Steady-state analytical model for vapour-phase VOCs diffusion in layered landfill composite cover systems

<table>
<thead>
<tr>
<th>Journal:</th>
<th>Canadian Geotechnical Journal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>cgj-2016-0293.R3</td>
</tr>
<tr>
<td>Manuscript Type:</td>
<td>Article</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>04-Jun-2017</td>
</tr>
</tbody>
</table>
| Complete List of Authors: | Xie, Hai-Jian; Zhejiang university, College of Civil Engineering and Architecture  
Wang, Qiao; Zhejiang University  
Yan, Huaxiang; Zhejiang University  
Chen, Yun Min; Institute of Geotechnical Engineering, |
| Keyword: | Vapor phase volatile organic compound, Diffusion, landfill layered cover, Degree of water saturation, analytical model |
Steady-state analytical model for vapour-phase VOCs diffusion in layered landfill composite cover systems

Haijian Xie¹*, Qiao Wang¹, Huaxiang Yan¹, Yunmin Chen¹

¹College of Civil Engineering and Architecture, Zhejiang University, 866 Yuhangtang Road, Hangzhou, 310058, China

Haijian Xie (Email: xiehaijian@zju.edu.cn)
Qiao Wang (Email: 21512082@zju.edu.cn)
Huaxiang Yan (Email: yanhua@zju.edu.cn)
Yunmin Chen (Email: chenyunmin@zju.edu.cn)

*Corresponding author:
Dr. Haijian Xie
College of Civil Engineering and Architecture, Zhejiang University, 866 Yuhangtang Road, Hangzhou, 310058, China
Email: xiehaijian@zju.edu.cn
Tel: +86-571-88981608; Fax: +86-571-88208793
Abstract

An analytical model for one-dimensional vapour-phase volatile organic compounds (VOCs) diffusion through four-layered landfill composite cover system consisting of a protective layer, a drainage layer, a geomembrane (GMB), and a compacted clay liner (CCL) is developed. Effects of degree of water saturation ($S_r$), adsorption, and degradation on vapour-phase VOCs diffusion in cover system were then analyzed. Vapour-phase benzene concentration profile increases with increase of $S_r$ in the drainage layer and protective layer. When $S_{r1} = S_{r2} = 0.5$ ($S_{r1}$ and $S_{r2}$ are degree of water saturation of protective layer and drainage layer, respectively.), surface flux for the case with the degree of water saturation of CCL layer $S_{r4} = 0.3$ is 1.3 and 1560 times larger than that with $S_{r4} = 0.7$ and $S_{r4} = 0.9$, respectively. Effect of adsorption of VOCs in CCL on performance of cover system is more important than that in drainage layer and protective layer. Surface flux and concentration of benzene tends to be zero when CCL is amended with 0.5% biochar due to increase of retardation factor. The effect of degradation rate on benzene concentration increases with increase of degree of water saturation. The influence of half-life of VOCs in soil layer $t_{1/2}$ on vapour-phase VOCs concentration can be neglected when $S_r \leq 0.3$.

**Keywords:** vapour-phase volatile organic compound, diffusion, landfill layered cover, degree of water saturation, analytical model.
Introduction

Anaerobic decomposition of organic matter in refuse produces landfill gas (LFG), commonly consisting of methane (~50-60% by vol.), carbon dioxide (~40% by vol.) and more than 100 types of non-methane VOCs (USEPA, 1991; Tassi et al. 2009). LFG emanation of VOCs is estimated to constitute 10% of the VOCs emissions occurring in the entire US (Kim et al. 2008). Under the regulations of New Source Performance Standards (NSPS), all landfill facilities with an annual emission rate above 50 Mg nonmethane organic compounds (NMOC) are forced to flare or to utilize LFG (Kim et al. 2008). Moreover, the impact of VOCs on the environment and potentially on human health may be more significant than that of the bulk gases (e.g., CH₄ and CO₂) (Chiriac et al. 2007). For example, significant levels of a range of chlorofluorocarbons could potentially contribute to both stratospheric ozone depletion and greenhouse effect (IPCC 1990). Alkylbenzenes, limonene, certain esters and organosulfur are responsible for the undesirable odor. Prolonged exposure to the landfill gas consisting of benzene and chlorinated hydrocarbons can cause severe health problems on human being, especially on landfill operators (Zou et al. 2003). The most common vapour-phase VOCs found in LFG are benzene, toluene, ethylbenzene, and xylenes (m, p, o-xylene) (BTEX) (Zou et al. 2003; Kim et al. 2008; Durmusoglu et al. 2010). For instance, aromatics represent the dominant group (71.5% of total VOCs) in the landfill cover soil gases reported by Tassi et al. (2009). The Chinese Integrated emission standards of air
pollutants (NEPAC 1996) recommended the emission limits for benzene, toluene, and xylenes are 0.4, 2.4, and 1.2 mg/m$^3$, respectively. However, it is reported that the concentrations of benzene, toluene, and xylenes in LFG are 49-114000 µg/m$^3$, 345.0-1461920 µg/m$^3$, and 95.1-440000 µg/m$^3$ (Parker et al. 2002; Allen et al. 1997; Durmusoglu et al. 2010), respectively, which are much larger than those specified in the standard.

There are two main contaminant transport mechanisms regarding vapour-phase VOCs transport through unsaturated soils: diffusion and advection (Conant et al. 1996; Choi et al. 2002; You and Zhan 2013). The main influences (environmental conditions) that control the VOCs transport through unsaturated soils are gas pressure, temperature and the permeability of the soils (You and Zhan 2013). Conant et al. (1996) found out that transport of VOCs was diffusion dominated, but density-induced advection was an important component of VOCs transport under summer conditions, when the concentration of vapour VOCs were higher. Choi et al. (2002) concluded that atmospheric pressure changes can induce gas flow in the unsaturated zone to such an extent that the advective flux of organic vapours in unsaturated zone soil gas can be significant relative to the gas phase diffusion flux of these organic vapours. Falta et al. (1989) and Mendoza and Frind (1990) demonstrated that density-driven flux can sometimes dominate gas phase transport of VOCs with high vapour pressures and high molecular weights in an unsaturated zone with high permeability. You and Zhan (2013) investigated the relative significance of gas phase VOCs fluxes in the unsaturated zone, diffusive
flux, pressure driven advective flux and density-driven advective flux under various hydrogeological conditions and found that under most of the field conditions the net contribution of the advective flux is one to three orders of magnitude less than the diffusive flux, and the influence of the density-driven flux is undetectable. Bohy et al. (2006) showed that the transport of TCE (trichloroethylene) and PCE (tetrachloroethylene) vapours in the vadose zone occurred mostly by diffusion.

