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Modeling volatilization of residual VOCs in unsaturated zones: A moving boundary problem

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ABSTRACT

It is of practical interest to investigate the natural evaporation of volatile organic compounds (VOCs) after the removal of a leaking tank situated on the top of the soil. This study aims to develop a mathematical model to predict mole fraction distributions and migration of evaporation front for two VOCs emanating from residual non-aqueous phase liquid (NAPL) due to the leak from the tank in a homogeneous soil. Considering the location of the front and the regions above and below the front, a numerical model for the diffusive transport of VOCs in unsaturated soils was developed using the finite difference method with a moving grid approach. The model was further simplified to the case of single VOC and solved analytically by Boltzmann's transformation with a moving boundary. Analytical expressions for the depth and moving speed of the front for a single VOC were then obtained for practical use. Finally, the developed model was used to predict the concentration distributions of VOCs below the land surface and examine the factors affecting the location and moving speed of the evaporation front.

1. Introduction

Subsurface contamination by volatile organic compounds (VOCs) has been one of important issues to environmental problems. Especially, the leak from an underground storage tank is an important source for the spill of VOCs in unsaturated soils. Once leak occurs, some VOCs may reside in soils as residual non-aqueous phase liquid (NAPL) [1,2]. Moreover, the VOCs may distribute among gas, liquid, and adsorbed phases in soils [3]. The transport mechanisms and fates of VOCs in unsaturated soils include advection, diffusion, dispersion, sorption, volatilization, interphase mass transfer, and chemical and biological reactions. Diffusion is generally the key mechanism under natural condition, especially, for gas transport in low-permeability soils. Most of the studies neglected advection for migration of organic vapors and gases in unsaturated soils [4–7]. Falta et al. [8] indicated that density driven advection is insignificant if the magnitude of soil permeability is less than 1×10^{-11} m^2. Massmann and Farrier [9] mentioned that advection induced by atmospheric pressure fluctuation is not substantial for gas transport in unsaturated soil with permeabilities less than 1×10^{-14} m^2 under normal weather conditions.

In the past, several mathematical models were developed to assess the fate and transport of VOCs in unsaturated soils [1,9–13] or in biological reactors [14]. Rivett et al. [15] presented a review of unsaturated zone transport and attenuation of plumes leached from shallow VOC source zones. Jury et al. [16] developed an analytical solution for a single pesticide species partitioning to gas, water and adsorbed phases undergoing first-order decay in an unsaturated soil. Later, Jury et al. [17] introduced an analytical model to evaluate the relative volatilization losses of some organic compounds under standard soil conditions. Lin and Hildemann [18] developed an analytical model including the mechanisms such as leachate flow, diffusion, adsorption, degradation, and volatilization to predict emissions of volatile organic compounds from hazardous or sanitary landfills. Shoemaker et al. [19] used the solution developed by Jury et al. [16] to study the effect of vapor phase sorption on the transport of organic compounds. Yates et al. [20] presented an analytical model to study the diffusion of organic vapors and other gases in layered soil systems. However, these models did not consider the existence of residual NAPL in soils and could underestimate the amounts of mass of VOCs residing in soil and migrating to the atmosphere. Sun et al. [21] developed an analytical solution for reactive transport of multiple volatile contaminants with assuming linear reaction kinetics and linear equilibrium partitioning between vapor, liquid, and solid phases in the unsaturated soil.

In unsaturated soils, the upper boundary of VOCs in NAPL while moving downward with time can be considered as an evaporation

