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MODELING THE FATE OF TOLUENE IN A CHAMBER WITH ALFALFA PLANTS
1. THEORY AND MODELING CONCEPTS

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ABSTRACT

A model was developed to investigate the fate of organic contaminants in soils in the presence of vegetation. The model has two modules. The first module simulates the soil-water and root-water pressure heads under the influence of water extraction by the roots of growing vegetation. Evapotranspiration due to alfalfa plants is an outflux boundary condition at the soil surface for this model. The distributions for water and air contents and Darcy water flux are obtained from the soil-water pressure heads. The second module simulates the fate of soil constituents in the porous medium using the Darcy water flux. The constituents assumed to be present in vegetated soil were contaminant, biomass, oxygen, and root exudates. A Galerkin finite element method was used to solve the model equations in two dimensions to enable comparison with an experimental system. The domain simulating the experimental chamber was assumed to be comprised of rectangular elements with bilinear shape functions which represented the variations within each element. Convergence to solution for the non-linear equations was accomplished using the Picard iterative algorithm. The time derivative was approximated using an implicit Crank-Nicholson scheme.

Key words: *soil, modeling, toluene, gas diffusion, phytoremediation, finite element model*

INTRODUCTION

Soil and groundwater pollution is of significant concern because hazardous organic pollutants in soil threaten the long-term quality of potable groundwater. The remediation of these pollutants usually is expensive. Bioremediation, in general, is effective in remediating sites contaminated with biodegradable organics (Lee et al., 1988; Hinchee and Olfenbuttel, l991a; Hinchee and Olfenbuttel, l991b). In recent years, bioremediation in the presence of plants has developed as a feasible technology (Erickson et al., 1994; Schnoor et al., 1995; Davis et al., 1998). This technology, referred to as phytoremediation or treemediation, is an emerging, effective, and economical method for cleaning up pollutants from contaminated sites. Successful engineering and application of this technology have been demonstrated in pilot and field scale studies (Cunningham and Berti, 1993; Gatliff, 1994; Narayanan et al., 1995; Schnoor et al., 1995; Davis et al., 1998).

Plants are beneficial at contaminated sites in several ways (Erickson et al., 1994; Schnoor et al., 1995; Davis et al., 1998). The exudates from the root tips enrich the root zone with a variety of carbon and energy yielding compounds including enzymes. The diverse indigenous soil microflora are maintained on these compounds and degrade the hazardous organics. Roots of the plants also help in immobilization and stabilization of contaminants by removing water and adsorbing the compounds onto root and soil surfaces. Evapotranspiration associated with plants, in general, helps in the upward move-

ment of groundwater and dissolved pollutants from subsurface to rhizosphere soil. The root zone of the soil is also relatively rich in oxygen because oxygen is constantly diffusing from the atmosphere into the top soil. In the root zone, biodegradation of organic contaminants is enhanced by both indigenous soil microorganisms and plant enzymes (Anderson et al., 1993; Shimp et al., 1993; Schnoor et al., 1995; Davis et al., 1998). Phytoremediation may be limited to less toxic and less recalcitrant compounds, but its limits are not yet defined.

Mathematical models of vegetative bioremediation are helpful tools for assessing the practical implications of phytoremediation. Simulation results help to predict the feasibility of proposed phytoremediation schemes. Knowledge of the groundwater hydrology, soil-water fluxes, site geological characteristics, contaminant phytotoxicity, and environmental factors are critical in modeling plant-based bioremediation. In this first of two papers, we focus on a mathematical model for analyzing the transport and fate of contaminants in the rhizosphere. The model incorporates processes that describe the movement of water in soil and roots which in turn impact the transport processes of contaminants, biomass, oxygen, and root exudates in the vegetated system. One of the objectives of mathematical modeling was to study the impact of plants on the upward movement of groundwater and dissolved solutes into the rhizosphere where microbes sustained on exudates degrade them. Another objective was to model the effects of vegetation on soil moisture, gas phase transport, root exudate concentration, and microbial populations.

The bioremediation model was previously validated for one-dimensional simulations and proposed in two-dimensions (Davis et al., 1993; Tracy et al., 1993; Tracy et al., 1994). The model has been extended to three dimensions and may be applied to study the movement of solutes in vegetation-mediated reclamation of any contaminated site. In order to compare experimental results from a two-dimensional chamber, the model proposed in three dimensions was modified and implemented in two dimensions in this study. The method of solution is described in some detail to assist others who wish to extend the model to other applications. The comparison of the modeling results to experimental laboratory results performed to study the fate of toluene in the presence of alfalfa plants is discussed in Narayanan et al. (1998a).

Researchers have developed models to study movement of water in vegetated soils under the influence of evapotranspiration (Feddes et al., 1975; Neuman et al., 1975; Marino and Tracy, 1988). Marino and Tracy (1988) proposed and verified a macroscopic root-soil water flow model that simulated the movement of water through a vegetated environment. The model includes processes such as water storage effects in the root system, and limiting and wilting root-water potentials that affect the plant's transpiration rate. The model is represented as a set of soil-water and root-water transport equations coupled through a root extraction term. In the work reported here, a similar approach is taken to mathematically model the movement of water in soil and roots.

Several models were developed to study the fate and transport of solutes in contaminated aquifers

(Borden and Bedient, 1986; Borden et al., 1986; Molz et al., 1986; Jinzhong, 1988; Rifai et al., 1988; Kindred and Celia, 1989; Sleep and Sykes, 1989; Chen et al., 1992; Malone et al., 1993; Essaid et al., 1995); however, some of these have not yet been employed in comparison with laboratory observations or field measurements (Molz et al., 1986; Kindred and Celia, 1989; Sleep and Sykes, 1989). Borden et al. (1986) simulated plume migration in contaminated aquifers and reported that microbial growth is oxygen limited quite instantaneously at the contaminated zones. They described the growth kinetics of microbes using a multiplicative Monod relation. Chen et al. (1992) developed a model, based upon five nonlinear partial differential equations, to simulate the degradation of aqueous benzene and toluene using two electron acceptors, oxygen and nitrate, and one trace nutrient. Sensitivity analyses and comparison with column data suggested that results were sensitive to microbial kinetic parameters such as maximum specific growth rate and saturation constant in the microbial growth model.

Essaid et al. (1995) developed and tested a two-dimensional multispecies reactive solute transport model for a contaminant plume at a Bemidji, Minnesota, crude oil spill site. They described aerobic and anaerobic biodegradation with sequential use of electron acceptors such as O_2, NO_3^-, Mn^{+2}, and Fe^{+2} associated with substrate and nutrient limitation. However, they did not incorporate transport of biomass in aquifers. Malone et al. (1993) discussed various biological models with substrate degradation limited due to oxygen depletion in aquifers contaminated with toluene as residual NAPL. They also included transport of toluene degradation intermediates that may play a role in biomass growth kinetics.

Several of the above cited models assumed constant groundwater velocity (pore water velocity) during the transport of solutes. However, in real-world aquifer situations that may not be appropriate. This is because groundwater velocities may change with precipitation and seasonal events which vary the watertable. Moreover, under the influence of vegetation, groundwater velocities in the horizontal and vertical directions may change. Other models included the effect of changing convective groundwater flux in the remediation process (Jinzhong, 1988; Sleep and Sykes, 1989). In this paper, transport due to varying soil-water fluxes is considered in the model.

Another significant term which should be included in the modeling of toluene is the diffusional flux. Gas-phase diffusional transport can be several orders of magnitude higher than liquid phase transport processes in soils when dealing with highly volatile solutes (Sleep and Sykes, 1989; Jin et al., 1994; Narayanan et al., 1998b). Gas-phase diffusional flux is incorporated in the study using the first-form (popular form) of the Millington-Quirk equation (Millington, 1959). The equation accounts for the tortuosity in the vapor phase during volatile transport through the soil-gas.

Models developed to study the fate and transport of contaminants in the presence of vegetation are relatively limited (Davis et al., 1993; Boersma et al., 1988; Trapp and McFarlane, 1995; Briggs et al., 1982). During phytoremediation there is a possibility of uptake and translocation of the contaminants

into plants depending on solute hydrophobicity. Boersma et al. (1988) modeled the passive and active uptake of xenobiotic chemicals by a compartmental representation of the physical and chemical processes in terrestrial plants. They also accounted for movement of water and organic nutrients within plants. Models considering active and passive processes for uptake of volatile and non-volatile contaminants interacting with roots and shoots have also been studied (Trapp and McFarlane, 1995). In our study, however, the uptake of toluene by plants is represented as a passive phenomenon based on models proposed by Briggs et al. (1982).

CONCEPTUAL MODEL AND GOVERNING EQUATIONS

To predict the fate of any solute in a rooted soil requires the integration together of several different process models, these being: (1) the movement of water; (2) the transport of solutes; and (3) the chemical and biological adsorption and transformation of solutes in a root-soil environment. In many practical problems, simulations of the fate of solutes in a root-soil environment can be performed in a one- or two-dimensional modeling domain. However, it should be noted that a significant assumption made when a one- or two-dimensional modeling domain is used is that variations in the model parameters and state variables are insignificant in the dimensions normal to the modeling domain. Under this assumption, the behavior of the state variables can be predicted as an average value over the dimensions normal to the modeling domain. Therefore, even if the simulations are performed in one or two dimensions, the conceptual model should be fully developed in a three-dimensional modeling domain. Thus, each of these process models are developed in a three-dimensional cartesian coordinate system, and integrated into a set of partial differential equations that govern the fate of solutes in a root-soil environment.