Gas transport through the GMBs is always controlled by molecular diffusion since the frequency of defects of the GMBs in well controlled landfills is relatively low (Foose 2002; Stark and Choi 2005). Diffusion characteristics of polyvinyl chloride (PVC) and linear low-density polyethylene (LLDPE) GMBs with respect to VOCs dissolved in water and VOCs in the vapour phase were studied by McWatters and Rowe (2009). Four polyethylene based vapour barriers and six different GMBs were examined for diffusion properties with respect to benzene, toluene, ethylbenzene, and xylenes (BTEX) (Jones and Rowe 2016). It is indicated that the vapour-phase VOCs can readily transport in the intact GMBs by diffusion and partition process (McWatters and Rowe 2009, 2010; Jones and Rowe 2016). Transport of VOCs in the landfill cover system is also shown to be primarily induced by diffusion (Yao et al. 2013; You et al. 2013; Shackelford 2014; Su et al. 2015). Su et al. (2015) demonstrated that toluene diffusion might be the main reason for the toluene reduction in the deeper zones of landfill covers. Therefore, the transport of vapour-phase VOCs transport in the landfill cover system
consisting of a CCL layer, an intact GMB layer, a drainage layer and a protective layer can be treated as a diffusion-dominated process.

Degradation of vapour-phase VOCs in landfill cover system also plays a significant role in reducing the emission amount of vapour-phase VOCs to the atmosphere (Eganhouse et al. 2001; Abreu and Johnson 2006; Verginelli and Baciocchi 2011; Su et al. 2015). Eganhouse et al. (2001) demonstrated that degradation is the process primarily responsible for the observed attenuation of the VOCs at a municipal solid waste landfill site. The mechanism of VOCs degradation in landfill cover system was also investigated (Davis and Madsen 1996; Hohener et al. 2003; Su et al. 2014). Davis and Madsen (1996) investigated the effect of substrate concentration, soil type, and relative soil moisture on the rate of toluene biodegradation in the soils. Results show that toluene degradation rate decreased with the decrease of soil moisture content. The biodegradation of toluene was completely eliminated when the soil water content of the soil was reduced to 2% (air dried). Hohener et al. (2003) mixed 13 typical VOCs to study the biodegradation kinetics of fuel vapour-phase VOCs in homogeneous unsaturated alluvial sand by laboratory batch experiments. Tassi et al. (2009) carried out the field investigation on VOCs behavior in the landfill cover soils and found that the aromatics in the landfill gas were significantly affected by degradation at aerobic conditions. Su et al. (2014) found that the toluene degradation rates in both landfill covers soils and waste biocover soils fitted well with the Michaelis–Menten model.

Mathematical models have been developed for gas transport in the soils. The
diffusion process of landfill vapour phase VOCs through the composite barriers can be predicted by the numerical models such as COMPASS (Thomas et al. 1999; Thomas et al. 2012) and COMSOL (Zhang et al. 2013, 2015). Sedighi et al. (2015) provided the verifications and preliminary applications related to the development of COMPASS-PHREEQ for reactive transport of multicomponent chemicals in unsaturated soils in the solid, aqueous, and gas phases of the unsaturated soils. Jones and Rowe (2016) used the finite-layer method based software Pollute v7 to assess the relative performance of the different vapour barriers. However, the effect of degree of water saturation of the soils on gas transport in the layered cover system cannot be evaluated by Pollute. Although many problems can be solved by numerical models, it is still necessary to use analytical models. Using analytical solutions, a better understanding of the mechanism of contaminant diffusion can be obtained, the movement of contaminant plumes can be predicted, the field parameters related to contaminant diffusion can be measured, and the results of numerical modeling can be verified (Xie et al. 2015a). Yates et al. (2000) presented analytical solutions for a one-dimensional gas diffusion in the system consisting of either two finite soil layers or a finite layer adjacent to an infinite soil layer. Bouchard et al. (2011) developed an analytical model for stable isotope ratios of VOCs transport in the unsaturated zone. The analytical models for aqueous-phase VOCs diffusion in the layered system are also available in the literature. For example, Foose (2002) provided the analytical model for VOCs diffusion in semi-infinite composite liners. Cleall and Li (2011) presented analytical solutions
to analyze VOCs diffusion through intact composite liners. Xie et al. (2013) presented an analytical solution for one-dimensional diffusion of organic contaminants through a composite liner considering the effect of degradation. The analytical models for aqueous VOCs transport in the landfill liner system are also available (Xie et al. 2015a, b). However, these analytical models are focused on aqueous VOCs transport in the saturated landfill bottom liner systems. Landfill final cover system usually consists of a protective layer, a drainage layer, a GMB layer, a CCL layer, and a gas recovery layer (Qian et al. 2001). The cover soils are usually unsaturated and the effect of degree of water saturation on vapour VOCs diffusion and adsorption in the cover system should be considered. Moreover, the influence of GMB on performance of the four-layered cover system needs to be investigated. There is no analytical model available for the diffusion of vapour-phase VOCs in this multi-layered unsaturated cover system.

The objective of this paper is to develop an analytical model capable of predicting vapour-phase VOCs diffusion in the four-layered composite cover system consisting of a protective layer, a drainage layer, a GMB, and a CCL. The effect of VOCs degradation in the soil liner will be considered. Vapour-phase VOCs transport in the four soil layers is assumed to be one-dimensional and a steady state process. The degradation model used in the present paper is assumed to be first-order kinetics. Parametric studies will be carried out to investigate the effect of the degree of water saturation, degradation rate and adsorption on VOCs concentration profiles and surface flux on the basis of the proposed analytical
solution.

**Mathematical model**

**Basic assumptions**

A four-layered cover system consisting of a protective layer, a drainage layer, a GMB layer, and a CCL layer is considered here (see Fig.1). The concentration of vapour-phase VOCs in the gas recovery layer is assumed to be a constant, i.e., \( C_0 \). This may be the case when the gas recovery layer is assumed to be out of order in the late phase of the landfills (Zeiss 2006). The protective layer is assumed to be composed of loess or silt (Zhan et al. 2014). This is the typical Chinese landfill cover system specified in the national standard (MCC 2007). The analytical model for vapour-phase VOCs diffusion in the layered cover was developed on the basis of the following assumptions: (1) One-dimensional steady-state diffusion, degradation and adsorption of vapour-phase VOCs transport in layered cover system is considered; (2) The cover layers are homogeneous; (3) Diffusion obeys Fick’s law; (4) Vapour-phase VOCs adsorption in the cover system is a linear and equilibrium process; (5) VOCs transport follows mass balance; (6) Temperature is assumed to be a constant, i.e., 25°C; and (7) The GMB layer is intact and with negligible holes, cracks or defects. Park et al. (1996) and Foose et al. (2002) demonstrated that for well-constructed composite barriers, there are few defects in geomembranes and mass flux of volatile organic compounds through intact portions of a composite barrier can be four to six orders of magnitude greater than that through defects.
Governing equations

Based on the assumptions mentioned above, the governing equations for each layer can be written as follows.

