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Transport and fate of volatile organic chemicals in unsaturated, nonisothermal, salty porous media: 1. Theoretical development

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Abstract

A wide variety of volatile organic chemicals (VOC) have been applied to agricultural land or buried in chemical waste sites. The fate of these chemicals depends upon several mechanisms such as sorption, degradation, and transport in liquid and gaseous phases. Understanding the transport mechanisms affecting the volatile chemicals can lead to better management strategies. A theory describing inorganic solute transport, water and heat transfer, and the fate and transport of VOC in porous media has been developed. This theory includes matric water pressure head, solution osmotic pressure head, gravity pressure head, temperature, inorganic solute concentration, and VOC concentration gradients as driving forces for heat and mass transfer. The effect of surface tension, as a function of VOC concentration and temperature, on the matric water pressure head is included. The VOC can be associated with gas, liquid, and solid phases of the porous media. The gas and liquid phases are mobile, but the solid phase is immobile. The transfer of VOC across the gas/liquid, liquid/solid, and gas/solid interfaces is included using sorption–equilibrium assumptions at the interfaces. The VOC can degrade. This degradation is described by a first-order decay rate. The theory can be used to predict spatial and temporal variations of water content, temperature, inorganic concentration and the total concentration of VOC within a porous medium. The concentration of VOC in each phase can be predicted also. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Heat and mass transfer; Soil; Porous media; Soil temperature; Unsaturated flow; Solute transport

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1. Introduction

Leakage of volatile organic chemicals (VOC) from underground storage tanks and landfills, spills, and application of soil fumigants represent major sources of soil and groundwater contamination. There are many soil properties that affect the transfer processes of VOC in soils: soil-organic content; water potential; temperature; bulk density and clay content; chemical properties such as vapor density, solubility in water; Henry's law constant; ionizability; and reactivity with soil materials, and to climatic condition such as precipitation, evaporation, and air temperature [1]. Studies have been performed to describe the effect of one or more of these factors on organic chemical fate and movement in soil. Mayer et al. [2] studied the movement of pesticides in unsaturated Gila silt loam soil. They found that in the absence of appreciable mass transfer of water, a diffusion process accounted mainly for the movement of pesticides to the soil surface to replace that lost by volatilization. According to the relative values of certain physical and chemical properties of an organic compound, such as vapor pressure and water solubility, vapor-phase diffusion can be a major transport mechanism for controlling movement of the compound through a soil cover to the atmosphere [3]. Karimi et al. [4] showed that the volatilization flux of benzene through a soil cover is greatly reduced (i.e. between 7.6 and 12%) by increasing the soil–water content and soil bulk density. Similarly, Voudrias and Li [5] reported that a diffusion equation described benzene distribution well when compared with experimental values under dry soil conditions, but the diffusion equation performed poorly for wet soil.

Models including multiple transport mechanisms were successful in predicting VOC transport. Wagenet et al. [6] modeled the transport of DBCP (1,2-dibromo-3-chloropropane) in unsaturated soils. Their model included the molecular diffusion of solute in both gaseous and liquid phases and the convection in the liquid phase as well. Abriola and Pinder [7] developed a model to describe organic chemical distributions in three physical forms: as a nonaqueous phase, as a soluble component of an aqueous phase and as a mobile fraction of a gas phase. The effects of matrix and fluid compressibility, gravity, phase composition, interphase mass exchange, capillarity, diffusion and dispersion were all considered. Falta et al. [8] found that density-driven flow in unsaturated soil was significant in dense-vapor flow. The magnitude of this flow depended on vapor pressure, molecular weight, gas phase permeability, and the gas phase retardation coefficient. Similar results for 1,1,1-trichloromethane (TCE) were reported by Mendoza and Frind [9].

Mass and energy transfer are also influenced by soil solution surface tension, which depends on the concentration and type of solute. Levine [10] reported that the majority of organic compounds reduce the surface tension. Smith and Gillham [11] presented a model to describe movement of dissolved organic chemical and water in soils based upon a matric water pressure head gradient. They included the effect of surface tension on the pressure head and found that surface tension might significantly affect the water and chemical fluxes in porous media. Desai et al. [12] (quoted by Ref. [10]) measured the influence of cationic surfactant cetyl trimethyl ammonium bromide (CTAB) on capillary pressure–saturation relationships. They stated that the presence of surface-ac-

tive contaminants in the unsaturated zone would be expected to have a significant effect on the flow of water and its dissolved constituents.

All of the studies mentioned earlier considered VOC transfer for isothermal soil conditions. However, large temperature and inorganic solute concentration gradients often exist in the upper layer of a soil profile. Lindstrom and Piver [13] presented a model of low-water-solubility chemical transport for an unsaturated nonisothermal soil condition. The model is useful because it includes most of the significant processes that affect chemical transport in soils. However, the convection of solute transfer in the vapor phase and the effect of solution osmotic pressure head on water transfer were ignored in their model. Cohen and Ryan [14] included effects of temperature and water content on the transport and partitioning parameters of dieldrin in unsaturated soil. They reported differences in the predicted volatilization fluxes of dieldrin between day and night time by a factor of 25. Bear and Bensabat [15] present a theory of multiphase flow in porous media based on momentum transfer across the interface. The theory included advective flux caused by surface tension gradient associated with temperature and/or solute concentration gradient. From the theory, it is concluded that the classical Darcy formulation may be insufficient for describing flow in a multiphase system, especially when temperature or solute concentration distributions are present. Water flow was reduced in the presence of large salt concentration in unsaturated nonisothermal soil or in unsaturated isothermal soil [16–18]. So, thermal and osmotic effects in addition to the matric water pressure head effect should be considered when describing energy and mass transfer in porous media.