Soil-water and Root-water Flow Equations

The movement of soil-water in variably saturated soils (saturated and unsaturated) is important for the prediction of solute movement. The movement of soil-water and root-water is simulated based on a modified Richards equation (Marino and Tracy, 1988). If we consider a small three-dimensional element in a vegetated soil, then a soil-water flux mass balance results in a modified Richards equation (for derivation see Cooley, 1983):

$$\left[\beta S_s + S_y \frac{dS_e}{d\psi_s}\right]\frac{\partial \psi_s}{\partial t} = \frac{\partial}{\partial x_i}\left[K_{s,ij}\frac{\partial}{\partial x_j}\left(\psi_s + x_3\right)\right] - q \quad i,j = 1,2,3 \tag{1}$$

where, i and j are direction indices in a Cartesian coordinate system such that $x_1 = x$, $x_2 = y$ are horizontal directions and $x_3 = z$ is the vertical direction. A repetition of subscript symbols in the model equations indicates summation over all possible values of the subscripts. $K_{s,ij}$ represents the components of the hydraulic conductivity tensor of the soil and ψ_s is the pressure head of soil water. A description of various symbols used in this model representation is included in the notation section. Equation (1) is assumed to govern the flow of soil-water in the unsaturated and saturated regions (Marino and Tracy, 1988). A similar balance for root-water flowing through a root segment present in this soil element yields the following form of root-water flow equation (for derivation see Marino and Tracy, 1988):

$$R_d \frac{\partial}{\partial t}\left(WC_r\right) + WC_r \frac{\partial R_d}{\partial t} = \frac{\partial}{\partial x_i}\left[K_{r,ij} R_d \frac{\partial}{\partial x_j}\left(\psi_r + x_3\right)\right] + q \quad i,j = 1,2,3 \tag{2}$$

The root-water extraction term, q in Eqs. (1) and (2), as defined by Marino and Tracy (1988), is the rate of water extracted by vegetation averaged over a representative horizontal area of the soil element. The expression for q is:

$$q = S_w R_d \Gamma\left(\psi_s - \psi_r\right) \tag{3}$$

where Γ is a lumped parameter describing the permeability of a plant's root system. It may be noted that in the above Eqs. (2) and (3), the total amount of water extracted by roots (q) is a function of the pressure head gradient ($\psi_s - \psi_r$) across root boundaries, degree of soil saturation (S_w), rooting depth (z) and rooting density (R_d) of the vegetation. Additional empirical soil characteristic relationships used to interrelate values of ψ_s, $K_{s,ij}$, and S_e are:

$$S_e = \frac{A}{A + \left(\psi_a - \psi_s\right)^c} \qquad \psi_s < \psi_a \tag{4}$$
$$S_e = 1 \qquad \psi_s \geq \psi_a$$

and

$$K_{s,ij} = K_{sat}\left(S_e\right)^d \tag{5}$$

where S_e is the effective saturation, defined as

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \frac{S_w - S_r}{1 - S_r} \tag{6}$$

where degree of saturation, S_w, is equal to θ/η and S_r is the residual saturation (Corey, 1977). A, c, and d are empirically determined soil characteristic parameters and ψ_a is the air entry value of soil-water pressure head which is often assumed to be zero. Equation (4) is the generalized form of Brutsaert equation (Brutsaert, 1966). Equations (5) and (6) were proposed by Brooks and Corey (Corey, 1977). The influence of A, c, and d on the curves of S_e versus ψ_s and $K_{s,ij}$ versus S_e are well discussed by Winter (1983).

Equations (1) and (2) together now represent the soil-root water flow model in a vegetated soil. The superficial groundwater velocity or Darcy flux (V_i) may be obtained from Eqs. (1) and (2) after determining the soil-water pressure head (ψ_s) in the system. Darcy flux of soil-water may be written as:

$$V_i = -K_{s,ij}\frac{\partial}{\partial x_j}\left(\psi_s + x_3\right) \tag{7}$$

The Darcy soil-water fluxes can then be used to determine the convective flux in the transport equations for soil constituents.

Initial and Boundary Conditions

The soil-water and root-water equations need to be supplemented with appropriate initial and boundary conditions for obtaining the soil-water (ψ_s) and root-water pressure heads (ψ_r). For initial conditions, pressure heads in the entire domain Ω at time $t = 0$ need to known. i.e.,

$$\psi_s(x_i,0) = \Psi_{so}(x_i) \tag{8}$$

$$\psi_r(x_i,0) = \Psi_{ro}(x_i) \tag{9}$$

where $\Psi_{so}(x_i)$ and $\Psi_{ro}(x_i)$ are known distributions of soil and root-water pressure heads, respectively, at time $t = 0$. For boundary conditions, one must specify either the soil-water pressure heads [$\Psi_s(x_i,t)$] (Dirichlet kind of boundary condition)

$$\psi_s(x_i,t) = \Psi_s(x_i,t) \qquad on \ \Gamma_1 \tag{10}$$

or the normal flux of soil-water (V_w) (Neuman kind of boundary condition)

$$-K_{s,ij}\left(\frac{\partial}{\partial x_j}\left(\psi_s + x_3\right)\right)n_i = V_w \qquad on \ \Gamma_2 \tag{11}$$

where G_1 is a segment of the boundary of domain W along which the pressure heads are specified and G_2 is a complementary segment of G_1 along which normal fluxes may or may not be specified. n_i is the ith component of the unit vector normal to the boundary G_2 with positive direction as inward. V_w is taken positive for influx and negative for outflux of water.

At the soil surface, the soil-water flux boundary condition for soil-water flow, Eq. (1), depends on the evaporation and transpiration rates. The potential evaporation rate of water or limiting evaporation rate of water is based on the soil moisture content and atmospheric conditions (Neuman and Davis, 1983). Hence, the evaporation flux at the surface may be written as:

$$K_{s,ij}\left(\frac{\partial}{\partial x_j}\left(\psi_s + x_3\right)\right) = E \quad at \ surface \tag{12}$$

in which E is the limiting evaporation rate from highly dried soils when $\psi_s < \psi_{s,lim}$ at the soil surface and E is the potential evaporation rate (E_p) for conditions when $\psi_s > \psi_{s,lim}$ at the soil surface. E may vary with time in the simulation. In this simulation study, the potential rate of evaporation, E_p, used as soil-water flux boundary condition at the soil surface is calculated from the total observed evapotranspiration rate as follows:

$$E_p = ET\left(\exp\left(-b \ LAI\right)\right) \tag{13}$$

Similarly, the root-water flux boundary condition for the root-water flow Eq. (2) at the soil-surface may include specification of the transpiration rate of water by the vegetation. The rate of transpiration is also subject to a limiting value or potential value based on the prevailing atmospheric conditions and rate of change of water in the plants. This boundary condition may be represented as:

$$K_{r,ij}R_d\left(\frac{\partial}{\partial x_j}\left(\psi_r + x_3\right)\right) = T \quad at \ surface \tag{14}$$

wherein

$$T = T_p \qquad \psi_r\left(x_i,t\right) > \psi_{r,lim}\left(x_i,t\right) \tag{15}$$

and

$$T = T_p\left[1 - \frac{\left(\psi_r - \psi_{r,lim}\right)}{\left(\psi_{r,wilt} - \psi_{r,lim}\right)}\right] \quad \psi_{r,wilt} < \psi_r < \psi_{r,lim} \tag{16}$$

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where $\psi_{r,wilt}$ is the wilting root-water pressure head based on atmospheric conditions and plants used for bioremediation and finally,

$$T = 0 \qquad \psi_r(x_i,t) < \psi_{r,wilt}(x_i,t) \tag{17}$$

The potential transpiration rate by plants, T_p, can be obtained from total observed evapo-transpiration (*ET*) associated with both the plants and the soil based on plant growth period (Feddes et al., 1975; Neuman et al., 1975). The expression for T_p is:

$$T_p = ET\left(1 - \exp\left(-b\ LAI\right)\right) \tag{18}$$

where parameters *b* and *LAI* are plant related parameters. Leaf area index (*LAI*) may change with time due to plant growth though it is assumed to be constant in this simulation study. The above mentioned boundary conditions are handled conveniently using the finite element method.

Solute and Biomass Transport Equations

The soil matrix is assumed to be an isotropic and variably saturated porous medium. The interstitial spaces between the soil particles may be occupied by water and gas phases. Below the water table, the soil is fully saturated with water (no gas phase), while in the vadose zone (which usually includes the rhizosphere) water and gas phases are both present. Thus, in the saturated zone the water content, θ, is equal to the porosity. i.e.,

$$\theta = \theta_s = \eta \tag{19}$$

In the unsaturated zone, the void fraction, θ_a, occupied by the gas phase is

$$\theta_a = \eta - \theta \tag{20}$$

The solutes and biomass assumed to be present in a vegetated soil environment and accounted for in this model development are the organic contaminant (subscript *s*), aerobic microorganisms (subscript *b*), atmospheric oxygen (subscript *o*), and exudates secreted by roots (subscript *r*).