The steady state transport of vapour-phase VOCs through the protective layer can be modeled by

$$\frac{D_{d1}}{R_{d1}} \frac{\partial^2 C_1}{\partial z^2} - \lambda_1 C_1 = 0$$  (1)

where $C_1$ is the vapour-phase VOCs concentration in the protective layer; $D_{d1}$ is the vapour-phase VOCs diffusion coefficient in the protective layer; $R_{d1}$ is the retardation factor of vapour-phase VOCs in the protective layer; $z$ is the soil depth; $\lambda_1$ is the vapour-phase VOCs degradation rate in the protective layer, which can be described as (Aronson and Howard 1997)

$$\lambda_1 = \ln 2 / t_{1/2,1}$$  (2)

where $t_{1/2,1}$ is the half-life of vapour-phase VOCs in the protective layer.

The governing equation for vapour-phase VOCs transport in the drainage layer is

$$\frac{D_{d2}}{R_{d2}} \frac{\partial^2 C_2}{\partial z^2} - \lambda_2 C_2 = 0$$  (3)

where $C_2$ is the vapour-phase VOCs concentration in the drainage layer; $D_{d2}$ is the diffusion coefficient of VOCs vapour-phase in the drainage layer; $R_{d2}$ is the retardation factor of vapour-phase VOCs in the drainage layer; $\lambda_2$ is the vapour-phase VOCs degradation rate in the drainage layer.

$$\lambda_2 = \ln 2 / t_{1/2,2}$$  (4)

where $t_{1/2,2}$ is the half-life of vapour-phase VOCs in the drainage layer.
Based on Fick’s second law, the equation for vapour-phase VOCs transport in GMB can be written as (McWatters and Rowe 2010)

\[
D_{33} \frac{\partial^2 C_3}{\partial z^2} = 0
\]  
(5)

where \( C_3 \) is vapour-phase VOCs concentration in the GMB; and \( D_{33} \) is vapour-phase VOCs diffusion coefficient in the GMB.

The governing equation for vapour-phase VOCs transport in the CCL layer is

\[
\frac{D_{44}}{R_{d4}} \frac{\partial^2 C_4}{\partial z^2} - \lambda_4 C_4 = 0
\]  
(6)

where \( C_4 \) is the vapour-phase VOCs concentration in CCL layer; \( D_{44} \) is the diffusion coefficient in the CCL; \( R_{d4} \) is the vapour-phase VOCs retardation factor in the CCL; \( \lambda_4 \) is the vapour-phase VOCs degradation rate in the CCL.

\[
\lambda_4 = \ln 2 / t_{1/2,4}
\]  
(7)

where \( t_{1/2,4} \) is the half-life of vapour-phase VOCs in the CCL.

In the cases of CCL and silt (protective layer), the retardation factor can be determined by (Petersen et al. 1994)

\[
R_{d} = 1 + \frac{\theta_{wi}}{\theta_{wi} K_H} + \frac{\rho \theta_{ai} K_d}{\theta_{ai} K_H} (i=1, 4)
\]  
(8)

where \( \theta_{wi} \) is the volumetric water content of the \( i \)th soil layer; \( K_H \) is Henry’s constant (dimensionless, \( \text{cm}^3 \) (aqueous phase)/\( \text{cm}^3 \) (gas phase)); the Henry’s constant of benzene is 0.218 (Tucker and Nelken 1982); \( \rho \) is the bulk density of the soil; \( \theta_{ai} \) is volumetric soil-air content of the \( i \)th layer, which can be determined by

\[
\theta_{ai} = n \times (1 - S_r)
\]  
(9)

where \( n \) is the total porosity of soil; and \( S_r \) is the degree of water saturation of soil.
$K_d$ is the distribution coefficient (cm$^3$/g), which is equal to the quantity of sorbed chemical per gram of dry soil divided by the concentration of nonsorbed chemical in the gas phase (Hoff et al. 2002; Batterman et al. 1995)

$$K_d = K_{oc} f_{oc}$$  \hspace{1cm} (10)

where $K_{oc}$ is the Octanol-water partition coefficient; $f_{oc}$ is soil’s organic carbon fraction (Krickhoff et al. 1979). In this study, $f_{oc}$ is assumed to be 0.005, which is a moderate organic carbon fraction (Batterman et al. 1995).

For the drainage layer (sandy layer), the retardation factor can be determined by Eq. (11). The following four primary phase-partitioning processes is considered: (i) adsorption at the air-water interface, (ii) partitioning or dissolution into the bulk aqueous phase, (iii) sorption by the solid phase of the soil from the aqueous phase, and (iv) sorption at the solid surface from the gas phase (Kim et al. 2001a, 2005):

$$R_{d2} = \beta_g + \beta_w + \beta_i + \beta_d$$  \hspace{1cm} (11)

where $\beta$ represents the partial retardation factor with the subscripts g, w, i, and d referring to vapour-phase VOCs retention in the gas phase, in the aqueous phase, at the air–water interface, and sorbed at the solid domain of the soil, respectively:

$$\beta_g = 1$$  \hspace{1cm} (12)

$$\beta_w = \frac{\theta_{wi}}{K_i \theta_{ai}}$$  \hspace{1cm} (13)

$$\beta_i = \frac{\alpha_i K_i}{\theta_{ai}}$$  \hspace{1cm} (14)

$$\beta_d = \frac{\rho_s K_d}{K_i \theta_{ai}}$$  \hspace{1cm} (15)

where $\alpha_i$ is the specific air-water interfacial area (cm$^2$/cm$^3$ bulk soil); and $K_i$ is the
interfacial adsorption coefficient \( \text{cm}^3 / \text{cm}^2 \) (gaseous phase) / \( \text{cm} \) (air-water interface (cm)).

The effect of adsorption at the interface on the gas transport of VOCs was previously either neglected (Conant et al. 1996), or incorporated with \( K_i \) values (Conklin et al. 1995). There are several experiments on the adsorption of VOCs through sandy soil considering the effect of VOCs adsorption at the air-water interface (Kim et al. 1997; Popovičová and Brusseau 1998; Schaefer et al. 2000; Chen and Kibbey 2006).

However, there is no data available for VOCs adsorption on the air-water interface for clayey soils. Therefore, the effect of air-water interface on adsorption of vapour-phase VOCs in CCL and silty soils (the protective layer) is not considered.

The effective diffusion coefficient for vapour-phase VOCs diffusion in soil can be determined by (Moldrup et al. 2005)

\[
D_s = D_0(\theta_i^{10/3} / n^2)
\]

where \( D_0 \) is the gas diffusion coefficient in free air; \( D_s \) is gas diffusion coefficient in soil.

**Boundary conditions**

\( C_3^* \) is introduced to simplify the equations regarding VOCs diffusion in the GMB

\[
C_3^* = \frac{C_3}{S_{gf}}
\]

where \( S_{gf} \) is the partition coefficient between vapour-phase VOCs and GMB; and \( C_3^* \) is the vapour-phase VOCs concentration on the surface and bottom of the GMB.