According to our literature review, the simultaneous transfer of VOC, inorganic solutes, water and heat under the combined effect of temperature, total water potential and surface tension has not been considered completely. Therefore, our objective is to develop a new theory describing the transfer of volatile organic chemicals, inorganic solute, water, and heat in unsaturated, nonisothermal, salty porous media.

2. Theory

The theory developed here describes simultaneous transport of water, heat, and inorganic and organic chemicals in porous media. The inorganic chemicals are assumed to reside and move only in the liquid phase and do not interact (adsorb or combine) with the solid materials of the porous medium, and the organic chemical is assumed to reside in all three phases of the porous media (liquid, vapor, and solid phases) and move in liquid and vapor phases of the porous medium.

2.1. Water transfer

A theory was developed by Nassar and Horton [19] to describe water, heat and inorganic noninteracting solute transfers under the combined effects of matric water pressure head, solution osmotic pressure head and temperature gradients in unsaturated, nonisothermal, salty porous media. Our theory will be extended to include the transfer and fate of volatile organic chemicals in a porous system.

2.1.1. Transfer of water vapor

A porous system (i.e., soil) might include several types of gases such as water vapor, carbon dioxide, carbon monoxide, nitrous oxides, and organic gases resulting from pesticide or herbicide decomposition. These gas combinations can be called a multicomponent mixture. Fick's law can be used to describe molecular diffusion for the gas mixtures in soils with some limitations. These limitations are: differences among the binary diffusion coefficients of gases are less than a factor of two [20], the molar flux ratio of gases is in a range of 0.8 to 1.2 [21] and the mole fraction is not significant [22,23]. According to these assumptions, the ordinary molecular diffusive flux can be described as:

$$q_v = -D_{wm} \nabla \rho_v \quad (1)$$

where q_v is water vapor flux density ($\text{kg}/\text{m}^2 \text{ s}$); ρ_v is density of water vapor (kg/m^3); and D_{wm} is molecular diffusivity of water vapor in a gas mixture (i.e. air, water vapor and vapor of VOC, m^2/s). D_{wm} can be obtained from Ref. [24] as:

$$D_{wm} = 1 / [y'_2/D_{i-2} + y'_3/D_{i-3} + \dots y'_n/D_{i-n}] \quad (2)$$

where D_{i-n} is the molecular diffusivity for the binary pair, i.e., water vapor diffusive through components n , and y'_n is the mole fraction of component n in the gas mixture evaluated on a component-water vapor-free basis, that is

$$y'_2 = y_2 / [y_2 + y_3 + \dots y_n] \quad (3)$$

Eq. (2) is called Blanc's law [22] and it is applicable when the mole fraction of a gas is small.

Movement of water vapor in porous media is affected by the air filled porosity and the tortuosity of the porous media. So, Eq. (1) can be modified to describe the diffusive water vapor flux in a porous media as:

$$q_v = -D_{wm} \Omega \theta_a \nabla \rho_v \quad (4)$$

where $\Omega = (S - \theta)^{2/3}$ is a factor accounting for tortuosity [25], dimensionless; S = soil porosity, dimensionless; θ = volumetric liquid water content, dimensionless; and θ_a = air-filled porosity, dimensionless.

Eq. (4) is Fick's law, which describes diffusion of water vapor in a porous medium under isothermal and isobaric conditions. Considering changes in the molecular diffusion coefficient of water vapor resulting from the multicomponent gas mixture, and conditions of nonisothermal, unsaturated, salty porous media, the following equation from Ref. [19] can describe water vapor flow:

$$q_v / \rho_w = - (D_{Tv} \nabla T) - (D_{mv} \nabla \psi_m) - D_{ov} \nabla \psi_o \quad (5)$$

where D_{Tv} is thermal vapor diffusivity ($\text{m}^2/\text{s } ^\circ\text{C}$), D_{mv} is the isothermal vapor diffusivity (m/s), D_{ov} is osmotic vapor diffusivity (m/s) and ρ_w is the density of liquid water (kg/m^3). All of these diffusivities are functions of temperature, T ; matric water pressure head, Ψ_m ; and solution osmotic pressure head, Ψ_o . In the present study, Ψ_m is a function of the liquid water content, θ ; the surface tension, γ ; and temperature, T . γ is the surface tension as a function of VOC concentration in the liquid phase, C_{ow} [11]. The solution osmotic pressure head is a function of the inorganic solute concentra-

tion, C , and temperature. It is assumed that the concentration of VOC in the liquid phase is small, and its effect on Ψ_o is negligible.