There are a number of physical and chemical phenomena associated with the fate and transport processes of solutes in variably saturated soil. Each of the solutes and biomass may undergo subsurface transport either due to convection, dispersion, or diffusion. For the organic contaminant and oxygen, gas-phase diffusional transport may be predominant because of high volatility and vapor pressure associated with these solutes. For others, convective-dispersive fluxes may be the only important mechanism for transport. However, in general, the governing mass balance equation for any soil constituent *k* in a variably saturated porous medium may be written as:

$$\frac{\partial}{\partial t}\left[C_k\theta + R_dP_k + \rho S_k + \theta_aC_{g,k}\right] =$$

$$= \frac{\partial}{\partial x_i}\left[\theta D_{ij}\frac{\partial}{\partial x_j}(C_k) + D_{eff,k}\frac{\partial}{\partial x_j}(C_{g,k}) - V_iC_k\right] \pm G_k \qquad (21)$$

where subscript k may represent s, b, o, or r. C_k, P_k, S_k, and $C_{g,k}$ are concentration of constituent k in water, plant roots, soil solid, and gas phases, respectively. By assuming linear local equilibrium partitioning of constituents between the various phases, we can correlate the local concentrations of constituent in each phase to one another. To describe the equilibrium relationships, solid phase concentration, S_k, is proportional to the aqueous phase concentration C_k and is written as:

$$S_k = K_{dk}\ C_k \qquad (22)$$

K_{do}, adsorption coefficient of oxygen, is set to be zero in this simulation study. K_{ds}, the adsorption coefficient of contaminant, is usually dependent upon the soil-organic carbon content (f_{oc}) and K_{oc} value tabulated in literature according to the relationship:

$$K_{ds} = K_{oc}\ f_{oc} \qquad (23)$$

Similarly, gas phase concentration, $C_{g,k}$ is proportional to aqueous phase concentration C_k:

$$C_{g,k} = H_kC_k \qquad (24)$$

where H_k is the Henry's law constant of constituent k which can be obtained for contaminant and oxygen from tabulated values in literature. H_b is assumed to be zero as the microbial biomass is not volatile and H_r is assumed to be arbitrarily set to 1.0.

The coefficient $D_{eff,k}$ is the effective gaseous diffusion coefficient of soil constituent k in the subsurface soil gas. This effective diffusion coefficient depends on the tortuosity factor in subsurface soil. The equation defining the $D_{eff,k}$ may be represented using the popular form of Millington-Quirk equation in soil environments. i.e.,

$$D_{eff,k} = \frac{\theta_a^{10/3}}{\eta^2}D_{ak} \qquad (25)$$

Using Eqs. (24) and (25), we represent the diffusional flux in the gas phase as follows:

$$Gas\ Diffusional\ flux = \frac{\theta_a^{10/3}}{\eta^2}D_{ak}H_k\frac{\partial C_k}{\partial x_j} = \xi_kD_{ak}\frac{\partial C_k}{\partial x_j} \qquad (26a)$$

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where:

$$\xi_k = \frac{\theta_a^{10/3}}{\eta^2} H_k \tag{26b}$$

Convective flux in the water phase (or Darcy flux of soil-water), V_i, is employed from the values calculated from Eq. (7). Gas phase convective transport is assumed to be insignificant in this study; however, this phenomenon may be significant in pressure-driven processes such as soil-vapor extraction or density-driven processes during volatilization. The hydrodynamic dispersion term D_{ij} in Eq. (21) is calculated based on the Darcy's soil-water fluxes (V_i) and the dispersivity factors (a_L and a_T) which are characteristic to the soil utilized. The relationship for dispersion tensor, D_{ij}, is defined by:

$$\theta D_{ij} = \alpha_T |V| \delta_{ij} + (\alpha_L - \alpha_T)(V_i V_j / |V|) \tag{27}$$

Molecular diffusion in the aqueous phase is considered to be negligible in this study. However, at very low groundwater velocities this phenomenon may be the controlling mechanism. The term G_k in Eq. (21) represents the source term (positive) or sink term (negative) contributions for soil constituent k due to plant uptake and microbially mediated biodegradation processes.

Microbial degradation

Several conceptual models for microbial growth and transport that influence contaminant biodegradation have been investigated. One approach for expressing biomass activity in soils is by representing it as biofilm and microcolonies in microscopic growth models, which include mass transfer coefficients associated with diffusion of substrates and nutrients across a film present on the biophase (Molz et al., 1986; Chen et al., 1992). In the macroscopic approach, microbial biomass is transported and sorbed to the soil particles and root surfaces. Also, biomass growth is assumed to be nutrient and substrate limited (Borden et al., 1986; Kindred and Celia, 1989). Since microbial growth may be limited by more than one substrate or nutrient, a Monod kinetic model based on multiple substrates and nutrients is often employed (Bailey and Ollis, 1986; Molz et al., 1986). The carbon substrate is generally the principal constituent that limits the growth of biomass in soil environments. Oxygen can also limit aerobic bioremediation processes in soil environments. Limitations to growth of microorganisms may occur due to other micronutrients such as nitrogen and phosphorous. However, in this model, the focus is only on carbon and oxygen as the two essential nutrients limiting the growth of indigenous aerobic microorganisms. A two-substrate Monod kinetic model is used to describe this behavior.

The rhizosphere supports an enhanced microbial population because root exudates contain a variety of carbon compounds which act as growth substrates. The concentration of root exudates is included as growth substrate in the Monod model for vegetated soils; i.e.,

$$G_b = -Y_o G_o = \mu_m (\theta + R_d R_b + \rho K_{db}) C_b \left[\frac{C_s + C_r}{(K_{rs} + C_s + C_r)} \left(\frac{C_o}{K_o + C_o} \right) \right] \qquad (28a)$$

Similarly, the contaminant and root exudate degradation may be represented as:

$$G_s = -\left(\frac{\mu_m}{Y_s} \right) (\theta + R_d R_b + \rho K_{db}) C_b \left[\frac{C_s}{(K_{rs} + C_s + C_r)} \left(\frac{C_o}{K_o + C_o} \right) \right] \qquad (28b)$$

$$G_r = -\left(\frac{\mu_m}{Y_r} \right) (\theta + R_d R_b + \rho K_{db}) C_b \left[\frac{C_r}{(K_{rs} + C_s + C_r)} \left(\frac{C_o}{K_o + C_o} \right) \right] \qquad (28c)$$

The endogenous decay or specific decay parameters (k_{d1} and k_{d2}) of indigenous microorganisms in soils may not be constant during long time periods of biodegradation studies (Essaid et al. 1995). The rate may be a function of the concentration of toxic intermediates and/or a function of biomass concentration (Kindred and Celia, 1989). In this model, the endogenous decay rate is assumed to be a function of biomass concentration. This is because, when there is high concentration of biomass, substrate and nutrient concentrations become limiting due to competition. This may result in high death rate and depletion in biomass concentration. Moreover, in the presence of large microbial populations, protozoal grazing of bacteria in soils can reduce the biomass concentration. Hence, the endogenous decay in this model is assumed as shown below.

$$G_b = -(\theta + R_d R_b + \rho K_{db})(k_{d1} + k_{d2} C_b) C_b \qquad (29)$$

Mathematically, when C_b is relatively high, the death rate term which is second order with respect to biomass concentration increases rapidly and thereby limits the biomass concentration. However, at low C_b values, endogenous decay follows simple first-order kinetics.

Plant-related processes

Evapotranspiration is a significant process that influences the vertical movement of water in the soil. Dissolved contaminants may also be transported in the vertical direction because of this phenomenon. The contaminants may be immobilized on the roots or taken up and translocated in the transpiration stream of the plant. It was reported that the extent of uptake or translocation of organic contaminants or solutes, in general, in vegetation can be expressed using mathematical relationships developed by Briggs et al. (1982). Sorption by the roots is expressed in terms of the root concentration factor (R_{cf}) and shoot uptake is modeled by a transpiration stream concentration factor (T_{scf}). R_{cf} is defined as the ratio of the solute concentration in the roots to that of the

concentration in the soil-water, whereas T_{scf} is defined as the ratio of the solute concentration in the transpiration stream to that of the concentration in the soil-water.

The R_{cf} and T_{scf} are correlated via log K_{ow} (the octanol-water partition coefficient) values that are characteristic to the solutes involved and determine the extent of passive uptake of solutes by plants. The octanol-water partition coefficient (K_{ow}) is defined as the ratio of the concentration of solute in the octanol phase to that in the aqueous phase. The extent of plant uptake of solutes with different log K_{ow} values is well discussed in Cunningham and Berti (1993). Equations (30) and (31) shown below are the mathematical relations between R_{cf}, T_{scf}, and log K_{ow} as proposed by Briggs et al. (1982) based on regression analysis obtained after their study on the uptake of several classes of pesticidal chemicals by barley plants. It should be noted that these are non-volatile compounds which accumulate within the plant. The following relationships used in this model account for the uptake and translocation of the contaminants in the plants.

$$R_{cf} = 0.82 + 10^{(0.77\log K_{ow} - 1.52)} \tag{30}$$

$$T_{scf} = 0.784 \ \exp\left(-\frac{(\log K_{ow} - 1.78)^2}{2.44}\right) \tag{31}$$

Using these relationships the extent of root uptake (P_k) in Eq. (21) for substrate s is given by:

$$P_s = R_{cf} \ C_s \tag{32a}$$

and P_b for biomass and P_r for root exudates are given as:

$$P_b = R_b C_b; \qquad P_r = R_r \ C_r \tag{32b}$$

However, R_o for oxygen is assumed to be zero. The extent of plant uptake of contaminant may then be written as:

$$G_s = qT_{scf}C_s \tag{33a}$$

while the extent of plant uptake of oxygen and root exudates may be represented as:

$$G_o = -qT_o \ C_o; \qquad G_r = -qT_r \ C_r \tag{33b}$$

However, G_b is assumed to be zero. The root density (R_d) is assumed to vary with depth such that R_d is larger near the soil surface, and very small or zero at the bottom of the channel. An exponential relation as shown below is used for this representation.

$$R_d = R_{d,s} \exp(-d_r\, h) \tag{33c}$$

where vertical dimension h is measured from the soil surface, coefficient d_r is the root index drop rate, and $R_{d,s}$ is the root density at the soil surface (Tracy and Marino, 1989). This relationship is assumed constant throughout the time period of simulation.

