VEGETATED TREATMENT OF VEHICLE WASH SEDIMENTS: MATHEMATICAL MODELING OF GROUNDWATER AND SOLUTE TRANSPORT

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ABSTRACT

In modeling a phytoremediation strategy, the transport and fate processes of soil water are influenced by subsurface groundwater flow, precipitation events, microbial activity, and transpiring vegetation. This transport is modeled in a variably saturated environment in a vertical dimension and is represented by a Richards equation supported with a van Genuchten model as its constitutive relations. The fate and transport of solutes considers various physicochemical phenomena such as adsorption, volatilization, gas-phase diffusion, with biodegradation by soil microbes and plant uptake, as fate processes of the solutes. Volatilization of contaminants is treated as an open-contaminant, evaporative-flux boundary condition at the soil surface. Vegetation may play an important role by enhancing indigenous soil microbial degradation and by absorbing or transpiring the contaminants. The validated model will be employed to investigate the fate and transport processes occurring in an actual hydrocarbon-contaminated field site. The model results will be used as part of a decision support system to predict the soil conditions, plant activities, and contaminant fate processes in the soil environments for the simulation period.

Key words: *soil-water transport, van Genuchten model, petroleum hydrocarbons*

INTRODUCTION

Mathematical models of vegetative bioremediation are useful tools in assessing the practical implications of phytoremediation. In this study, a mathematical model was designed for use as a prediction tool in a decision support system. In a decision support system, models are incorporated as predictive tools for "what-if" scenarios. Decision support systems are systems designed for non-technical users so that they can access information that helps them to make a decision. The decision support system supplements the person's background and can point to additional sources of data that the user may not be aware of. In the case of phytoremediation, common questions that practicing environmental professionals have are: "How long will it take for the contaminant to be remediated to regulatory standards?" and "What is the risk to groundwater?" The decision support system being designed needs to address those questions. In order to address either question, a model of the contaminant's behavior in the vegetated-contaminated soil system needs to be developed. Several models are currently available that simulate solute fate and transport in a vegetated contaminated soil (Davis et al., 1993; Boersma et al., 1988; Trapp and McFarlan, 1995; Briggs et al., 1982). For our purposes, a new model, which is tailored to the specific needs of the decision support system, is being developed. The existing models are quite robust but at times require a great number of inputs and longer computation times. The non-technical users of the decision support system are looking for simple answers, and they do not typically have the background to interpret some of the complex results from some of the computational models. With an appropriate mathematical model and proper input, answers to these questions can be calculated.

MODEL ASSUMPTIONS

The model presented is a simple flow-and-transport model for one dimension. Gas-phase transport was assumed to occur only by molecular diffusion. Phase-equilibrium partitioning occurs between the local solid, water, and gas phases. Diurnal change in soil temperature and its effect on soil-moisture distribution are assumed negligible. An atmospheric soil-surface boundary layer (1-5 cm thick) exists so that solute concentration in this layer is in equilibrium with solute concentration in surface soilwater.

MODEL DESCRIPTION

The model has a series of governing equations for the individual processes being modeled. Definitions for each of the variables in the following equations are listed at the end of this paper. The soil-water flow equations are considered first, with the governing soil-water flow equation given by:

$$\left(\beta S_S + S_y \frac{dS_e}{d\psi_S}\right)\frac{\partial \psi_s}{\partial t} = \frac{\partial}{\partial z}\left(K\frac{\partial}{\partial z}(\psi_s + z)\right) - R \quad (1)$$

Eq. (1) describes the soil-water flow in the form of Richard's equation in the vertical (z) direction under the influence of root-water uptake from the soil. Each term within the equation accounts for a particular aspect of soil-water flow. The terms on the right side of the equation relate to the movement of the water in the vertical direction, z, or removal from the volume of soil being represented, R. The terms on the left side of the equation represent the change in the soil's storage of water, as related to the specific storativity of the soil, S_s, effective saturation, S_e, and the soil's specific yield, S_y. Both of these terms are related to the amount of water that a soil can hold. The term S_e, effective saturation, is defined in terms of the soil-water pressure head, ψ_s, and parameters α, m, and n, described by van Genuchten (1980). These parameters are based on the clay, sand, and carbon content of the soil and are used to describe the soil- water retention curve for the soil. The equation describing this relationship is shown below.

$$S_e = \left[\frac{1}{1+(\alpha\psi_S)^n}\right]^m \text{ when } \psi_S < 0$$

$$S_e = 1 \quad \text{when} \quad \psi_S \geq 0 \quad (2)$$

and $dS_e/d\psi_S$ is given by

$$\frac{dS_e}{d\psi_S} = \frac{\alpha m}{1-m}\left(1 - S_e^{1/m}\right)^m S_e^{1/m} \quad (3)$$

and m and n are related as follows

$$m = 1 - \frac{1}{n} \quad (4)$$

K, hydraulic conductivity, is given by

$$K = K_S S_e^{1/2}\left(1 - \left(1 - S_e^{1/m}\right)^m\right)^2 \quad (5)$$

Equations (2) through (5) are essential constitutive relationships based on van

Genuchten's model (1980) for predicting hydraulic conductivity of unsaturated soils in order to obtain closure to Eq. (1).