For the top surface boundary, the surface of the four layered cover system is assumed to be atmosphere. The concentration of VOCs is then assumed to be zero in the top surface boundary.
\[ C_1(z) \big|_{z=0} = 0 \]  

(18)

At the interface between the protective layer and the drainage layer \((z=l_1)\), the boundary conditions are as follows

\[ C_1(z) \big|_{z=l_1} = C_2(z) \big|_{z=l_1} \]  

(19)

\[ \theta_{a1} D_{s1} \frac{\partial C_1(z)}{\partial z} \big|_{z=l_1} = \theta_{a2} D_{s2} \frac{\partial C_2(z)}{\partial z} \big|_{z=l_1} \]  

(20)

At the interface between drainage layer and GMB \((z=l_1+l_2)\), the boundary conditions are (Rowe et al. 2004; Li and Cleall 2010)

\[ C_2(z) \big|_{z=l_1+l_2} = C_3^*(z) \big|_{z=l_1+l_2} \]  

(21)

\[ \theta_{a2} D_{s2} \frac{\partial C_2(z)}{\partial z} \big|_{z=l_1+l_2} = S_{gf} D_{s3} \frac{\partial C_3^*(z)}{\partial z} \big|_{z=l_1+l_2} \]  

(22)

At the interface between GMB and CCL \((z=l_1+l_2+l_3)\), the boundary condition is (Rowe et al. 2004)

\[ C_3^*(z) \big|_{z=l_1+l_2+l_3} = C_4(z) \big|_{z=l_1+l_2+l_3} \]  

(23)

\[ S_{gf} D_{s3} \frac{\partial C_3^*(z)}{\partial z} \big|_{z=l_1+l_2+l_3} = \theta_{a3} D_{s4} \frac{\partial C_4(z)}{\partial z} \big|_{z=l_1+l_2+l_3} \]  

(24)

At the bottom boundary, the concentration of vapour-phase VOCs is assumed to be constant

\[ C_4(z) \big|_{z=L} = C_0 \]  

(25)

where \(L\) is the thickness of the cover system, i.e., \(L=l_1+l_2+l_3+l_4\).

There are a variety of external boundary conditions that can exist for composite landfill cover system. The concentrations of landfill gas have been shown to fluctuate widely over time (Duan et al. 2014; Lu et al. 2015). No single type of boundary condition has been shown to be representative of conditions in a wide variety of
modern landfills. Furthermore, gas recovery system is usually discontinued and out of order after several years of landfill operation (Zeiss 2006). In this study, the boundary conditions are assumed to be constant for conservative predictions of VOCs transport.

**Analytical solution of the model**

The general solutions to the ordinary differential Eqs. (1), (3) and (6) are as follows:

\[ C_i = A_i e^{m_i z} + B_i e^{-m_i z} \quad i=1, 2, 4 \]  

(26)

where

\[ m_i = \sqrt{\frac{\lambda_i R_i}{D_i}} \quad i=1, 2, 4 \]  

(27)

The general solution for the ordinary differential Eq. (5) is:

\[ C_3^* = \frac{(A_i z + B_i)}{D_3} \]  

(28)

Substituting Eq. (26) into Eqs. (19)-(24) results in Eqs. (29) and (30):

\[ C_i(z) = C_{i+1}(z) \quad i=1, 2, 3 \]  

(29)

\[ \theta_{ai} D_{si} \frac{\partial C_i(z)}{\partial z} = \theta_{ai+1} D_{s(i+1)} \frac{\partial C_{i+1}(z)}{\partial z} \quad i=1, 2, 3 \]  

(30)

where \( \theta_{a3} = S_{gf} \).

The relationships between \( A_{i+1}, B_{i+1} \) and \( A_i, B_i \) can be obtained as follows

\[ A_{i+1} = \frac{1}{2} (1 + \alpha_i) e^{\left(m_i, m_{i+1}\right) z_i} A_i + \frac{1}{2} (1 - \alpha_i) e^{-\left(m_i, m_{i+1}\right) z_i} B_i \quad i=1, 2, 3 \]  

(31)

\[ B_{i+1} = \frac{1}{2} (1 - \alpha_i) e^{\left(m_i, m_{i+1}\right) z_i} A_i + \frac{1}{2} (1 + \alpha_i) e^{-\left(m_i, m_{i+1}\right) z_i} B_i \quad i=1, 2, 3 \]  

(32)

\[ \alpha_i = \frac{\theta_{ai} D_{si} m_i}{\theta_{ai+1} D_{s(i+1)} m_{i+1}} \quad i=1, 2, 3 \]  

(33)

where \( z_i \) is relative depth in the \( i \)th layer.

Eqs. (31) and (32) can be written in the matrix form:

https://mc06.manuscriptcentral.com/cgj-pubs
\[
\begin{bmatrix}
A_{i+1} & B_{i+1}
\end{bmatrix} = N \begin{bmatrix}
A_i & B_i
\end{bmatrix} = \sum_{i=1}^{N} \begin{bmatrix}
A_i & B_i
\end{bmatrix} \quad i=1, 2, 3
\]

where

\[
N_i = \begin{bmatrix}
\frac{1}{2} (1 + \alpha_i) e^{(m_i - m_{i+1}) z_i} & \frac{1}{2} (1 - \alpha_i) e^{-(m_i - m_{i+1}) z_i} \\
\frac{1}{2} (1 - \alpha_i) e^{(m_i - m_{i+1}) z_i} & \frac{1}{2} (1 + \alpha_i) e^{-(m_i - m_{i+1}) z_i}
\end{bmatrix} \quad i=1, 2, 3
\]

Substituting Eqs. (26) into Eq. (18) and Eq. (25) results in

\[
A_i + B_i = 0 \quad (36)
\]

\[
A_i e^{m_i (l_i + l_{i+1})} + B_i e^{-m_i (l_i + l_{i+1})} = C_0 \quad (37)
\]

\[
\begin{bmatrix}
A_4 & B_4
\end{bmatrix} = N_3 N_2 N_1 \begin{bmatrix}
A_1 & B_1
\end{bmatrix} \quad (38)
\]

Set \( N_3 N_2 N_1 \) as

\[
N_3 N_2 N_1 = \begin{bmatrix}
M_1 & M_2 \\
M_3 & M_4
\end{bmatrix} \quad (39)
\]