The effect of VOC concentration on the matric water pressure head can be included via the surface tension model [11] as:

$$\psi_m = \psi_m(T_o)(\gamma_m/\gamma_w) \quad (6)$$

where T_o is an arbitrary reference temperature ($^{\circ}\text{C}$), $\Psi_m(T_o)$ is the matric pressure head at the reference temperature, γ_w is the surface tension of a free-water system at the reference temperature (J/m^2), and γ_m is surface tension at VOC concentration of C_{ow} (J/m^2).

The effect of temperature on the matric water pressure head was considered through the surface tension model [26] as:

$$\psi_m = \psi_m(T_o)\exp[-\beta(T - T_o)] \quad (7)$$

where β is a surface tension–temperature dependent coefficient and its value equal to $2.09 \times 10^{-3} \text{ K}^{-1}$ [27].

The combined effect of temperature and VOC concentration on the matric water pressure head can be described as:

$$\psi_m = \psi_m(T_o)(\gamma_m/\gamma_w)\exp[-\beta(T - T_o)] \quad (8)$$

Eq. (5) describes the diffusive flux of water vapor under nonisothermal, unsaturated, salty soil conditions. The right-hand side of the equation includes three terms of vapor fluxes. The first term is diffusive flux resulting from a temperature gradient, the second term is vapor flux resulting from a the matric water pressure head gradient, and the third term is diffusive flux of water vapor resulting from a solution osmotic pressure head gradient. The gravity pressure head effect on vapor flow is neglected.

2.1.2. Transfer of liquid water

Water flow in liquid form can be described using Darcy's law for isothermal solute-free soil condition. In order to describe the liquid movement of water in nonisothermal unsaturated salty soil, Nassar and Horton [19] introduced the following equation:

$$q_1/\rho_1 = -\left(K\frac{\partial\psi_m}{\partial T}\nabla T\right) - (K\nabla\psi_m) - (K\sigma\nabla\psi_o) - Kk \quad (9)$$

where q_1 = liquid water flux ($\text{kg}/\text{m}^2 \text{ s}$); K is the unsaturated hydraulic conductivity (m/s); k is a unit vector in the positive vertical position and ρ_1 is the density of soil solution (kg/m^3). Eq. (9) describes the liquid water flux under nonisothermal, unsaturated, salty porous media. The liquid water moves in the porous media under temperature, matric water pressure head, solution osmotic pressure head, and gravity pressure head gradients, respectively. The effect of organic chemical on liquid flow was included via the surface tension–matric pressure relation (Eq. (6)). The third term in the equation was multiplied by an osmotic efficiency coefficient, σ , because the solute is not completely restricted by the soil matrix [28]. The value of this coefficient is less than or equal to 1.

2.1.3. Total water transfer

Total water flux is the vapor and liquid fluxes combined together. By combining Eqs. (5) and (9) we have

$$q_1/\rho_1 + q_v/\rho_w = - \left(K \frac{\partial \psi_m}{\partial T} + D_{Tv} \right) \nabla T - (K + D_{mv}) \nabla \psi_m - (\sigma K + D_{ov}) \nabla \psi_o - Kk \quad (10)$$

Eq. (10) describes the steady-state water flux in liquid and vapor phases under temperature, matric water pressure head, solution osmotic pressure head, and gravity pressure head gradients.

2.1.4. Transient water transfer

The principles of mass conservation for water can be expressed in the following form of the continuity equation:

$$\frac{\partial \theta_t}{\partial t} = - \nabla \left(\frac{q_1}{\rho_1} + \frac{q_v}{\rho_w} \right) \quad (11)$$

where t is time (s), and θ_t is the total volumetric water content (liquid and vapor). ρ_1 is assumed to be constant.

The total volumetric water content was described [29] as:

$$\theta_t = \theta + \frac{\rho_v}{\rho_w} \theta_a \quad (12)$$

By differentiating Eq. (12) with time and substituting $\partial \theta_a / \partial t$ by $-\partial \theta / \partial t$ and Eq. (10) into Eq. (11), Nassar and Horton [19] reported that:

$$\begin{aligned} & \left[1 - \frac{\rho_v}{\rho_w} + \frac{\theta_a}{\rho_w} \frac{\partial \rho_v}{\partial \psi_m} \frac{\partial \psi_m}{\partial \theta} \right] \frac{\partial \theta}{\partial t} + \left[\frac{\theta_a}{\rho_w} \frac{\partial \rho_v}{\partial \psi_o} \frac{\partial \psi_o}{\partial C} \right] \frac{\partial C}{\partial t} + \left[\frac{\theta_a}{\rho_w} \frac{\partial \rho_v}{\partial T} \right] \frac{\partial T}{\partial t} \\ & = \nabla \left[(K + D_{mv}) \nabla \psi_m + \left(K \frac{\partial \psi_m}{\partial T} + D_{Tv} \right) \nabla T + (\sigma K + D_{ov}) \nabla \psi_o - Kk \right] \quad (13) \end{aligned}$$

Eq. (13) describes the spatial and temporal changes of soil-moisture content under nonisothermal, unsaturated, salty porous media. In addition, a soil includes both inorganic and organic solutes. The organic solutes have an effect on the surface tension which affects water flow as well.

