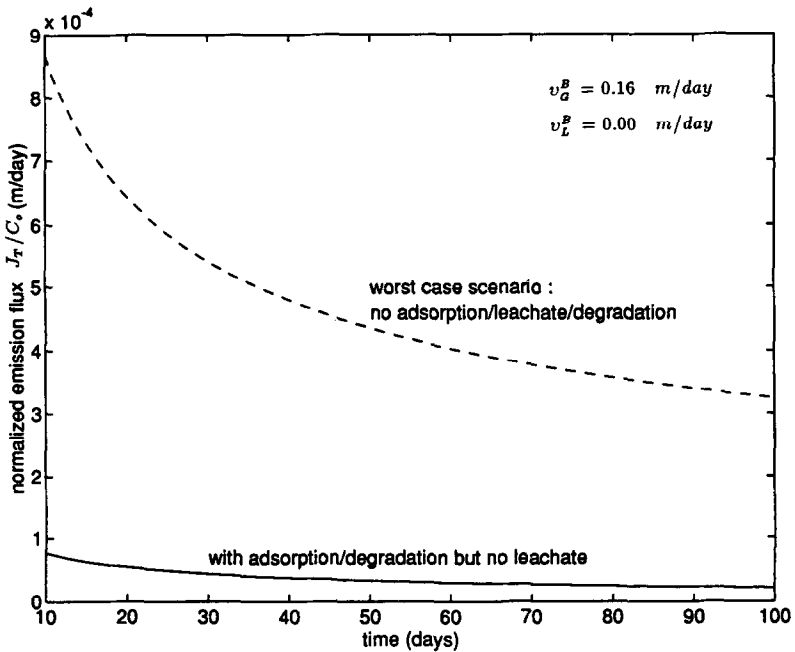


Fig. 9. The effect of the adsorption and degradation mechanisms on the predicted normalized emission rate of lindane.

As can be seen in Figs. 6–8, very complex emission behavior can result under certain circumstances. A more thorough examination of this behavior would certainly lead to a better fundamental understanding of the relative importance of the various mechanisms contributing to the rate of atmospheric emissions. While such an analysis is beyond the scope of this paper, it is planned for the future.

7. Conclusions

A nonsteady-state analytical model was developed to predict emissions of volatile organic compounds (VOCs) from hazardous or sanitary landfills. The model incorporates the following important mechanisms occurring in the unsaturated subsurface landfill environment: biogas flow, leachate, diffusion, adsorption, degradation, volatilization and mass transfer limitations through the top cover.

Examinations of three selected compounds using this model show a complicated interaction of the mechanisms involved. The Henry's law constant has the most significant effect on emissions to the atmosphere. Biogas flow and leachate act as two competing mechanisms for the removal of contaminants from the soil, whereas adsorption retains chemicals and prolongs the period of time over which emissions are released. The model is able to predict changes in subsurface concentrations and emission fluxes with time, an improvement over currently-available screening-level models.

8. Nomenclature

C_a	ambient concentration in atmosphere, ML^{-3} .
C_0	initial concentration, ML^{-3} .
C_G	concentration in gas phase, ML^{-3} .
C_L	concentration in liquid phase, ML^{-3} .
C_T	bulk concentration or total concentration, ML^{-3} .
d	landfill cover depth, L.
D_G	gaseous molecular diffusion coefficient in soil, L^2T^{-1} .
D_G^{air}	molecular diffusion coefficient in air, L^2T^{-1} .
D_G^E	effective gaseous diffusion coefficient in soil, L^2T^{-1} .
D_G^{Ecover}	effective gaseous diffusion coefficient in cover soil, L^2T^{-1} .
D_L	aqueous molecular diffusion coefficient in soil, L^2T^{-1} .
D_L^E	effective aqueous diffusion coefficient in soil, L^2T^{-1} .
D_L^{water}	molecular diffusion coefficient in water, L^2T^{-1} .
D_T	defined in (15), L^2T^{-1} .
erfc	complementary error function.
f_G	equilibrium mass fraction in gas phase, dimensionless.
f_L	equilibrium mass fraction in liquid phase, dimensionless.
f_{oc}	fraction of organic carbon in the soil, dimensionless.
f_s	equilibrium mass fraction in sorbed phase, dimensionless.

$f(z)$	concentration gradient function, dimensionless.
H_T	defined in (23), LT^{-1} .
J_G	gaseous contaminant flux, $ML^{-2}T^{-1}$.
J_L	aqueous contaminant flux, $ML^{-2}T^{-1}$.
J_T	total flux, defined in (19), $ML^{-2}T^{-1}$.
k	mass transfer coefficient in the air-soil boundary layer, LT^{-1} .
K_G	linear adsorption coefficient between gas and solid phase, L^3M^{-1} .
K_H	Henry's law constant (concentration basis), dimensionless.
K_L	linear adsorption coefficient between liquid and solid phase, L^3M^{-1} .
K_{OC}	organic carbon partition coefficient, L^3M^{-1} .
K_{OW}	octanol-water partition coefficient, dimensionless.
K_T	overall mass transfer coefficient through top soil cover, LT^{-1} .
L	landfill depth, L.
L_D	vertical depth of contamination, L.
L_P	distance of the source plane beneath the surface, L.
m	mass remaining underground, ML^{-2} .
m_0	initial mass underground, ML^{-2} .
M	contaminant release strength in plane source, ML^{-2} .
p	Laplace variable with respect to z .
q	concentration sorbed onto solid surface (mass of contaminant per mass of dry solid), MM^{-1} .
R_G	partitioning coefficient for vapor phase, dimensionless.
R_L	partitioning coefficient for liquid phase, dimensionless.
R_S	partitioning coefficient for sorbed or solid phase, ML^{-3} .
s	Laplace variable with respect to t .
$\partial S_G/\partial t$	rate of mass transfer in vapor phase, $ML^{-3}T^{-1}$.
$\partial S_L/\partial t$	rate of mass transfer in liquid phase, $ML^{-3}T^{-1}$.
$\partial S_S/\partial t$	rate of mass transfer in solid phase, $MM^{-1}T^{-1}$.
t	time, T.
$T_{1/2}$	half-life, T.
v_G	gaseous interstitial velocity, LT^{-1} .
v_G^B	bulk or apparent gas velocity, LT^{-1} .
v_L	aqueous interstitial velocity, LT^{-1} .
v_L^B	bulk or apparent water velocity, LT^{-1} .
V_T	defined in (14), LT^{-1} .
W	defined in (37).
z	vertical distance, positive downwards, L.
δ	Dirac delta function.
μ_T	overall degradation rate, defined in (16), T^{-1} .
μ_G	first order rate constant in gas phase, T^{-1} .
μ_L	first order rate constant in liquid phase, T^{-1} .
μ_S	first order rate constant in solid phase, T^{-1} .
ϕ	total porosity, dimensionless.
ρ_B	bulk density of soil, ML^{-3} .
θ_G	volumetric air content or gas-filled porosity, dimensionless.

θ_L	volumetric water content or liquid-filled porosity, dimensionless.
ξ	integration variable.

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