Uniting Eqs. (36)-(39) results in

\[
A_i = \frac{C_0}{(M_1 - M_2) e^{m_i l_i} + (M_3 - M_4) e^{-m_i l_i}} \quad (40)
\]

\[
B_i = -\frac{C_0}{(M_1 - M_2) e^{m_i l_i} + (M_3 - M_4) e^{-m_i l_i}} \quad (41)
\]

where

\[
M_1 = \frac{1}{8} \begin{bmatrix}
(1 + \alpha_i)^3 \exp[(m_i - m_2) z_i + (m_2 - m_1) z_2 + (m_3 - m_4) z_3] + \\
(1 - \alpha_i)^2 (1 + \alpha_i) \exp[(-(m_i + m_2) z_i + (m_2 + m_3) z_2 + (m_3 - m_4) z_3)] + \\
(1 - \alpha_i)^2 (1 - \alpha_i) \exp[(m_i - m_2) z_i - (m_2 - m_3) z_2 + (m_3 + m_4) z_3] + \\
(1 - \alpha_i)^2 (1 - \alpha_i) \exp[-(m_i + m_2) z_i + (m_2 + m_3) z_2 + (m_3 + m_4) z_3]
\end{bmatrix}
\]

\[
M_2 = \frac{1}{8} \begin{bmatrix}
(1 + \alpha_i)^3 (1 - \alpha_2) \exp[(m_i - m_2) z_i + (m_2 - m_1) z_2 - (m_3 + m_4) z_3] + \\
(1 - \alpha_i)^2 (1 - \alpha_2) \exp[-(m_2 + m_1) z_i + (m_2 + m_3) z_2 - (m_3 + m_4) z_3] + \\
(1 - \alpha_i)^2 (1 + \alpha_2) \exp[(m_i - m_2) z_i - (m_2 + m_3) z_2 + (m_4 - m_3) z_3] + \\
(1 - \alpha_i)^2 (1 + \alpha_2) \exp[-(m_2 + m_1) z_i + (m_3 - m_2) z_2 + (m_4 - m_3) z_3]
\end{bmatrix}
\]
Diffusive flux of vapour phase VOCs in unsaturated cover soils can be expressed as follows (McCarthy and Johnson 1995; Healy et al. 1996; Rowe et al. 2004):

\[ J_{si} = -\theta_{wi} D_{si} \frac{\partial C_i}{\partial z} \]  

(46)

where \( J_{si} \) is the diffusive flux of VOCs in the \( i \)th layer.

The surface flux at the top of the cover system \( J_{s0} \) can then be obtained as follows:

\[ J_{s0} = \frac{-2\theta_{w0} D_{s0} C_{o} m_{i}}{(M_1 - M_2) e^{m_{1}L} + (M_3 - M_4) e^{-m_{4}L}} \]  

(47)

**Parametric analysis for vapour-phase VOCs diffusion in four-layered cover system**

**Parameters for the model**

A typical landfill four-layered cover system consisting of a protective layer, a drainage layer, a GMB layer, and a CCL layer (see Fig.1) was considered for parametric study with respect to vapour-phase VOCs diffusion. The volumetric water content \( \theta_w \) of the sandy layer ranges from 0.04 to 0.36 (Ogorzalek et al. 2008; Abdolahzadehamir et al. 2011; Vachon et al. 2015; Ng et al. 2015c). For CCL and protective layer, the ranges of volumetric water content are 0.1-0.58 (Ng et al. 2015a;
2015b; 2015c) and 0.1-0.55 (Zhan et al. 2014), respectively. The porosity of each layer and corresponding reference are listed in Table 1. So in this paper ranges from 0.1 to 0.9, which is relevant to the ranges mentioned above. Benzene is chosen to represent VOCs in the landfill gas because the most common vapour-phase VOCs found in LFG are benzene, toluene, ethylbenzene, and xylenes (m,p,o-xylene) (BTEXs) (Durmusoglu et al. 2010). Jones and Rowe (2016) pointed out that benzene, with its much lower air quality guidelines and larger diffusion coefficient values in GMBs than other chemicals, is likely to govern design.

Diffusion coefficient in free air for benzene is 9.6×10^{-6} m^2/s (24°C) (Tucker and Nelken 1982). The values of diffusion coefficients of vapour-phase benzene in protective layer, drainage layer and CCL here are evaluated by the model given by Moldrup et al. (2005) (see Eq. (16)). The diffusion coefficient of GMBs (including LLDPE GMB, high density polyethylene (HDPE) GMB, PVC GMB, polyamide nylon coextruded GMB, and ethylene vinyl-alcohol (EVOH) coextruded GMB) for vapour-phase benzene ranges from 0.045×10^{-13} to 10×10^{-13} m^2/s (McWatters and Rowe 2009, 2010; McWatters 2010). The partition coefficient for vapour-phase benzene migration through GMBs ranges from 80 to 200 (McWatters and Rowe 2009, 2010). LLDPE GMB is chosen here since it is widely used in the landfill cover system in China (MCC 2007). The diffusion coefficient for vapour-phase benzene in LLDPE GMB is 3.5×10^{-13} m^2/s (McWatters 2010). The thickness of LLDPE GMB is 2 mm and the partition coefficient is 150 (McWatters 2010). The determination models for retardation factor for different soils are different. For sandy layer, the retardation
factors are evaluated by Eq. (11) (Kim et al. 2001a, 2005). For the clayey and silty layer, the retardation factors are evaluated by Eq. (8) (Petersen et al. 1994). It is implied that adsorption of vapour-phase VOCs in soils is highly dependent on the water content in the soils.

Degradation rates vary with soil properties and types. Different soil types with different organic content, pH, temperature, oxygen, nutrients and moisture content can have different half-lives (Dunfield et al. 1993; Schuetz et al. 2003). Soils with high organic content usually have higher degradation rate (Kim et al. 2001b). Vapour-phase VOCs degradation rates in soil ranges from $2 \times 10^{-11}$ s$^{-1}$ to $1.60 \times 10^{-7}$ s$^{-1}$ (Jury et al. 1990; Howard and Printup 1991; Baehr and Baker 1995; Franzmann et al. 1999; Turczynowicz and Robinson 2001). Degradation rate for vapour-phase benzene in biologically active surface zone of soil is $2.20 \times 10^{-8}$ s$^{-1}$ (Jury et al. 1990). Half-lives of benzene in the cover soils here are assumed to be 1 year, 10 years and 100 years for the parametric analysis, which are close to results obtained by Baehr and Baker (1995), Jury et al. (1990), and Howard and Printup (1991), i.e., $2 \times 10^{-11}$-$1.60 \times 10^{-7}$ s$^{-1}$ (0.14-1000 years). The values of the parameters are shown in Tables 1 and 2. The degradation rates $\lambda_1$, $\lambda_2$ and $\lambda_4$ presented in Table 1 are cited from the references directly. The source concentration of the vapour-phase benzene is assumed to be 100 µg/m$^3$, which falls in the range of 49.0-402.3 µg/m$^3$ reported by Durmusoglu et al. (2010).

**Comparison with the numerical method**

To demonstrate the method and to verify that this approach yields the correct results,
the contaminant concentration profiles obtained by the proposed analytical solution are compared with those obtained by the finite-element method based commercial software COMSOL Multiphysics 5.1 (COMSOL 2014). Different values of degree of water saturation of the cover soils were chosen for comparisons. The parameters are listed in Table 1 and 2. The concentration profiles for the different cases with different values of degree of water saturation are shown in Fig.2. It is shown that the results obtained by the proposed analytical model and the numerical model are in good agreement.