2.2. Heat flow

Milly and Eagleson [29] described heat flow in terms of conduction, latent heat, and sensible heat transfer mechanisms. They included temperature and matric pressure head gradients as driving forces for heat flow in unsaturated, nonisothermal, solute-free soils. They included several soil heat sources. These sources are the heat of dry soil, latent heat of vapor, heat content of vapor, heat content of liquid, and heats of wetting. Milly and Eagleson's [29] partial differential equation describing the spatial and temporal

variation in soil temperature for unsaturated, nonisothermal, solute-free soil, was extended for application to unsaturated, nonisothermal, salty porous material [19]. The extended equation is

$$\alpha_1 \frac{\partial T}{\partial t} + \alpha_2 \frac{\partial \theta}{\partial t} + \alpha_3 \frac{\partial C}{\partial t} = \nabla \left[\lambda \nabla T + \rho_w L D_{mv} \nabla \psi_m + \rho_w L D_{ov} \nabla \psi_o - C_L (T - T_o) (q_v + q_1) \right] \quad (14)$$

where

$$\begin{aligned} \alpha_1 &= C_s + [L_o + C_p (T - T_o)] \theta_a \frac{\partial \rho_v}{\partial T} \\ \alpha_2 &= [L_o + C_p (T - T_o)] \theta_a \frac{\partial \rho_v}{\partial \psi_m} \frac{\partial \psi_m}{\partial \theta} + C_L \rho_1 (T - T_o) - \rho_w w \\ &\quad - C_p \rho_v (T - T_o) - L_o \rho_v \\ \alpha_3 &= [L_o + C_p (T - T_o)] \theta_a \frac{\partial \rho_v}{\partial \psi_o} \frac{\partial \psi_o}{\partial C} \\ L(T) &= L_o - (C_L - C_p) (T - T_o) \\ C_s &= C_d + C_p \rho_v \theta_a + C_L \rho_1 \theta \end{aligned}$$

$L(T)$ is latent heat of vaporization (J/kg), C_s is bulk heat capacity of soil (J/m³ °C), C_d is the heat capacity of dry soil (J/m³ °C), C_p is specific heat of water vapor at constant pressure (J/Kg °C), C_L is the specific heat of soil solution (J/kg °C), L_o is the latent heat of vaporization (J/kg) evaluated at the reference temperature, W is the differential heat of wetting (J/kg), and λ is the effective thermal conductivity of the medium including the transport of latent heat by vapor distillation resulting from a temperature gradient (W/m °C).

Eq. (14) includes temperature and matric and osmotic pressure head gradients. This equation can be reduced for application to unsaturated, nonisothermal, solute-free porous material by neglecting the osmotic pressure head effects.

2.3. Inorganic solute transfer

Movement of inorganic solute in porous media might occur by several mechanisms: molecular diffusion, hydrodynamic dispersion, thermal diffusion, salt sieving and gravity descent [30]. The salt thermal diffusion does not contribute significantly in solute diffusion [31]. The theory of Nassar and Horton [19] describes the movement of solute in unsaturated, nonisothermal, salty soil. The driving forces for solute movement are matric water pressure head, solute concentration, and temperature gradients. In this study, we make use of the water matric pressure head gradient, and neglect the salt thermal diffusion, which enables us to rewrite the equation of Nassar and Horton [19] as:

$$\frac{\partial(C\theta)}{\partial t} = \nabla [D_{sh} \nabla C - D_{sv} \nabla \psi_m - V\theta C] \quad (15)$$

where D_{sh} is a diffusion–dispersion coefficient of inorganic solute (m^2/s), D_{sv} is a diffusion coefficient of solute resulting from salt sieving ($mol/m^2 s$), and $V (= q_1/(\rho_1\theta))$ is an average pore–water velocity of soil solution (m/s).

2.4. Organic solute transfer

Volatile organic chemicals may reside in liquid, gaseous, and solid phases [32]. Their movement can be a function of the physical and chemical properties of these phases as well as the properties of the chemicals. The movement of VOC in a porous system can differ from the movement of inorganic solutes discussed earlier. Therefore, new equations describing the VOC fluxes in the liquid and gaseous phases will be developed. Lin and Hildemann [33] introduced a theory to describe VOC movement by diffusion and convection in liquid and vapor phases in soil under isothermal conditions. Here, we extend their theory to consider the movement of VOC in nonisothermal, unsaturated salty soil. (Note: It is assumed that salinization of soil is primarily the result of the inorganic solute concentration.) The movement of a VOC is modeled as a one-dimensional flow: gas is moving with an average pore velocity $V_g (= q_v/(\rho_w\theta_a))$ [33], whereas liquid is moving with an average pore velocity V . The sorbed phase organic chemicals are considered to be immobile.