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Nomenclature

C	a constant parameter
C_G	gas-phase concentration (kg/m^3)
C_G^0	saturated gas concentration (kg/m^3)
C_G^P	equilibrium gas concentrations of pure component (kg/m^3)
C_L	liquid-phase concentration (kg/m^3)
C_L^0	saturated liquid concentration (kg/m^3)
C_L^P	equilibrium liquid concentrations of pure component (kg/m^3)
C_S	adsorbed-phase concentration (dimensionless, kg/kg)
C_S^0	saturated adsorbed concentration (dimensionless, kg/kg)
C_T	total concentration (kg/m^3)
C_T^0	saturated total concentration (kg/m^3)
d	stagnant air boundary layer with thickness (m)
D_E	effective diffusion coefficient (m^2/s)
D_G	diffusion coefficient in gas phase in soil (m^2/s)
D_G^{air}	diffusion coefficient in air (m^2/s)
dt	time interval (day)
dz	initial grid size (m)
dz_{N-r}	grid size below the front (m)
dz_r	grid size above the front (m)
f	mass fraction of organic compound in NAPL
f_{oc}	soil organic carbon fraction
h	D_G^{air}/d (m/s)
i	number of component
K_D	distribution coefficient (m^3/kg)
K_H	Henry's law constant
K_{oc}	organic carbon partition coefficient (m^3/kg)
L	depth of lower boundary (m)
M	molecular mass of the VOC (kg/mole)
n	soil porosity
P^0	saturated vapor pressure of the VOC (kPa)
$\Re$	ideal gas constant (J/mole K)
s	evaporation front (m)
S_0	initial NAPL saturation
S_G	saturation of gas-phase
S_L	saturation of liquid-phase
S_R	saturation of NAPL
t	time (s)
T	absolute temperature (K)
u	mole fractions of organic compounds in the NAPL phase
u_0	initial mole fraction
U_f	moving speed of evaporation front (m/s)
z	depth from surface (m)
δ_i	η_i/D_G (s/m^2)
η_i	$\phi S_G + (\phi S_W + \rho_b K_{Di})/K_H$
θ_G	volumetric content of gas-phase
θ_G^0	initial volumetric content of gas-phase
θ_L	volumetric content of liquid-phase
θ_L^0	initial volumetric content of liquid-phase
θ_R	volumetric content of NAPL
θ_R^0	initial volumetric content of NAPL
μ_i	$\sigma_i M_i/D_G$ (kg s/mole m^2)
ρ_b	soil bulk density (kg/m^3)
ρ_R	density of NAPL (kg/m^3)
σ_i	$\rho_R n/C_{Gi}^P$

front. The location of the front, considered as a moving boundary, changes with time [22]. Mostly, the phenomenon of moving boundary occurs in the problems of heat flow with phase changes and in some diffusion problems, e.g., [23–25].

The objective of this paper is to develop a model to predict the concentration distributions of VOCs as well as the migration of the evaporation front of NAPL with two VOCs after the removal of a leaking storage tank in a homogeneous unsaturated soil. To our knowledge, all the existing models for simulating the natural evaporation of NAPL VOCs in unsaturated soils employ specific boundary conditions at fixed boundaries in the problem domain. On the other hand, the present model considers the moving boundary in describing the downward movement of evaporation front of NAPL. The moving boundary divides the polluted area into two regions, i.e., the regions above and below the front. A numerical model is developed by the finite difference method with a moving grid approach for the location of the evaporation front and concentration distributions of two VOCs in these regions. The model is further simplified for a single VOC case and solved analytically using Boltzmann's transformation with a moving boundary. The prediction obtained from the analytical solution is then compared with those given by other analytical model and the developed numerical model for a single VOC case. In addition, analytical expressions developed from the analytical solution for the location and moving speed of the front are used to assess the time of vanish of NAPL at a specific location below the land surface.

2. Methods

2.1. Problem description

Fig. 1a shows a storage tank situated on the top of land surface and filled with VOCs. The VOCs, if leaking from the tank, exhibit four different phases (namely, gas, aqueous, adsorbed and residual NAPL phases) in the unsaturated soil. Assume that VOCs have equilibrium concentrations in these phases and the liquid phase is uniformly distributed in the soil with an initial NAPL saturation S_0. The saturation of each phase represents the volume percentage in the soil pore and the sum of saturation of each phase equals one. In addition, the evaporation front of the NAPL, denoted as $s(t)$, initially stays right at the land surface, i.e., $z = s(0) = 0$ where z is the vertical axis and moves downward with time. Fig. 1b shows the scenario in which the gas phase VOCs begins to diffuse to atmosphere and the NAPL starts to vaporize to gas phase once the tank is removed. Assume that the NAPL evaporates fully above the front and the front migrates instantaneously when the evaporation occurs. Therefore, the NAPL saturation, S_R, equals zero between the land surface and the front and the residual NAPL still persists below the front.

2.2. Model formulation

Corapcioglu and Baehr [26] developed a mathematical model based on mass conservation for each VOC component in gas, water, adsorbed and NAPL phases in the unsaturated soil. Moreover, Baehr and Corapcioglu obtained a one-dimensional mass conservation equation [27, Eq. 1] for each VOC component based on following three assumptions: (1) both NAPL and air phases are immobile, (2) molecular diffusion of each VOC component within aqueous phase and NAPL is insignificant, and (3) abiotic transformation is negligible. By further neglecting biodegradation and gas phase advection and assuming that the water phase of VOC and NAPL are immobile, the equation of mass conservation for each VOC component in gas,