**Effect of degree of water saturation**

Fig.3 and Fig.4 show the effect of \( S_{r1} \) and \( S_{r2} \) on the concentration profiles and steady-state surface flux. The degree of water saturation \( (S_r) \) has great influence on steady-state surface flux and concentration profiles of benzene in the cover soils. The increase of \( S_{r1} \) and \( S_{r2} \) would decrease surface flux and increase vapour-phase benzene concentration. When \( S_{r2} = S_{r4} = 0.5 \), concentration at the depth \( z/L = 0.2 \) for the case with \( S_{r1} = 0.7 \) is 8 times larger than that with \( S_{r1} = 0.3 \) (see Fig.3). With \( S_{r1} = S_{r4} = 0.5 \), the surface flux for the case with \( S_{r1} = 0.1 \) is 155.7 mg/ha/year, which is 31 times greater than that for \( S_{r1} = 0.9 \) (see Fig.4). It is indicated that increasing \( S_r \) in the drainage layer and the protective layer can effectively decrease the flux releasing of benzene in the cover soils. According to the governing equations (Eqs.(1), (3), and (6)) and the determination of surface flux (see Eq.(47)), the increase of retardation factor and decrease of diffusion coefficient in the cover soils with the increase of \( S_r \) leads to the decrease of benzene surface flux. For example, the retardation factor for the case with
\( S_{r1} = 0.9 \) can be 3.6 and 14 times greater than that of the case with \( S_{r1} = 0.7 \) and \( S_{r1} = 0.3 \), respectively (see Table 2).

The effect of \( S_{r4} \) on the concentration profile and the surface flux are shown in Fig. 5. There is no obvious difference of the surface fluxes when \( S_r \leq 0.5 \). The surface flux changes greatly when \( S_r \) reaches 0.9. When \( S_{r1} = S_{r2} = 0.5 \), surface flux for the case with \( S_{r4} = 0.3 \) is 1.3 and 1560 times larger than those with \( S_{r4} = 0.7 \) and \( S_{r4} = 0.9 \), respectively (see Fig. 5). The decrease of diffusion coefficient of VOCs and the increase of adsorption in CCL due to the increase of the degree of saturation are the major reason for this on the basis of the governing equations (Eqs. (1), (3), (6)). When \( S_{r4} \) increases from 0.7 to 0.9, the diffusion coefficient of benzene decreases from \( 7.1 \times 10^{-8} \) to \( 1.8 \times 10^{-9} \text{ m}^2/\text{s} \), while the retardation factor increases from 11.7 to 42.3. A saturated, crack free CCL makes an excellent barrier to gas migration (Qian et al. 2001).

Benzene concentration decreases with the increase of \( S_r \) in the CCL layer, which is opposite to the rules found in the drainage layer and the protective layer. With \( S_{r1} = S_{r2} = 0.5 \), relative concentration at the depth \( z/L = 0.8 \) for the case with \( S_{r4} = 0.7 \) is 0.8, which is 40 times greater than that for \( S_{r4} = 0.9 \) (see Fig. 5). It is shown that the relative concentration at the top surface of GMB increases with the increase of \( S_r \) in the protective layer and the drainage layer. For example, with \( S_{r1} = S_{r4} = 0.5 \), the benzene concentration at the top surface of GMB for the case with \( S_{r2} = 0.9 \) can be 5 and 19 times larger than those with \( S_{r2} = 0.7 \) and \( S_{r2} = 0.5 \), respectively (see Fig. 4). At the interface between drainage layer and GMB layer (\( z = l_1 + l_2 \)), conservation of mass
requires that the contaminant fluxes in the layers are the same at their interface (see Eq. 20). When $\theta_{a2}$ and $D_{r2}$ decrease with the increase of $S_r$ in the drainage layer, the flux at the interface between the drainage layer and the GMB will be reduced. This results in the accumulation of vapour benzene at the interface. Therefore, the concentrations increase with the decrease of $S_r2$. As for the case considering the decrease of $S_r4$, the vapour-phase benzene concentration in the CCL is reduced due to the increase of adsorption capacity of the CCL, especially when $S_r4>0.7$ (see Fig. 5). It is indicated that the increase of degree of water saturation in the CCL will result in lower concentration values in the cover system than the cases considering increase of degree of water saturation in the protective layer and the drainage layer.

**Effect of VOCs adsorption**

Effects of adsorption on the concentration profile and surface flux of the cover system are shown in Fig. 6. Six cases were chosen to investigate the effect of retardation factor of the cover soils on the benzene concentration profiles and surface flux released. Case 1 is the scenario without consideration of adsorption and dissolution of VOCs in all layers with $R_{d1}=R_{d2}=R_{d4}=1$. The adsorption of vapour benzene in the protective layer, the drainage layer, and the CCL is considered in the case 2, 3, and 4, respectively. The retardation factor is assumed to be 25 for the corresponding layer for the cases considering the adsorption effect, i.e., $R_{d1}=25$, $R_{d2}=25$, and $R_{d4}=25$ for the cases 2, 3, and 4, respectively. Case 5 is chosen to evaluate the effect of adsorption in the CCL amended with biochar. The CCL layer is assumed to be amended with 0.5% biochar in case 5 with $R_{d1}=25$, $R_{d2}=25$, and $R_{d4}=200$ (Breus
and Mishchenko 2006; Chen and Yuan 2011). Case 6 is chosen to investigate the influence of GMB on the concentration profile. The GMB is not included in the cover system in case 6. Retardation factors for case 6 are the same as case 1.

It is indicated that adsorption in the protective layer and drainage layer has little influence on the concentration profile and surface flux since the concentration profiles of the cases 1-3 are almost overlapped. The surface flux for case 1 is 139.1 mg/ha/year, which is close to that of case 2 and case 3. It is also indicated that the influence of adsorption in CCL is much stronger than that in the drainage layer and the protective layer (see Fig.6). At the depth of $z/L=0.8$, concentration for case 4 is 0.70, which is 1.3 times less than that for case 1. The surface flux for case 4 is 1.3 times less than that for case 1. According to the determination of the surface flux (Eq.(47)), larger gradient of VOCs concentration results in larger surface flux. The concentration gradient of VOCs on the surface for case 4 is 1.34 times less than that for case 3. Besides, VOCs concentration in CCL is much larger than that in the drainage layer. The surface flux of the cover system can thus be more effectively reduced by the increase of adsorption capacity in this layer.

Soils amended with biochar have attracted much attention recently. CCL amended with biochar is shown to have a much greater retardation factor, i.e., 200 (Bushnaf et al. 2011; Chen and Yuan 2011). It is demonstrated that the surface flux and concentration of benzene tends to be zero when the CCL is assumed to be amended with 0.5% biochar (see Fig.6). The surface flux for case 5 is 7.5 times less than that for case 3 (see Fig.6). This is due to the much larger retardation factor of the amended soil.
GMB also plays an important role in impeding benzene diffusion. Benzene concentration and surface flux increase when GMB is not considered. At the depth of $z/L=0.6$, concentration for case 5 is 0.64, which is 2.5 times greater than that for case 3. Surface flux for case 5 is 253.5 mg/ha/year, which is 1.8 times greater than that for case 3. This is due to the low diffusion coefficient of GMB. It is indicated that GMB is a good barrier for vapour-phase benzene diffusion.