2.4.1. Liquid flux of VOC

The mechanisms for VOC transport in the liquid phase are diffusion, convection, and hydrodynamic dispersion [33]. Therefore, the net liquid flux of VOC, J_{ow} , can be described as:

$$J_{ow} = -D_{ow}\nabla C_{ow} + V\theta C_{ow} \quad (16)$$

where J_{ow} is chemical flux in liquid phase ($mol/m^2 s$), $D_{ow} = D_{dw} + D_{hw}$ is a diffusion–dispersion coefficient for VOC (m^2/s), $D_{dw} = D_o \epsilon \exp(T^*\theta)$ is the diffusion coefficient of VOC in porous media, and ϵ and T are empirical constants related to the texture of the porous media [34]. Values of 0.001 and 10.0 are for ϵ and T , respectively. D_o is the diffusion coefficient of VOC in a free-water system (m^2/s), and D_{hw} is the dispersion coefficient of VOC (m^2/s).

Eq. (16) describes the liquid flux of VOCs by diffusion–dispersion and mass flux of soil solution.

2.4.2. Vapor flux of VOC

Assuming that the vapor-phase movement of a VOC can occur by diffusion under its concentration gradient and by convection in mass flow of gas, we have

$$J_{og} = -D_{og}\nabla C_{og} + \theta_a C_{og} V_g \quad (17)$$

where J_{og} is the gas flux of VOC in gaseous phase ($mol/m^2 s$), $D_{og} = D_{dg} + D_{hg}$ is a diffusion–dispersion coefficient for VOC (m^2/s) in gaseous phase, $D_{dg} = D_{mg} \Omega \theta_a$ is the diffusion coefficient of VOC in porous media (m^2/s), D_{gm} is the molecular-diffusion coefficient of an organic compound in a multicomponent mixture (water vapor, air and vapor of the VOC) (see Eq. (2)) (m^2/s), D_{hg} is the dispersion coefficient of VOC

[9] (m^2/s), and C_{og} is the concentration of VOC in the gaseous phase (mol/m^3). Mendoza and Frind [9] introduced hydrodynamic dispersion of solute in the gas phase, and they assumed that the dispersion coefficient of VOC in the gaseous phase can be a function of the average pore velocity of gas. For a small degree of water saturation, the dispersivity of solute in the gaseous phase is assumed to be equal to the dispersivity of the solute in the liquid phase in the same porous media.

2.4.3. Total flux of VOC

The overall flux of VOC (J_{ot}) is the combination of the vapor and liquid fluxes. Adding Eqs. (16) and (17) together, yields the overall flux equation for VOC.

$$J_{\text{ot}} = -D_{\text{ow}} \nabla C_{\text{ow}} - D_{\text{og}} \nabla C_{\text{og}} + V\theta C_{\text{ow}} + \theta_a V_g C_{\text{og}} \quad (18)$$

Eq. (18) describes the steady-state organic solute flux in a porous medium that occurs in liquid and gaseous phases. The medium is an unsaturated nonisothermal, salty condition. The right-hand side of the equation includes four flux terms. The first term describes the flux resulting from diffusion–dispersion in the liquid phase. The second term describes the flux resulting from diffusion–dispersion in the gaseous phase. The third term describes the flux of VOC resulting from mass flow of water in the liquid phase, and the fourth term describes the convective VOC flux in the vapor phase.

2.4.4. Phase partitioning

Mass partitioning occurs between two individual phases, namely liquid/solid, solid/vapor, or vapor/liquid. Partitioning to the solid phase, known as adsorption or desorption, influences the movement and fate of compounds. 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. Petersen et al. [35] found that the adsorption coefficient of trichloroethylene (TCE) in dry soil was nonlinearly related to water content equal to or less than four molecular layers of water, but it was linearly related to the water content in wet soil. In the present study, local chemical equilibrium for the VOC between the phases is assumed. So, the concentration of VOC in a phase can be estimated from the concentration of VOC in another phase. The chemical equilibrium between the vapor/solid, liquid/solid, and vapor/liquid are linear and described, respectively, as follows [32]:

$$C_{\text{os}} = K_{\text{sg}} C_{\text{og}} \quad (19)$$

where K_{sg} is the linear adsorption coefficient between the solid and gas phase (m^3 of gas/kg of solid);

$$C_{\text{os}} = K_{\text{sl}} C_{\text{ow}} \quad (20)$$

where K_{sl} is the linear adsorption coefficient between the solid and liquid phase (m^3 of liquid/kg of solid);

$$C_{\text{og}} = K_{\text{gl}} C_{\text{ow}} \quad (21)$$

where $K_{\text{gl}} = C_{\text{og}}/C_{\text{ow}}$, (m^3 of liquid/ m^3 of gas) is Henry's law constant, C_{og} is the saturated vapor concentration of the VOC and C_{ow} is the solubility of VOC in water [3].

Effect of temperature on C_{og} can be considered via the ideal gas law [8], and effect of inorganic solute concentration on C_{ow} can be considered through an empirical relation [36].

In order to reduce the dependent variables, the individual concentration in each phase (C_{og} , C_{ow} , and C_{os}) and the fluxes of liquid and vapor phases of the organic chemicals (J_{ow} and J_{og}) are expressed as a function of the total concentration, C_t , which has been chosen as the only dependent variable. The total concentration of miscible volatile adsorbed solute can be given by the sum of each contributing phase [6]:

$$C_t = \theta_a C_{og} + \theta C_{ow} + \rho_b C_{os} \quad (22)$$

where ρ_b is the bulk density of soil (kg/m^3).