Assumptions in the model

The significant assumptions involved in the model are as follows:

(1) The model is in three dimensions. It can be reduced to two dimensions depending on the study where one dimension is in the horizontal direction, along the direction of groundwater flow, and the other the vertical direction, representing the movement due to evapotranspiration;

(2) The mass balances are written for elements present in the root zone of plants;

(3) Plants are assumed to be well-adapted and tolerant to the concentration of organics;

(4) The root density decreases exponentially from the surface to the bottom of the channel.

(5) Mass transport processes in the liquid phase are predominantly in the form of advective and dispersive transport while diffusional mass transport in liquid phase is negligible;

(6) Gas-phase diffusional transport for oxygen and volatile organics in the soil is considered;

(7) Contaminants present in the soil and groundwater are in the form of dissolved contaminants in the aqueous phase rather than existing as non-aqueous phase liquid (NAPL) blobs;

(8) Microbial growth is limited only by carbon and oxygen substrates;

(9) Microbial degradation is only due to aerobic soil microorganisms;

Governing equations

If we represent the governing model equations for contaminant in the vegetated soil based on Eq. (21) and incorporate Eqs. (22), (24), (26a), (28b), (32a) and (33a), we have

Rate of change in contaminant concentration   *Plant uptake*

$$\frac{\partial}{\partial t}\left[C_s\left(\theta + R_d R_{cf} + \rho K_{ds} + \theta_a H_s\right)\right] = -q T_{scf} C_s$$

Contaminant transport

$$+ \frac{\partial}{\partial x_i}\left[\theta D_{ij}\frac{\partial}{\partial x_j}(C_s) + \left(\xi_s D_{as}\right)\frac{\partial}{\partial x_j}(C_s) - V_i C_s\right] \tag{34}$$

Contaminant degradation by biomass

$$-\left(\frac{\mu_m}{Y_s}\right)\left(\theta + R_d R_b + \rho K_{db}\right)C_b\left[\frac{C_s}{K_{rs} + C_s + C_r}\left(\frac{C_o}{K_o + C_o}\right)\right]$$

The governing differential equation for the microorganisms can be represented based on Eq. (21) and incorporating Eqs. (22), (28a), (29), and (32b).

Rate of change in biomass concentration   *Biomass decay*

$$\frac{\partial}{\partial t}\left[C_b\left(\theta + R_d R_b + \rho K_{db}\right)\right] = -\left(\theta + R_d R_b + \rho K_{db}\right)\left(k_{d1} + k_{d2} C_b\right)C_b$$

Biomass transport

$$+\frac{\partial}{\partial x_i}\left[\theta D_{ij}\frac{\partial}{\partial x_j}\left(C_b\right) - V_i C_b\right] \tag{35}$$

Biomass growth

$$+\mu_m\left(\theta + R_d R_b + \rho K_{db}\right)C_b\left[\frac{C_s + C_r}{K_{rs} + C_s + C_r}\left(\frac{C_o}{K_o + C_o}\right)\right]$$

Similar governing differential equations for the oxygen and root exudates may be written as:

Rate of change in exudate concentration   *Plant uptake*   *Exudate loading*

$$\frac{\partial}{\partial t}\left[C_r\left(\theta + R_d R_r + \rho K_{dr} + \theta_a H_r\right)\right] = -q T_r C_r \quad + \quad q_r C_{rr}$$

Exudate transport

$$+\frac{\partial}{\partial x_i}\left[\theta D_{ij}\frac{\partial}{\partial x_j}\left(C_r\right) + \left(\xi_r D_{ar}\right)\frac{\partial}{\partial x_j}\left(C_r\right) - V_i C_r\right] \tag{36}$$

Exudate consumption by biomass

$$-\left(\frac{\mu_m}{Y_r}\right)\left(\theta + R_d R_b + \rho K_{db}\right)C_b\left[\frac{C_r}{K_{rs} + C_s + C_r}\left(\frac{C_o}{K_o + C_o}\right)\right]$$

Rate of change in oxygen concentration   *Plant uptake*

$$\frac{\partial}{\partial t}\left[C_o\left(\theta + \theta_a H_o\right)\right] \qquad = \qquad -q T_o C_o$$

Oxygen transport

$$+\frac{\partial}{\partial x_i}\left[\theta D_{ij}\frac{\partial}{\partial x_j}\left(C_o\right) + \left(\xi_o D_{ao}\right)\frac{\partial}{\partial x_j}\left(C_o\right) - V_i C_o\right] \tag{37}$$

Oxygen consumption by biomass

$$-\left(\frac{\mu_m}{Y_o}\right)\left(\theta + R_d R_b + \rho K_{db}\right)C_b\left[\frac{C_s + C_r}{K_{rs} + C_s + C_r}\left(\frac{C_o}{K_o + C_o}\right)\right]$$

Equations (34)-(37) are used to describe the biodegradation of a contaminant by microbes in the presence of oxygen and root exudates in the root zone of well-adapted and growing plants.

Initial and Boundary Conditions

In order to solve Eqs. (34)-(37) simultaneously, one must specify the initial and boundary conditions for the problem. For the initial conditions, concentration of soil constituent k must be specified at time $t = 0$. i.e.,

$$C_k(x_i,0) = \overline{C}_{o,k}(x_i) \tag{38}$$

where $\overline{C}_{o,k}(x_i)$ is the prescribed concentration of soil constituent k at time $t = 0$. The boundary conditions for constituent k may be a specified concentration $(\overline{C}_{in,k})$ along a boundary G_3 (Dirichlet kind of boundary condition) on domain W,

$$C_k(x_i,t) = \overline{C}_{in,k}(x_i,t) \quad on\ \Gamma_3 \tag{39}$$

and/or a specified normal flux (F_k) along a boundary G_4 (Neuman kind of boundary condition) on domain W, i.e.,

$$-\left(\theta D_{ij}\frac{\partial}{\partial x_j}(C_k) + \xi_k D_{ak}\frac{\partial}{\partial x_j}(C_k) - V_i C_k\right)n_i = F_k \tag{40}$$

and/or a zero normal flux boundary condition at the boundary G_5 on domain W.

$$\frac{\partial}{\partial x_i}(C_k) = 0 \quad on\ \Gamma_5 \tag{41}$$

where, n_i is the ith component of the unit vector normal to the boundary G_4 with positive direction as inward. F_k is taken positive for influx and negative for outflux of soil constituent k.

Finite Element Formulation

The developed model Eqs. (1), (2), and (34)-(37) are applicable to a three-dimensional Cartesian coordinate system. In order to enable a comparison of numerical results with an experimental chamber (Narayanan et al., 1995; Narayanan et al., 1998a), the finite element formulation described in this paper for Eqs. (1), (2), and (34)-(37) are restricted to two dimensions (x and z). The variation in the y direction is assumed negligible in our system. The model was originally validated for Eqs. (1), (2), and (34) in one dimension (Tracy and Marino, 1989). The limiting cases of model Eqs. (1), (2), and (34)-(37) in one dimension were discussed in Tracy et al.,

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(1993) and Tracy et al., (1994). The Galerkin finite element approach in conjunction with a specific discretization scheme is employed in this study.