**Effects of degradation rate on VOCs concentration profile**

The effect of degradation rate on VOCs concentration profile is shown in Fig. 7. The corresponding parameters are given in Table 3. It is indicated that with an increase of the degree of water saturation, the effect of the degradation rate on the benzene concentration profile and the surface flux will be increased. With $t_{1/2,1}=t_{1/2,2}=t_{1/2,4}=1$ year, the surface flux of benzene for the case with $S_{r1}=S_{r2}=S_{r4}=0.7$ is 51.1 mg/ha/year, which is 2 times less than that with $t_{1/2,1}=t_{1/2,2}=t_{1/2,4}=100$ years (see Fig. 7). It is indicated that the increase of the degradation rate in the cover system results in the decrease in VOCs concentrations. At the depth of $z/L=0.7$, concentration of VOCs for the case with $t_{1/2,1}=t_{1/2,2}=t_{1/2,4}=100$ years for $S_{r1}=S_{r2}=S_{r4}=0.7$ is 1.3 times more than that for $t_{1/2,1}=t_{1/2,2}=t_{1/2,4}=1$ year. Larger degradation rates of VOCs in the cover system means higher levels of nutrients, organic matter and electron acceptors in the layer, which results in the faster decrease of the VOCs concentration in cover system. Degradation effect of VOCs in the covers should be considered, especially for the cases with $t_{1/2}<1$ year. It is also found that half-lives of VOCs in the cover soils have greater influence on concentration profiles for the case with $S_{r1}=S_{r2}=S_{r4}=0.7$ than
that for the case with $S_{r1}=S_{r2}=S_{r4}=0.3$ (see Fig.7). When $S_{r1}=S_{r2}=S_{r4}=0.3$, concentration profile for the case with $t_{1/2}=1$ year is almost overlapped with that for $t_{1/2,1}=t_{1/2,2}=t_{1/2,4}=100$ years (see Fig.7). The surface flux for the case with $t_{1/2,1}=t_{1/2,2}=t_{1/2,4}=1$ year is close to the case with $t_{1/2,1}=t_{1/2,2}=t_{1/2,4}=100$ years for the case with $S_{r1}=S_{r2}=S_{r4}=0.3$. It is indicated that the influence of $t_{1/2}$ on VOCs concentration could be neglected when $S_r \leq 0.3$ (see Fig.7). On the basis of the governing equations (Eqs. (1), (3), (6)), this is due to the fact that diffusion and adsorption are more important when $S_{r1}=S_{r2}=S_{r4}\leq 0.3$.

Conclusions

An analytical model is developed for vapour-phase VOCs diffusion in the four-layered landfill unsaturated cover systems. Parametric studies were carried out to investigate the effect of degree of water saturation, retardation factor, degradation rate and GMB on the performance of the cover system. The following conclusions can be drawn:

(1) The degree of saturation ($S_r$) has great influence on performance of the cover system regarding benzene diffusion. With the increase of $S_r$ in the drainage layer and the protective layer, the vapour-phase benzene concentration profile increases. Vapour-phase benzene concentration decreases with the increase of $S_r$ in the CCL layer. When $S_{r2}=S_{r4}=0.5$, concentration at the depth $z/L=0.2$ for the case with $S_{r1}=0.7$ is 8 times larger than that with $S_{r1}=0.3$. The surface flux does not change greatly when $S_r \leq 0.5$ and it decreases sharply when $S_r$ reaches 0.9. When $S_{r1}=$
$S_r^2=0.5$, surface flux for the case with $S_r^4=0.3$ is 1.3 and 1560 times larger than that with $S_r^4=0.7$ and $S_r^4=0.9$.

(2) Influence of adsorption in CCL is much stronger than that in the drainage layer and protective layer. Surface flux for the case with $R_d^1=R_d^2=1$, $R_d^4=25$ is 1.3 times less than that for the case without consideration of adsorption in all layers. Surface flux and concentration of benzene tends to be zero when the CCL layer is assumed to be amended with 0.5% biochar due to much greater retardation factor ($R_d=200$).

(3) Degradation effect of VOCs in the covers should be considered, especially for the case with $t_{1/2,1}=t_{1/2,2}=t_{1/2,4}<1$ year. The flux of VOCs for $S_r^1=S_r^2=S_r^4=0.7$ on the surface of the cover system is 51.1 mg/ha/year with $t_{1/2,1}=t_{1/2,2}=t_{1/2,4}=1$ year, which is 2.0 times less than that with $t_{1/2,1}=t_{1/2,2}=t_{1/2,4}=100$ years. The effect of the degradation rate on the benzene concentration profile will be increased with the increase of the degree of water saturation. It is indicated that the influence of $t_{1/2}$ on VOCs concentration can be neglected when $S_r^4<0.3$.

(4) The proposed analytical model is relatively simple and can be used in preliminary design and evaluation of landfill cover system and verification of more complicated numerical model.

(5) The transient behavior for vapour phase VOCs diffusion in the cover system should be considered in the further studies. For example, the effect of gas transmission rate in the recovery layer on vapour-phase VOCs transport in the cover systems should be considered in the following further studies. Another limitation is that the analytical solutions used for analyses are for simplified boundary conditions.
Assuming that the concentration of the VOCs boundary concentration remains constant over time is probably unrealistic. However, this assumption is conservative, facilitates development of the analytical solution for diffusion through composite covers, and there is a significant lack of field data collected from a wide variety of modern landfills to support using a more complex boundary condition. Besides, the analytical model in this study is applicable to the landfill with unknown and vague boundary conditions. The proposed analytical model is applicable to the cases that the GMB layer is intact and with negligible holes, cracks or defects. In these cases, the advection through the defects of GMB and then the soil covers can be neglected and diffusion is the dominant transport mechanism controlling VOCs transport in the four-layered cover system. Numerical models should be used for the cases that the advection flux through the defects of GMB cannot be neglected.

Acknowledgements

The financial supports from the National Natural Science Foundation of China (Grants Nos. 41672288, 51478427, 51278452, and 51008274), the National Basic Research Program of China (973 Program, Grant No.2012CB719806), the Fundamental Research Funds for the Central Universities (Grant No. 2017QNA4028), and Zhejiang Provincial Public Industry Research Project (Grant No. 2015C31005) are gratefully acknowledged.
Notations