The phase partitioning coefficient is defined as the ratio of total concentration to the concentration of an individual phase [33].

$$R_g = C_t/C_{og} = (\theta_a K_{gl} + \theta + \rho_b K_{sg} K_{gl})/K_{gl} \quad (23)$$

$$R_w = C_t/C_{ow} = \theta_a K_{gl} + \theta + \rho_b K_{sl} \quad (24)$$

$$R_s = C_t/C_{os} = (\theta_a K_{sl} + \theta K_{sg} + \rho_b K_{sl} K_{sg})/(K_{sg} K_{sl}) \quad (25)$$

where R_g , R_w , and R_s are gas, liquid, and solid partitioning coefficients, respectively.

2.4.5. Governing equation

Transient solute flow in a soil requires description of fluxes and solute concentration with time and depth. Based on the mass conservation law, the equilibrium assumptions, and the partitioning coefficients, and assuming that degradation of the total organic chemical concentration obeys first-order kinetics [32], we obtain a general partial differential equation as:

$$\partial C_t / \partial t = -\nabla J_{ot} - \Phi C_t \quad (26)$$

where Φ is a decay coefficient (s^{-1}). The second term on the right hand side represents a sink change rate. Substituting the partitioning coefficients and Eqs. (18) and (22) into Eq. (26), we obtain:

$$\partial C_t / \partial t = \nabla (D_t \nabla C_t - V_t C_t) - \Phi C_t \quad (27)$$

where

$$V_t = \frac{\theta_a V_g}{R_g} + \frac{\theta V}{R_w}$$

$$D_t = \frac{D_{og}}{R_g} + \frac{D_{ow}}{R_w}$$

V_t and D_t are an effective velocity and diffusion–dispersion coefficient, respectively, for VOC in porous media.

Eq. (27) describes the transient change of total organic solute concentration in a soil system. This equation can be reduced exactly to Lin and Hildemann's [33] model if the soil is isothermal and inorganic solute-free, and the dispersive flow of the organic solute in the gas and liquid phases and the salt sieving are neglected.

2.5. Coupled organic chemical, inorganic solute, water, and heat transport

Four partial differential equations (Eqs. (13)–(15) and (27)) are developed. The equations should be solved simultaneously in order to understand the mechanisms of energy and mass transfer in porous media. The equations can be used to describe the spatial and temporal variations of organic chemical, inorganic solute, water content, and temperature in porous media when the boundary and initial conditions and the transport parameters are available.

2.6. Soil parameters and characterization

To describe the simultaneous transfer of heat, water, inorganic solute and volatile organic chemicals in porous media, the transport parameters and partitioning coefficients should be obtained. The transport parameters of heat, water, and inorganic solute are discussed in detail by Nassar and Horton [19].

Effect of organic chemical concentration on the surface tension, γ_w/γ_m , can be estimated for nonionized organic solute using the following form [22]:

$$\gamma_m/\gamma_w = \left(\Gamma_w + \Gamma_o(\gamma_o/\gamma_w)^{1/4} \right)^4 \quad (28)$$

where γ_o is the surface tension of volatile organic chemical (J/m²), Γ_w and Γ_o are the superficial volume fraction of water and the volatile organic chemical in the surface layer.

The binary diffusion coefficients in the gaseous phase can be calculated following Fuller et al. [37] and Lyman et al. as quoted by Ref. [36] as a function of temperature and pressure:

$$D_{i-n} = \frac{0.00143(T + 273)^{1.75}}{P(M_{i-n})^{1/2}[(V_i)^{1/3} + (V_n)^{1/3}]^2} 10^{-3} \quad (29)$$

where D_{i-n} is the molecular diffusivity for gas i through gas n in the vapor phase of the porous media (m²/s); T is temperature (°C); P is vapor phase pressure (Mpa); $M_{i-n} = 2(1/\bar{\omega}_i + 1/\bar{\omega}_n)^{-1}$, V_i and V_n are the molar volumes for gases i and n , respectively (μm³/g mol), and the $\bar{\omega}_i$ and $\bar{\omega}_n$ are the molecular weights of the i th and n th constituents (g/mol), respectively. Eq. (29) can be used for determination of D_{i-n} that is necessary for calculating D_{wm} (Eq. (1)) and D_{gm} (Eq. (18)).

The diffusion coefficient of a nonelectrolyte in a free-water system can be calculated from the Wilke–Chang equation [24] as:

$$D_o = \frac{7.4 \times 10^{-12}(\omega_w M_w)^{0.5}(T + 273)}{\mu_w V_i^{0.6}} \quad (30)$$

where D_o is mass diffusivity of organic chemical through water (m²/s); ω_w is the solution association constant (2.26 can be used for aqueous solution), M_w is the molecular weight of water (g/mol), μ_w is the viscosity of water (Mpa s); and V_i is the molal volume of organic solute at the normal boiling point (μm³/g mol).