In the Galerkin finite element method, initially the entire domain W is assumed to be subdivided into a network of elements. Rectangular elements with the four corners designated as nodal points, are employed in this study. The approximate solutions for soil-water pressure head in Eq. (1), root-water pressure head in Eq. (2), and concentration of soil constituent k in any of the four Eqs. (34) through (37) at any given time in the entire system may be represented as:

$$\overline{\Psi}_s(x,z,t) = \sum_{i=1}^{Npt} N_i(x,z)\ \psi_{s,i}(t) \tag{42}$$

$$\overline{\Psi}_r(x,z,t) = \sum_{i=1}^{Npt} N_i(x,z)\ \psi_{r,i}(t) \tag{43}$$

$$\overline{C}_k(x,z,t) = \sum_{i=1}^{Npt} N_i(x,z)\ C_{k,i}(t) \tag{44}$$

In Eqs. (42) through (44), the coefficients $\psi_{s,i}(t)$, $\psi_{r,i}(t)$, and $C_{k,i}(t)$ are time dependent values at the ith nodal point of the soil-water pressure head (ψ_s) root-water pressure head (ψ_r) and soil constituent concentration (C_k), respectively. *Npt* represents the number of nodal points in the entire domain W. The symbols $\overline{\psi}_s$, $\overline{\psi}_r$, and $\overline{C}_k$ represent the approximate solution of the soil-water pressure head (ψ_s) root-water pressure head (ψ_r) and soil constituent concentration (C_k), respectively. $N_i(x,z)$ in Eqs. (42)-(44) represents the piecewise shape (or basis) function at node i in terms of x and z. The shape function for a node i defined in this study are such that at any nodal point j for $j = 1...Npt$

$$N_i(x,z) = \delta_{ij} \tag{45}$$

where, δ_{ij} is the Kronecker delta function defined to be 1.0 when $i = j$ and zero otherwise. In other words, $N_i(x,z)$ is 1.0 only when x and z are spatial coordinates of the ith nodal point in the domain W and zero at all other nodal points in the spatial domain. Further, the piecewise shape functions $N_i(x,z)$ possess the property that:

$$N_i(x,z) = \sum_{e=1}^{Ne} N_i^e(x,z) \tag{46}$$

where, N_i^e is the elemental shape function at node i associated with element e and *Ne* is the number of elements in the entire domain W. It must be noted that N_i^e at node i is 1.0 and zero at all other nodes of element e.

The elemental shape function at node i, N_i^e, varies monotonically within the element e which contains node i as one of its nodes or is zero otherwise. Any linear or non-linear functions such as quadratic or cubic (Hermite or Lagrange type) functions could be used as elemental shape functions. In the Galerkin method pursued in this study, the elemental shape function at node i, N_i^e, is assumed to vary linearly within the element from 1.0 at node i to zero at other nodes in the same element e.

On substituting the approximate solutions $\overline{\psi}_s$, $\overline{\psi}_r$, and $\overline{C}_k$ in Eqs (1), (2), and (34)-(37), a residual (R) results from the six principal Eqs. (1), (2), and (34)-(37). Each of the six principal model Eqs. (1), (2), (34), (35), (36), and (37) are from here on referred to by the index m such that $m = 1$ indicates Eq. (1), $m = 2$ indicates Eq. (2), $m = 3$ indicates Eq. (34) and so on. The statement of finite element formulation for any principal equation m in weighted residual form may then be written as:

$$\iint\limits_{\Omega} R_m\, N_i\, dxdz = 0; \quad i = 1,2,....,Ne \tag{47}$$

where, R_m is the residual (R) for equation m and N_i is the weighting function (in this case the same shape functions). Equation (47) may also be interpreted as setting the residual (R_m) orthogonal to all the shape functions N_i defined in Eqs. (42)-(44).

Quantities such as hydraulic conductivity, Darcy flux, q, $dS_e/d\psi_s$, S_e, R_d, m, and the reciprocal of the tortuosity factor for gas phase diffusion (x) vary either explicitly or implicitly with ψ_s, ψ_r or C_k according to some prescribed constitutive relationships described earlier for the domain Ω. For simplicity, the variation of these dependent quantities is assumed to be linear with x and z within any elemental domain. However, the variation of these dependent quantities from one nodal point to another nodal point is governed by the prescribed constitutive relationships. Hence, if f is one such varying dependent quantity in domain Ω then f for entire domain is defined as:

$$f\left(\psi_s, \psi_r, C_k\right) = \sum_{i-1}^{Npt} f\left(\psi_{s,i}, \psi_{r,i}, C_{k,i}\right)\, N_i(x,z) \tag{48}$$

By combining Eqs. (42)-(48) and using Green's first identity, one obtains a coupled system of six non-linear matrix differential equations which may be written as follows:

$$A_m\left(U_m\right)\left[\frac{dU_m}{dt}\right] + B_m\left(U_m\right)\left[U_m\right] = Q_m \tag{49}$$

where, U_m represents any of the unknowns ψ_s, ψ_r or C_k corresponding to the model equation m used to represent Eq. (49); A_m and B_m are matrices of dimensions $Npt\, X\, Npt$ and functions of

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variable U_m only. Matrix A_m resulting from the shape functions and time coefficient of differential equation m is called the mass matrix. Matrix B_m resulting from the spatial derivatives of the shape functions is called the conductivity matrix. Q_m of dimension $Npt \, X1$ is called the load matrix of the differential equation m. Development of the coefficients matrices are included in Appendix A for the governing differential Eq. (34). An exactly identical procedure may be adopted in developing Eq. (49) for the other principal differential Eqs. ((1), (2), (35)-(37)).

The derivative of variable U_m with respect to time in Eq. (49) can be approximated using a weighted Crank-Nicholson central difference scheme (Huyakorn and Pinder, 1983; Zienkiewicz and Morgan, 1983). Equation (49) may then be rewritten as:

$$\left\{ wB_m \, \Delta t^n + A_m \right\} \left[U_m^n \right] = \left\{ Q_m \Delta t^n \right\} + \left\{ A_m - (1-w) B_m \, \Delta t^n \right\} \left[U_m^{n-1} \right] \tag{50}$$

where, U_m^{n-l} represents the solution of the variable U_m (Y_s, Y_r or C_k) for equation m after the $(n-l)$th time step of simulation, w is a Crank-Nicholson weighting factor equal to 0.5, and $\mathrm{D}t^n$ is the nth time step increment for the simulation. Equation (50) represents a system of $Npt \, X \, m$ non-linear equations that needs to be solved iteratively at all the time steps of simulation. The iterative method of convergence followed in this formulation is the Picard iteration scheme (Huyakorn and Pinder, 1983; Zienkiewicz and Morgan, 1983). After each iteration, an improved value of variable U_m^n is obtained as shown below and re-substituted in coefficients of Eq. (50) to obtain the new converged solution for U_m^n at the nth time step.

$$U_m^n = \frac{U_m^n + U_m^{n-1}}{2} \tag{51}$$

After obtaining a satisfactory convergence according to a prescribed tolerance limit for variable U_m^n at nth time step, the guess values for the iteration at the $(n+l)$th time step are based on the extrapolation of the known values to values at time step $(n+1/2)$ as shown below:

$$U_m^{n+1/2} = U_m^n + \frac{\Delta t^n}{2\Delta t^{n-1}} \left(U_m^n - U_m^{n-1} \right) \tag{52}$$

where, $\mathrm{D}t^n$ and $\mathrm{D}t^{n-l}$ are nth and $(n-l)$th time steps, respectively. The coefficients of Eq. (50) are then again evaluated at the new guess values and iteration at the $(n+1)$th time step is initiated until a satisfactory convergence is achieved.

METHOD OF SOLUTION

The model Eqs. (1), (2), and (34)-(37) need to be solved simultaneously to obtain the approximate solutions ($\overline{\mathrm{Y}}_s$, $\overline{\mathrm{Y}}_r$ or $\overline{C}_k$). However, a decoupling mechanism of the soil and root-water flow model from the solute transport model can be employed which successfully helps to solve for the approximate solutions with rapidity. The coupled Eqs. (1) and (2) are, therefore, first

solved independently for both $\overline{y}_s$ and $\overline{y}_r$. Darcy flux of soil-water and soil-water content may then be obtained from Eq. (7), and Eq. (4) and Eq. (6), respectively. Subsequently, at the same time step, the Darcy flux V_i and calculated water content q are used in the transport model Eqs. (34)-(37) to obtain the approximate concentrations of soil constituent k. Figure 1 shows a schematic of the solution methodology.

To begin the simulation, Eq. (49) is first solved by ignoring the term containing the time derivative. This step is similar to solving for the approximate solution of the model Eqs. (1), (2), and (34)-(37) assuming a steady state situation. The solution at the first time step is then obtained by assuming the steady state solution as the initial condition for the simulation. Boundary conditions are always applied to Eq. (52) appropriately. Evaporation boundary conditions at the soil surface; influx, outflux, and no flux of water and solute at the known boundaries; or constant concentration of solute at given boundaries of the system are applied accordingly to Eq. (50) during the solution procedure. Numerical results are presented in Narayanan et al. (1998a).

CONCLUSIONS

A comprehensive phytoremediation model was developed in three dimensions. The model considers the movement of water in a variably saturated soil and in the roots of vegetation. The root-soil water model equations were solved for the pressure head distribution which was used to determine the Darcy flux and soil-water content distribution in the system. The movement and fate of soil constituents (contaminant, biomass, oxygen, and root exudates) was modeled with evapotranspiring vegetation. The set of model equations was solved using Galerkin finite element method with bilinear shape functions and Picard iterative algorithm for non-linearity. The solution methodology involved solving the soil-root water flow model first and then solving the transport equations at the same time step. The finite element formulation was developed for two dimensions in this paper in order to compare the simulation results with experimental data obtained in a laboratory chamber. The model can be easily employed to simulate the fate of contaminants in a vegetated soil particularly with relatively shallow unconfined aquifers.