- \( C_i \) VOCs concentration in the \( i \)th layer
- \( C_{3*} \) VOCs concentration on the surface and bottom of GMB
- \( C_0 \) VOCs concentration at the bottom the cover system
- \( D_{si} \) effective diffusion coefficient for VOCs in the \( i \)th layer
- \( D_o \) diffusion coefficient of the VOCs in air
- \( J_o \) surface flux of VOCs
- \( K_H \) dimensionless Henry’s constant
- \( K_d \) distribution coefficient
- \( K_{oc} \) octanol-water partition coefficient organic content of soil
- \( K_i \) interfacial adsorption coefficient
- \( L \) thicknesses of the cover system
- \( n \) total porosity of soil
- \( R_{di} \) retardation factor of the \( i \)th layer
- \( S_{gf} \) partition coefficient for between contaminants and GMB
- \( S_r \) degree of water saturation of soil
- \( t_{1/2} \) half-life of VOCs
- \( t_{1/2,i} \) half-life of VOCs of the \( i \)th layer
- \( z \) space coordinate
- \( z_i \) relative depth in the \( i \)th layer
- \( \alpha_i \) specific air-water interfacial area
- \( \beta_s \) partial retardation factor referring to VOC retention in the gas phase
\[ \beta_w \quad \text{partial retardation factor referring to VOC retention in the aqueous phase} \]

\[ \beta_i \quad \text{partial retardation factor referring to VOC retention at the air-water interface} \]

\[ \beta_s \quad \text{partial retardation factor referring to VOC retention sorbed at the solid domain of the soil from aqueous phase} \]

\[ \theta_{ai} \quad \text{volumetric soil-air content of the } i\text{th layer} \]

\[ \theta_{wi} \quad \text{volumetric soil-water content of the } i\text{th layer} \]

\[ \lambda_i \quad \text{VOCs degradation rate in the } i\text{th layer} \]

\[ \rho_s \quad \text{bulk density of the soil} \]
References


990–995.


McWatters, R. S., and Rowe, R. K. 2009. Transport of volatile organic compounds through PVC and LLDPE geomembranes from both aqueous and vapour phases.


Ng, C. W. W., Liu, J., Chen, R., and Xu, J. 2015b. Physical and numerical modeling of an inclined three-layer (silt/gravelly sand/clay) capillary barrier cover system under


Verginelli, I., and Baciocchi, R. 2011. Modeling of vapor intrusion from


Zeiss, C. A. 2006. Accelerated methane oxidation cover system to reduce greenhouse gas emissions from MSW landfills in cold, semi-arid regions. Water, Air, & Soil


List of Figures

Fig. 1 Mathematic model for Volatile organic compound diffusion through the composite cover barriers

Fig. 2 Comparisons of the proposed analytical solution with COMSOL Multiphysics 5.1

Fig. 3 Benzene concentration profiles with different $S_r$ for protective layer

Fig. 4 Benzene concentration profiles with different $S_r$ for drainage layer

Fig. 5 Benzene concentration profiles with different $S_r$ for CCL layer

Fig. 6 Benzene concentration profiles under different adsorption conditions

Fig. 7 Benzene concentration profiles under different degradation rates
Fig. 1 Mathematic model for volatile organic compound diffusion through the composite cover barriers
Fig. 2 Comparisons of the proposed analytical solution with COMSOL Multiphysics 5.1
Fig. 3 Benzene concentration profiles with different $S_r$ for protective layer
Fig. 4 Benzene concentration profiles with different $S_r$ for drainage layer
Fig. 5 Benzene concentration profiles with different $S_f$ for CCL layer
Fig. 6 Benzene concentration profiles under different adsorption conditions
Fig. 7 Benzene concentration profiles under different degradation rates
List of Tables

Table 1 Parameter values of cover materials

Table 2 Diffusion coefficient and retardation factor of VOCs under various $S_r$

Table 3 Parameters for analysis of effect of degradation rate on benzene concentration profile
Table 1 Parameter values of cover materials

<table>
<thead>
<tr>
<th>Cover system</th>
<th>Thickness (cm)</th>
<th>Relative depth (z/L)</th>
<th>Porosity (n)</th>
<th>Dry density $\rho_d$ (g/cm$^3$)</th>
<th>$S_{gf}$</th>
<th>$D_{s3}$ (m$^2$/s)</th>
<th>$\lambda$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protective layer</td>
<td>50</td>
<td>0.41</td>
<td>0.465$^g$</td>
<td>1.50$^g$</td>
<td></td>
<td></td>
<td>4.22×10$^{-10c}$</td>
</tr>
<tr>
<td>Drainage layered</td>
<td>30</td>
<td>0.25</td>
<td>0.379$^a$</td>
<td>1.59$^e$</td>
<td></td>
<td></td>
<td>1.05×10$^{-10d}$</td>
</tr>
<tr>
<td>GMB</td>
<td>0.2</td>
<td>0.01</td>
<td></td>
<td>150$^c$</td>
<td>3.5×10$^{-13c}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCL</td>
<td>40</td>
<td>0.33</td>
<td>0.51$^f$</td>
<td>1.25$^f$</td>
<td></td>
<td></td>
<td>1.93×10$^{-8b}$</td>
</tr>
</tbody>
</table>

a: Batterman et al. (1995); b: Turczynowicz and Robinson (2001); c: McWatters (2010); d: Baehr and Baker (1995); e: Jury et al. (1990); f: Ng et al., 2015b; g: Zhan et al. (2014).
### Table 2 Diffusion coefficient and retardation factor of VOCs under various $S_r$

<table>
<thead>
<tr>
<th>$S_r$</th>
<th>0.1</th>
<th>0.3</th>
<th>0.5</th>
<th>0.7</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{s1}(\times10^{-7})(m^2/s)$</td>
<td>24.3</td>
<td>10.5</td>
<td>3.43</td>
<td>0.63</td>
<td>0.016</td>
</tr>
<tr>
<td>$D_{s2}(\times10^{-7})(m^2/s)$</td>
<td>18.5</td>
<td>8.02</td>
<td>2.61</td>
<td>0.48</td>
<td>0.012</td>
</tr>
<tr>
<td>$D_{s4}(\times10^{-7})(m^2/s)$</td>
<td>27.53</td>
<td>11.91</td>
<td>3.88</td>
<td>0.71</td>
<td>0.018</td>
</tr>
<tr>
<td>Retardation factor $R_{d1}$</td>
<td>1.5</td>
<td>3.0</td>
<td>5.6</td>
<td>11.8</td>
<td>42.4</td>
</tr>
<tr>
<td>Retardation factor $R_{d2}$</td>
<td>7.76</td>
<td>10.4</td>
<td>15.2</td>
<td>26.3</td>
<td>82.0</td>
</tr>
<tr>
<td>Retardation factor $R_{d4}$</td>
<td>1.5</td>
<td>2.97</td>
<td>5.6</td>
<td>11.7</td>
<td>42.3</td>
</tr>
</tbody>
</table>

### Table 3 Parameters for analysis of effect of degradation rate on benzene concentration profile

<table>
<thead>
<tr>
<th>$S_r$</th>
<th>$t_{1/2}$=1 year</th>
<th>$t_{1/2}$=100 years</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>$D_{s1}(\times10^{-7})$ (m$^2$/s)</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>$D_{s2}(\times10^{-7})$ (m$^2$/s)</td>
<td>11.91</td>
</tr>
<tr>
<td></td>
<td>$D_{s4}(\times10^{-7})$ (m$^2$/s)</td>
<td>2.98</td>
</tr>
<tr>
<td></td>
<td>$R_{d1}$</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>$R_{d2}$</td>
<td>2.97</td>
</tr>
<tr>
<td>0.7</td>
<td>$t_{1/2}$=1 year</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>$t_{1/2}$=100 years</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>$R_{d4}$</td>
<td>26.3</td>
</tr>
</tbody>
</table>