The solubility of VOC (C_{ow}) in soil solution as a function of the inorganic solute concentration, C , can be calculated as [36]:

$$C_{ow} = S^\circ / (10^{kC}) \quad (31)$$

where S° is molar solubility in a free-water system, and k is an empirical salting parameter.

The decay coefficient (Φ), is described as a function of temperature, water content and soil depth [38] as:

$$\Phi = f_T f_\theta f_z K_{ref} \quad (32)$$

where f_T is a factor for the influence of soil temperature, f_θ is reduction factor for the influence of liquid water content, f_z is reduction factor for the influence of the depth, and K_{ref} is decay coefficient at reference condition (i.e., those in soil collected from the plow layer at 20°C and at a matric pressure of -1.0 m).

The rate coefficient at reference condition is related to the biochemical half-life under reference condition, H_{ref} , by the equation:

$$K_{ref} = \ln 2 / H_{ref} \quad (33)$$

$$f_T = \exp(\xi(T - T_o)) \quad (34)$$

where ξ is a function of T

$$f_\theta = \min(1, (\theta / \theta_{ref})^b) \quad (35)$$

where b is a constant, and θ_{ref} is the water content at a reference condition. The term f_z can be unity in the upper 0.30-m depth of the soil surface, but it is less than unity at a deeper depth.

3. Summary

An organic chemical applied to a soil might evaporate to the atmosphere or move by infiltrating water to the groundwater. Adsorption, degradation, dispersion, solubility of the organic chemical, and changes in water potential and temperature affect the evaporation and movement of organic chemicals in unsaturated soil. A theory was developed to describe simultaneous transfer of organic and inorganic solutes, and water and heat in unsaturated nonisothermal, salty porous media (i.e. soil). The theory considers that the organic chemical resides in liquid, vapor, and solid phases of the porous media, and the inorganic solute resides only in the liquid phase. The effect of organic chemical on the matric water pressure head was considered, and presence of gases in multicomponent mixtures was considered as well. The theory includes four partial differential equations: organic solute, inorganic solute, water, and heat transfer. Organic chemical transport in liquid and vapor phases was included in the theory. The movement in the liquid phase occurs by diffusion–dispersion and convective mechanisms. The movement in the vapor phase occurs by diffusion–dispersion and convective mass transfer of gas. The movement of VOC is affected by the phase partitioning coefficients. The inorganic solute moves in liquid by diffusion–dispersion, salt sieving

and convective mechanisms. Water moves in vapor and liquid phases. Both vapor and liquid movements are functions of matric water pressure head, solution osmotic pressure head, temperature, and gravitational pressure head. The heat flow equation describes heat flow by conduction and convection. Convection occurs by latent and sensible heat in conjunction with vapor and liquid transfer. The theory is appropriate for near surface soil exposed to nonisothermal conditions. The theory can be applied to management of pesticides in urban and agricultural soils, management of organic wastes stored in landfill areas, and heat and mass transfer in non-soil porous materials (catalysts, powders, heat exchangers, grain drying, and food storage).

Nomenclature

b	Coefficient in Eq. (35)
C	Inorganic solute concentration in liquid phase (mol m^{-3} of liquid)
C_d	Volumetric heat capacity of dry porous media ($\text{J m}^{-3} \text{ }^\circ\text{C}^{-1}$)
C_L	Specific heat of soil solution ($\text{J kg}^{-1} \text{ }^\circ\text{C}^{-1}$)
C_{og}	Concentration of VOC in gas phase (mol m^{-3} of gas)
C_{og}^*	Saturated concentration of VOC in gas phase (mol m^{-3} of gas)
C_{os}	Concentration of VOC in solid phase (mol m^{-3} of solid)
C_{ow}	Concentration of VOC in liquid phase (mol m^{-3} of liquid)
C_{ow}^*	Solubility of VOC in liquid phase (mol m^{-3} of liquid)
C_p	Specific heat of water vapor at constant pressure ($\text{J kg}^{-1} \text{ }^\circ\text{C}^{-1}$)
C_s	Volumetric heat capacity of wetted porous media ($\text{J m}^{-3} \text{ }^\circ\text{C}^{-1}$)
C_t	Total concentration of VOC in soil (mol m^{-3} of soil)
D_{dw}	Diffusion coefficient of VOC in liquid phase ($\text{m}^2 \text{ s}^{-1}$)
D_{gm}	Diffusion coefficient of organic vapor in gas mixture ($\text{m}^2 \text{ s}^{-1}$)
D_{dg}	Diffusion coefficient of VOC in gas phase ($\text{m}^2 \text{ s}^{-1}$)
D_{hg}	Dispersion coefficient of VOC in gas phase ($\text{m}^2 \text{ s}^{-1}$)
D_{hw}	Dispersion coefficient of VOC in liquid phase ($\text{m}^2 \text{ s}^{-1}$)
D_{i-n}	Binary diffusion coefficient for gas i through gas n ($\text{m}^2 \text{ s}^{-1}$)
D_{mv}	Matric pressure head-dependent diffusion coefficient for water vapor flow (m s^{-1})
D_o	Diffusion coefficient of VOC in free-water system ($\text{m}^2 \text{ s}^{-1}$)
D_{og}	Diffusion – dispersion coefficient of VOC in gas phase ($\text{m}^2 \text{ s}^{-1}$)
D_{ov}	Osmotic pressure head – dependent diffusion coefficient for water vapor flow (m s^{-1})
D_{ow}	Diffusion – dispersion coefficient of VOC in liquid phase ($\text{m}^2 \text{ s}^{-1}$)
D_{sh}	Diffusion – dispersion coefficient of inorganic solute ($\text{m}^2 \text{ s}^{-1}$)
D_{sv}	Diffusion coefficient of inorganic solute due to salt sieving ($\text{mol m kg}^{-1} \text{ s}^{-1}$)
D_t	Effective diffusion coefficient of VOC in soil ($\text{m}^2 \text{ s}^{-1}$)
D_{Tv}	Thermally induced diffusion coefficient for water vapor flow ($\text{m}^2 \text{ s}^{-1} \text{ }^\circ\text{C}^{-1}$)
D_{wm}	Diffusion coefficient of water vapor in gas mixture ($\text{m}^2 \text{ s}^{-1}$)
f_T	Coefficient in Eq. (32)
f_z	Coefficient in Eq. (32)
f_θ	Coefficient in Eq. (32)