ACKNOWLEDGMENTS

APPENDIX A

Derivation of coefficient matrices in Eq. (49)

Equation (34) is chosen to show the development of the coefficient matrices in Eq. (49) because of the presence of several different kinds of terms in the expression. To begin with, Eq. (34) may be rewritten as shown below.

$$\frac{\partial}{\partial t}\Big[C_s\big(\theta + R_d R_{cf} + \rho K_{ds} + \theta_a H_s\big)\Big] =$$
$$+ \frac{\partial}{\partial x_i}\Big[\theta D_{ij}\frac{\partial}{\partial x_j} + \big(\xi_s D_{as}\big)\frac{\partial}{\partial x_j} - V_i\Big] C_s \tag{A1}$$
$$- \Bigg(qT_{scf} + \frac{\mu_m\big(\theta + R_d R_b + \rho K_{db}\big)C_b C_o}{Y_s\big(K_{rs} + C_s + C_r\big)\big(K_o + C_o\big)}\Bigg) C_s$$

When the exact solution for the contaminant concentration (C_s) in the above equation is replaced with the an approximate solution ($\overline{C}_s$), a residual error term R_3 results in the expression as shown below. Subscript 3 is used for the residual term to indicate that it represents the third principal equation.

$$\frac{\partial}{\partial t}\big[\Delta_1\,\overline{C}_s\big] = -\Delta_2\,\overline{C}_s + \frac{\partial}{\partial x_i}\Big[\Delta_3\frac{\partial}{\partial x_j} - \Delta_4\Big]\overline{C}_s + R_3 \tag{A2}$$

where,

$$\Delta_1 = \big(\theta + R_d R_{cf} + \rho K_{ds} + \theta_a H_s\big)$$
$$\Delta_2 = \Bigg(qT_{scf} + \frac{\mu_m\big(\theta + R_d R_b + \rho K_{db}\big)\overline{C}_b\overline{C}_o}{Y_s\big(K_{rs} + \overline{C}_s + \overline{C}_r\big)\big(K_o + \overline{C}_o\big)}\Bigg)$$
$$\Delta_3 = \big(\theta D_{ij}\big) + \big(\xi_s D_{as}\big)$$
$$\Delta_4 = \big(V_i\big)$$

The approximate solution in Eq. (A2) may be substituted for by using Eq. (44) which yields,

$$\frac{\partial}{\partial t}\Big[\Delta_1 \sum N_i\,C_{s,i}(t)\Big] = -\Delta_2 \sum N_i\,C_{s,i}(t) + R_3$$
$$+ \frac{\partial}{\partial x_i}\Big[\Delta_3\frac{\partial}{\partial x_j}\big(\sum N_i\,C_{s,i}(t)\big)\Big] - \frac{\partial}{\partial x_i}\Big[\Delta_4 \sum N_i\,C_{s,i}(t)\Big] \quad i, j = 1...Npt \tag{A3}$$

The above expression can then be further simplified to give:

$$\sum N_i \, \Delta_1 \, \frac{\partial}{\partial t}\left[C_{s,i}\right] = -\sum N_i \, \Delta_2 \, C_{s,i} + R_3$$

$$+ \sum \frac{\partial}{\partial x_i}\left[\Delta_3 \, \frac{\partial}{\partial x_j}(N_i)\right] C_{s,i} - \sum \frac{\partial}{\partial x_i}\left[\Delta_4 N_i\right] \, C_{s,i} \tag{A4}$$

Using the property of the shape functions (N_i) described in Eqs. (45) and (46), and dropping the summation symbol for clarity, we can write Eq. (A4) for each element e in the domain W as:

$$N_i^e \, \Delta_1 \, \frac{\partial}{\partial t}\left[C_{s,i}\right] = -N_i^e \, \Delta_2 \, C_{s,i} + R_3^e$$

$$+ \frac{\partial}{\partial x_i}\left[\Delta_3 \, \frac{\partial}{\partial x_j}(N_i^e)\right] C_{s,i} - \frac{\partial}{\partial x_i}\left[\Delta_4 \, N_i^e\right] C_{s,i} \tag{A5}$$

Substituting the above expression in Eq. (47) and reiterating that the summation symbols have been dropped from the expression for clarity, we have the following weighted residual form of the finite element equation for each element e in the domain W :

$$\iint\limits_\Omega \left(N_i^e \, \Delta_1 \, \frac{\partial}{\partial t}\left[C_{s,i}\right]\right) N^e \; dxdz + \iint\limits_\Omega \left(N_i^e \, \Delta_2 \, C_{s,i}\right) N^e \; dxdz$$

$$-\iint\limits_\Omega \left(\frac{\partial}{\partial x_i}\left[\Delta_3 \, \frac{\partial}{\partial x_j}(N_i^e)\right] C_{s,i}\right) N^e \; dxdz \tag{A6}$$

$$+\iint\limits_\Omega \left(\frac{\partial}{\partial x_i}\left[\Delta_4 \, N_i^e\right] C_{s,i}\right) N^e \; dxdz = 0$$

The above integral states that the weighted sum of the residual error for the element e (R_3^e) is set to zero. N^e is the weighting functions within the element e. Since each element is assumed in the form of a quadrilateral in this finite element formulation, there would be four nodes for each element e. Consequently, N^e for an element with nodes $i, j, k,$ and l, will be equal to N^e_i at node i, and equal to N^e_j at node j and so on.

At any such node of element e, we then have the following equation:

$$\iint\limits_\Omega \Delta_1 N_i^e \, N_i^e \, dxdz \, \frac{\partial}{\partial t}\left[C_{s,i}\right] + \iint\limits_\Omega \Delta_2 N_i^e \, N_i^e \, dxdz \; C_{s,i}$$

$$-\iint\limits_\Omega \frac{\partial}{\partial x_i}\left[\Delta_3 \, \frac{\partial}{\partial x_j}(N_i^e)\right] N_i^e \; dxdz \; C_{s,i} \tag{A7}$$

$$+\iint\limits_\Omega \frac{\partial}{\partial x_i}\left[\Delta_4 N_i^e\right] N_i^e \; dxdz \; C_{s,i} = 0$$

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Using Green's identity, the third term on the left hand side of the above expression can be written as follows:

$$\iint_{\Omega} \Delta_3 \frac{\partial}{\partial x_i}\left(N_i^e\right)\frac{\partial}{\partial x_i}\left(N_i^e\right) \ dxdz \ C_{s,i} \tag{A8}$$

and the fourth term can be written as:

$$\iint_{\Omega} \Delta_4 N_i^e \frac{\partial}{\partial x_i}\left(N_i^e\right) \ dxdz \ C_{s,i} \tag{A9}$$

It must be noted here that Green's identity will introduce terms responsible for elemental flux boundary conditions along with Eqs. (A8) and (A9) across elemental boundaries as shown in Eqs.(11) and (40). However, these terms usually cancel with the flux terms of the neighboring elements sharing the same boundary upon assembling all the elements in the domain to finally yield the fluxes across the boundaries of the overall system. Representing these elemental fluxes across the elemental boundary by Q^e_3, and substituting Eqs. (A8) and (A9) into Eq. (A7) we have,

$$
\begin{aligned}
\iint_{\Omega} \Delta_1 N_i^e \ N_i^e \ dxdz \ \frac{\partial}{\partial t}\left[C_{s,i}\right] &+ \iint_{\Omega} \Delta_2 N_i^e \ N_i^e \ dxdz \ C_{s,i} \\
&- \iint_{\Omega} \Delta_3 \frac{\partial}{\partial x_i}\left(N_i^e\right)\frac{\partial}{\partial x_i}\left(N_i^e\right) dxdz \ C_{s,i} \\
&+ \iint_{\Omega} \Delta_4 N_i^e \ \frac{\partial}{\partial x_i}\left(N_i^e\right) dxdz \ C_{s,i} = Q^e_3
\end{aligned}
\tag{A10}
$$

Upon further simplification we have,

$$A_3^e\left[\frac{dC_{s,i}}{dt}\right] + B_3^e\left[C_{s,i}\right] = Q_3^e \tag{A11}$$

Similarly, equations can be represented for every other node within the same element and every other element within the domain. It must be restated that $A_3{}^e$ and $B_3{}^e$ are coefficients that are either explicit or implicit functions of the unknowns at each node. Dependent quantities such as q_a, R_d, D_{ij}, V_i, m, and the reciprocal of the tortuosity factor for gas phase diffusion (x_{as}) that appear in these coefficients also vary within the element e and therefore may be represented using Eq. (48) as shown below:

$$\theta \approx \sum_{i=1}^{Npt} \theta_i \ N_i\left(x,z\right) \tag{A12}$$

Summation of Eq. (A11) for all the nodes of an element with its dependent quantities represented by Eq. (A12) and for every element in the domain, we get Eq. (49) for the governing differential equation used to represent the contaminant transport (Eq. (34)). The coefficient matrices in Eq. (49) for the other governing differential equations (Eqs. (l), (2), (35)-(37)) can be developed by following a similar procedure.