g	Gravitational acceleration (m s^{-2})
H_{ref}	Biochemical half-life at reference condition (s)
k	Empirical salting parameter in Eq. (31)
K	Unsaturated hydraulic conductivity (m s^{-1})
\mathbf{k}	Unit vector factor
K_{sg}	Adsorption coefficient between solid/gas (m^3 of gas/kg of solid)
K_{ref}	Decay coefficient at reference condition (s^{-1})
K_{gl}	Henry's constant (dimensionless)
K_{sl}	Adsorption coefficient between solid/liquid (m^3 liquid/kg of solid)
K_s	Saturated hydraulic conductivity (m s^{-1})
L	Latent heat of vaporization (J kg^{-1})
L_o	Latent heat of vaporization at reference temperature (J kg^{-1})
M	Molecular weight of organic chemical (kg/mol)
M_w	Molecular weight of water (g/mol)
q_1	Liquid water flow rate ($\text{kg m}^{-2} \text{s}^{-1}$)
q_{og}	Flux density of VOC in gas phase ($\text{mol m}^{-2} \text{s}^{-1}$)
q_{ot}	Total flux density of VOC ($\text{mol m}^{-2} \text{s}^{-1}$)
q_{ow}	Flux density of VOC in liquid phase ($\text{mol m}^{-2} \text{s}^{-1}$)
q_v	Water vapor flow rate ($\text{kg m}^{-2} \text{s}^{-1}$)
q_w	Total water flow rate ($\text{kg m}^{-2} \text{s}^{-1}$)
P	Vapor pressure of VOC (MPa)
P°	Saturated vapor pressure of VOC (Mpa)
R	Universal gas constant ($\text{mJ/mol } ^\circ\text{C}$)
R_g	Partitioning coefficient for gas phase for VOC
R_s	Partitioning coefficient for adsorbed VOC on solid phase
R_w	Partitioning coefficient for liquid phase for VOC
S	Total porosity
S°	Molar solubility of VOC in free-water system (mol/m^3)
t	Time (s)
T	Temperature ($^\circ\text{C}$)
T_o	Reference temperature ($^\circ\text{C}$)
V	Average pore velocity of liquid water (m s^{-1})
V_g	Average pore velocity of organic vapor (m s^{-1})
V_i	Molar diffusion volume of VOC ($\mu\text{m}^3/\text{mol}$)
V_t	Effective convection velocity of VOC in soil (m s^{-1})
W	Differential heat of wetting (J kg^{-1})
y'_n	Mole fraction of component n in gas mixture

Greek symbols

β	Surface tension-temperature dependent coefficient ($^\circ\text{C}^{-1}$)
$\bar{\omega}_i, \bar{\omega}_n$	Molecular weight of gas i and n
θ	Volumetric water content in the liquid phase (m^3/m^3)
θ_a	Air-filled porosity (m^3/m^3)
θ_t	Total water content (m^3/m^3)
Ω	Tortuosity factor of air-filled pore space

μ_w	Dynamic viscosity of water (m^2/s)
λ	Effective thermal conductivity of porous media ($\text{W m}^{-1} \text{ }^\circ\text{C}^{-1}$)
ρ_b	Bulk density of soil (kg m^{-3})
ρ_l	Solution density (kg m^{-3})
ρ_v	Water vapor density (kg m^{-3})
σ	Osmotic efficiency coefficient
ϵ, τ	Constants for VOC diffusion coefficient in liquid phase
Φ	Decay coefficient (s^{-1})
Ψ_g	Gravity pressure head (m)
$\Psi_m(T_o)$	Matric water pressure head measured at reference temperature, T_o , (m)
Ψ_m	Matric water pressure head (m)
Ψ_o	Solution osmotic pressure head (m)
γ_w	Surface tension for free-water system (J/m^2)
γ_m	Surface tension of water as a function of VOC concentration (J/m^2)
ξ	Coefficient in Eq. (34)
ω_w	Association constant of aqueous solution

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