NOMENCLATURE

A	soil characteristic parameter (m)
A_m	mass matrix of dimension *Npt X Npt* for equation *m*
b	leaf area index coefficient
B_m	conductivity matrix of dimension *Npt X Npt* for equation *m*
c	soil characteristic parameter (dimensionless)
$C_{g,k}$	concentration of constituent k in gas phase (g/m^3)
C_k	concentration of constituent k in aqueous phase (g/m^3)
$\overline{C}_k$	approximate solution for concentration of constituent k in aqueous phase (g/m^3)
$\overline{C}_{in,k}$	specified concentration of constituent k in aqueous phase on boundary G_3 (g/m^3)
$\overline{C}_{o,k}$	initial prescribed concentration of constituent k in aqueous phase (g/m^3)
C_{rr}	concentration of root exudates flowing from plants (g/m^3)
d	soil characteristic parameter (dimensionless)
d_r	root index drop rate (dimensionless)
D_{ak}	gas phase diffusion coefficient of constituent k (m^2/hr)
D_{ij}	hydrodynamic dispersion coefficient (m^2/hr)
$D_{eff,k}$	effective gas phase diffusion coefficient of constituent k (m^2/hr)
$dS_e/d\gamma_s$	soil-capacity factor
E	limiting evaporation rate (m/hr)
E_p	potential evaporation rate (m/hr)
ET	total observed evapotranspiration rate (m/hr)
f	varying dependent quantity in domain W
f_{oc}	soil organic matter content (g/g)
F_k	specified normal flux on boundary G_4 (g/m^2/hr)
G_k	source or sink term for constituent k (g/m^3/hr)
h	height measured from soil surface (m)
H_k	Henry's law constant of solute k (g/(m^3 of air)/g/(m^3 of water)) (dimensionless)
K_{dk}	adsorption coefficient of constituent k onto soil particles (m^3/g)
K_o	Monod saturation constant for oxygen (g/m^3)
K_{oc}	carbon-water partition coefficient (g/m^3/g/m^3) (dimensionless)
K_{ow}	octanol-water partition coefficient (g/m^3/g/m^3) (dimensionless)
K_{rs}	Monod saturation constant for toluene substrate (g/m^3)
K_{sat}	saturated hydraulic conductivity in soil (m/hr)
$K_{s,ij;\ r,ij}$	hydraulic conductivity of soil and root, respectively (m/hr)
k_{d1}	first order constant for endogenous metabolism (l/hr)
k_{d2}	second order constant for endogenous metabolism (m^3/(g.hr))

L	outlet position for the chamber (m)
LAI	leaf area index
n_i	ith component of the unit vector normal to the boundary
$N_i(x,z)$	piecewise basis (or shape) functions of x and z
N_i^e	elemental shape function associated with element e
Ne	number of elements in the subdomain
Npt	number of nodal points in the subdomain
P_k	concentration of constituent k in plant root phase (g/m^3)
Q_m	load matrix of dimension $Npt\ X\ l$ for equation m
q	flux of water taken up by plants (m/hr)
q_r	root exudate loading factor (m^3/(m^3.hr))
R_m	residual of equation m
$R_{b,r}$	partition coefficient for biomass and root exudates, respectively, onto root surfaces (g/m^3/g/m^3) (dimensionless)
R_{cf}	root concentration factor (g/m^3/g/m^3) (dimensionless)
R_d	root density (m^3/m^3) (dimensionless)
$R_{d,s}$	root density at soil surface (m^3/m^3) (dimensionless)
S_e	effective saturation (m^3/m^3) (dimensionless)
S_k	concentration of constituent k in solid phase (g/m^3)
S_r	residual degree of saturation (m^3/m^3) (dimensionless)
S_s	specific storativity of soil (l/m)
S_w	degree of saturation (m^3/m^3) (dimensionless)
S_y	specific yield of soil (m^3/m^3) (dimensionless)
t	time (hr)
T	limiting transpiration rate by plants (m/hr)
T_o	transpiration stream concentration factor of oxygen (g/m^3/g/m^3) (dimensionless)
T_p	potential transpiration rate by plants (m/hr)
T_r	transpiration stream concentration factor of root exudates (g/m^3/g/m^3) (dimensionless)
T_{scf}	transpiration stream concentration factor of contaminant (g/m^3/g/m^3) (dimensionless)
U_m	variable of equation m
$|V|$	magnitude of the convective volumetric flux (Darcy flux) (m/hr)
V_i	convective volumetric flux in the ith direction (m/hr)
V_w	normal flux of water in the vertical direction (m/hr)
w	Crank-Nicholson weighting factor

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WC_r root-water content (m^3/m^3) (dimensionless)

Y_k yield of biomass from constituent k

x,z Cartesian coordinates (m) (axial and vertical directions, respectively)

Greek

a_L dispersivity factor in the soil in the longitudinal direction (m)

a_T dispersivity factor in the soil in the transverse direction (m)

b = 0 if ψ_s £ 0 and

             = 1 if ψ_s > 0

G lumped parameter describing the permeability of a plant's root

G_i boundary i in domain W

d_{ij} Kroneckar delta function defined to be

             = 1 if $i = j$; and = 0 if i ¹ j

Dt time interval of simulation

h soil porosity (m^3/m^3) (dimensionless)

q volumetric soil-water content (m^3/m^3) (dimensionless)

q_a volumetric gas porosity (m^3/m^3) (dimensionless)

q_r residual volumetric water content in soil (m^3/m^3) (dimensionless)

q_s saturated volumetric water content in soil (m^3/m^3) (dimensionless)

m_m maximum specific growth rate for biomass (l/hr)

x_k reciprocal of the tortuosity factor for gas phase diffusion in the soil

r bulk density of soil (g/m^3)

ψ_a air entry pressure head (m)

$\psi_{r,lim}$ limiting root-water pressure head (m)

$\psi_{r,wilt}$ wilting root-water pressure head (m)

$\psi_{s,lim}$ limiting soil-water pressure head (m)

$\psi_{s,r}$ approximate solution for soil and root-water pressure heads (m)

$\overline{\psi}_{s,r}$ soil-water and root-water pressure head (m)

$\psi_{so}(x_i)$ initial soil-water pressure heads (m)

$\psi_{ro}(x_i)$ initial root-water pressure heads (m)

$\psi_s(x_i,t)$ specified soil-water pressure head on boundary (m)

W physical domain

Subscripts and subscripts

e finite element

i{for i = 1,2,3}   spatial index

k contaminant (s), biomass (b), oxygen (o), or exudates (r)

m index for one of the six principal model equations

LITERATURE CITED

Anderson, T.A., E.A. Guthrie, and B.T. Walton, 1993. Bioremediation in the Rhizosphere, Environ. Sci. Technol., 27, pp. 2630-2636.

Bailey, J.E., and D.F. Ollis, 1986. Biochemical Engineering Fundamentals. McGraw-Hill, New York, NY.

Boersma, L., F.T. Lindstrom, C. McFarlane, and E.L. McCoy, 1988. Uptake of Organic Chemicals by Plants: A Theoretical Model, Soil Sci., 146 (6), pp. 403-417.

Borden, R.C., and P.B. Bedient, 1986. Transport of Dissolved Hydrocarbons Influenced by Oxygen-limited Biodegradation 1. Theoretical Development, Water Resour. Res., 22 (13), pp. 1973- 1982.

Borden, R.C., P.B. Bedient, M.D. Lee, C.H. Ward, and J.T. Wilson, 1986. Transport of Dissolved Hydrocarbons Influenced by Oxygen-limited Biodegradation 2. Field Application, Water Resour. Res., 22 (13), pp. 1983-1990.

Briggs, G.G., R.H. Bromilow, and A.A. Evans, 1982. Relationships Between Lipophilicity and Root Uptake and Translocation of Non-ionized Chemicals by Barley, Pestic. Sci., 13, pp. 495504.

Brutsaert, W., 1966. Probability Laws for Pore-size Distributions, Soil Sci., 101, pp. 85-92.

Chang, Y.Y., and M.Y. Corapcioglu, 1997. Effect of Roots on Water Flow in Unsaturated Soils, J. Irrig. and Drain. Engrg., ASCE, 123 (3), pp. 202-209.

Chen, Y.M., L.M. Abriola, P.J.J. Anid, and T.M. Vogel, 1992. Modeling Transport and Biodegradation of Benzene and Toluene in Sandy Aquifer Material: Comparison with Experimental Results, Water Resour. Res., 28 (7), pp. 1833-1847.

Cooley, R.L., 1983. Some New Procedures for Numerical Solution of Variably Saturated Flow Problems, Water Resour. Res., 19 (5), pp. 1271-1285.

Corey, A.T., 1977. Mechanics of Heterogenous Fluids in Porous Media, Water Resources Publication, Fort Collins, Colorado, pp. 40-41.

Cunningham, S.D., and W.R. Berti, 1993. Remediation of Contaminated Soils with Green Plants: An Overview, In Vitro Cell. Dev. Biol.-Plant, 29P, pp. 207-212.

Davis, L.C., L.E. Erickson, E. Lee, J. Shimp, and J.C. Tracy, 1993. Modeling the Effects of Plants on the Bioremediation of Contaminated Soil and Groundwater, Environ. Progress, 12, pp. 67-75.

Davis, L.C., M.K. Banks, A.P. Schwab, M. Narayanan, L.E. Erickson, and J.C. Tracy, 1998. Plant-based Bioremediation, In: S.K. Sikdar and R.L. Irvine (Eds.), Bioremediation: Principles and Practice, vol. 2, Technomic Publ. Co., Lancaster, PA, pp. 183-219.

Erickson, L.E., M.K. Banks, L.C. Davis, A.P. Schwab, M. Narayanan, K. Reilley, and J.C. Tracy, 1994. Using Vegetation to Enhance In-situ Bioremediation, Environ. Progress, 13, pp. 226-231.

Journal of Hazardous Substance Research 5a-27

Essaid, H.I., B.A. Bekins, E.M. Godsy, E. Warren, M.J. Baedecker, and I.M. Cozzarelli, 1995. Simulation of Aerobic and Anaerobic Biodegradation Processes at a Crude Oil Spill Site, Water Resour. Res., 31 (12), pp. 3309-3327.

Feddes, R.A., S.P. Neuman, and E. Bresler, 1975. Finite Element Analysis of Two-dimensional Flow in Soils Considering Water Uptake by Roots: II. Field Applications, Soil Sci. Soc. Am. J., 39, pp. 231-237.

Gatliff, E.G., 1994. Vegetative Remediation Process Offers Advantages Over Traditional Pump-and-Treat Technologies, Remediation, 4 (3), pp. 343-352.

Hinchee, R.E., and R.F. Olfenbuttel (Eds.), l991a. In-situ Bioreclamation, Butterworth-Heinemann, Boston, MA.

Hinchee, R.E., and R.F. Olfenbuttel (Eds.), l991b. On site Bioreclamation, Butterworth-Heinemann, Boston, MA.

Huyakorn, P.S., and G. F. Pinder, 1983. Computational Methods in Subsurface Flow, Academic Press, San Diego, CA.

Jin, Y., T. Streck, and W.A. Jury, 1994. Transport and Biodegradation of Toluene in Unsaturated Soil, J. Contam. Hydrol., 17, pp. 111-127.

Jinzhong, Y., 1988. Experimental and Numerical Studies of Solute Transport in Two-dimensional Saturated-unsaturated Soil, J. Hydrol., 97, pp. 303-322.

Kindred, J.S., and M.A. Celia, 1989. Contaminant Transport and Biodegradation, 2. Conceptual Model and Test Simulations, Water Resour. Res., 25 (6), pp. 1149-1159.

Lee, M.D., J.M. Thomas, R.C., Borden, and P.B. Bedient, 1988. Biorestoration of Aquifers Contaminated with Organic Compounds, Crit. Rev. Environ. Control, 18, pp. 29-89.

Malone, D.R., C.M. Kao, and R.C. Borden, 1993. Dissolution and Biorestoration of Nonaqueous Phase Hydrocarbons: Model Development and Laboratory Evaluation, Water Resour. Res., 29(7), pp. 2203-2213.

Marino, M.A., and J.C. Tracy, 1988. Flow of Water Through a Root-soil Environment, J. Irrig. and Drain. Engrg., ASCE, 114 (4), pp. 588-604.

Millington, R.J., 1959. Gas Diffusion in Porous Media, Science, 130, pp. 100-102.

Molz, F.J., M.A. Widdowson, and L.D. Benefield, 1986. Simulation of Microbial Growth Dynamics Coupled to Nutrient and Oxygen Transport in Porous Media, Water Resour. Res., 22(8), pp. 1207-1216.

Narayanan, M., L.C. Davis, J.C. Tracy, L.E. Erickson, and R.M. Green, 1995. Experimental and Modeling Studies of the Fate of Organic Contaminants in the Presence of Alfalfa Plants, J. Hazard. Mat., 41, pp. 229-241.

Narayanan, M., L.C. Davis, J.C. Tracy, and L.E. Erickson, 1998a. Modeling the Fate of Toluene in a Chamber with Alfalfa Plants 2. Numerical Results and Comparison Study, J. Hazard. Substance Res., in press.

Narayanan, M., N.K. Russell, L.C. Davis, and L.E. Erickson, 1998b. Fate of TCE in a Chamber with Alfalfa Plants, J. Environ. Qual., in press.

Neuman, S.P., 1973. Saturated-unsaturated Seepage by Finite Elements, J. Hydraul. Div., ASCE, 99 (HY12), pp. 2233-2250.

Neuman, S.P., and L.A. Davis, 1983. Documentation and Users Guide: UNSAT2-Variably Saturated Flow Model, Division of Waste Management, Office of Nuclear Material Safety and Safeguards, U.S. Nuclear Regulatory Commission, Washington D.C. 20555, NRC FIN B7361.

Neuman, S.P., R.A. Feddes, and E. Bresler, 1975. Finite Element Analysis of Two-dimensional Flow in Soils Considering Water Uptake by Roots: I. Theory, Soil Sci. Soc. Am. J., 39, pp. 224-230.

Rifai, H.S., P.B. Bedient, J.T. Wilson, K.M. Miller, and J.M. Armstrong, 1988. Biodegradation Modeling at Aviation Fuel Spill Site, J. Irrig. and Drain. Engrg., ASCE, 114(5), pp. 1007-1029.

Schnoor, J.L., L.A. Licht, S.C. McCutcheon, N.L. Wolfe, and L.H. Carreira, 1995. Phytoremediation of Organic and Nutrient Contaminants, Environ. Sci. Technol., 29, pp. 2905-2914.

Shimp, J.F., J.C. Tracy, L.C. Davis, E. Lee, W. Huang, L.E. Erickson, and J.F. Schnoor, 1993. Beneficial Effects of Plants in the Remediation of Soil and Groundwater Contaminated with Organic Materials, Crit. Rev. Environ. Sci. Tech., 23 (1), pp. 41-77.

Sleep, B.E., and J. F. Sykes, 1989. Modeling the Transport of Volatile Organics in Variably Saturated Media, Water Resour. Res., 25 (1), pp. 81-92.

Tracy, J.C., and M.A. Marino, 1989. Solute Movement Through Root-soil Environment, J. Irrig. and Drain. Engrg., ASCE, 115 (4), pp. 608-625.

Tracy, J.C., L.E. Erickson, and L.C. Davis, 1993. Rate-limited Degradation of Hazardous Organic Contaminants in the Root Zone of a Soil, Proc. of the Air and Waste Management Association, 86th Annual Meeting, Paper No. 93-WA-89.02.

Tracy, J.C., H. Ramireddy, L.E. Erickson, and L.C. Davis, 1994. Effects of Climatological Variability on the Performance of Vegetation Systems in Remediating Contaminated Soil, Proc. of the Air and Waste Management Association, 87th Annual Meeting, Paper No. 94-WA-86.01.

Trapp, S., and C. McFarlane (Eds.), 1995. Plant Contamination: Modeling and Simulation of Organic Chemical Processes, Lewis Publishers, Boca Raton, FL.

Winter, T.C., 1983. The Interaction of Lakes with Variably Saturated Porous Media, Water Resour. Res., 19 (5), pp. 1203-1218.

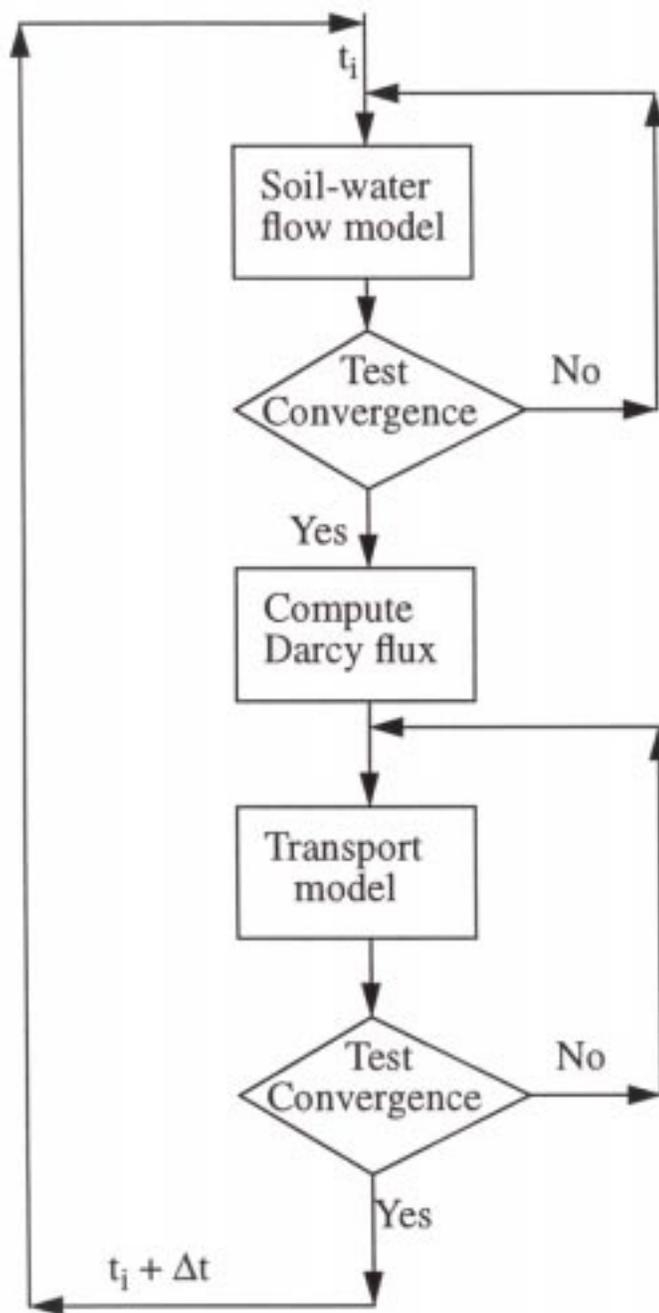Zienkiewicz, O.C., and K. Morgan, 1983. Finite Element and Approximation, John Wiley & Sons, New York, NY.

Figure 1. Schematic representation of the solution methodology for the model.