Soil-water uptake by roots depends on the root-length density, maximum root-water uptake, degree of saturation of soil, and the ratio of root-water and soil-water pressure heads (Campbell 1991). For our simulation, the variable *R*, from equation 1, is given by the equation

$$R = q_r L_d \qquad (6)$$

where q_r, the rate of soil-water uptake per unit length of roots, is represented as

$$q_r = \frac{q\max}{2} S_w \left(1 - \frac{\psi_r}{\psi_S} \right) \qquad (7)$$

where S_w, degree of soil saturation, is given by the equation

$$S_w = \frac{\theta}{\eta} = \frac{\theta}{\theta_S} \qquad (8)$$

θ , volumetric water content, is the sum of the residual volumetric soil-water content, and the amount of water held in storage by the soil. The equation describing this relationship is given below.

$$\theta = \theta_r + S_e \left(\theta_S - \theta_r \right) \qquad (9)$$

The last variable in equation 6, is L_d, the root-length density, and is represented by an exponential relationship as

$$L_d = L_{d,s} \exp\left(-dz \right) \qquad (10)$$

The subscript s denotes the root-length density as measured at the soil surface. The parameter d is a fitting parameter.

The top boundary condition used by equation (1) for our model is

$$K \frac{\partial \left(\psi_S + z \right)}{\partial z} = E \text{ at surface} \qquad (11)$$

The evapotranspiration rate of the system is represented by E in the above equation.

Upon solving equation (1) to convergence, the Darcy flux of soil water, *V*, is then computed as

$$V = -K \left(\frac{\partial \left(\psi_S + z \right)}{\partial z} \right) \qquad (12)$$

The solute transport portion of the model is written as a differential solute transport equation and is given by:

$$\frac{\partial}{\partial t} \left(C_T \right) = -\frac{\partial}{\partial z} \left(q_T \right) - S \qquad (13)$$

The total solute concentration in a soil element, C_r, is the sum of the soil water contained in the soil-water fraction, the soil-air fraction, and the soil-solid fraction of the soil and the amount of solute contained in the roots. This relationship is given by

$$C_T = \theta C_w + \theta_a C_a + \rho C_S + L_d A_{av} C_r \qquad (14)$$

The total solute flux, q_r, is affected by the amount of solute transported by the diffusion of the solute through the soil water, the amount that moves with the moving soil water, and the amount diffusing through the soil air. This sum is given by

$$q_T = -\theta D_w \frac{\partial}{\partial z} \left(C_w \right) + VC_w - D_{eff} \frac{\partial C_a}{\partial z} \qquad (15)$$

The sink term S, from equation 13, is represented as the sum of the solute degraded, therefore removed from the soil-water solution, and the amount of solute taken up by the plant and transported to the transpiration stream. Each of these factors depends on the concentration of solute in the soil water, C_w. The equation describing this relationship is shown below.

$$S = \theta k C_w + RT_{scf} C_w \qquad (16)$$

The various constitutive relations for closure of equations (14) through (16) are given by a series of equations based on physical and chemical principles. The first relationship is based on conservation of mass. It shows that the porosity of the soil is the sum of the volumetric water content and the volumetric air content.

$$\eta = \theta + \theta_a \qquad (17)$$

The next relationship relates the concentration of solute, in the soil solids, to the concentration of solute in the soil-water. This relationship is represented by a linear adsorption, with K_d defined as the sorption coefficient of solute onto soil solids.

$$C_S = K_d C_w \qquad (18)$$

The sorption coefficient has been shown to be related to the amount of organic matter contained within a soil and this relationship can also be represented by a linear function.

$$K_d = K_{oc} f_{oc} \qquad (19)$$

where K_{oc} is the carbon-water partitioning coefficient. The concentration of solute in the soil air depends on the concentration of solute in the soil water. The relationship describing this dependence is based on Henry's law and is shown below.

$$C_a = HC_w \qquad (20)$$

H, a dimensionless Henry's law coefficient, is dependent on the solute being studied. The concentration of solute in the roots is also represented as a linear adsorption relationship, with R_{cf} being the root concentration factor related to the octanol-water partitioning coefficient, K_{ow}, of the solute.

$$C_r = R_{cf} C_w \qquad (21)$$

$$R_{cf} = 0.82 + 10^{(0.77 \log k_{ow} - 1.52)} \qquad (22)$$

The dispersion coefficient is defined as

$$\theta D_w = \alpha_w V \qquad (23)$$

and the effective diffusion is given by

$$D_{eff} = \frac{\theta_a^{10/3}}{\eta^2} D_a \qquad (24)$$

The plant uptake of solute into the transpiration stream from soil water is described using the T_{scf}, transpiration stream concentration factor, that depends on k_{ow} value of the solute (Briggs et al., 1982).

$$T_{scf} = 0.784 \exp\left(- \frac{(\log k_{ow} - 1.78)^2}{2.44} \right) \qquad (25)$$

Finally, the governing solute transport equation, arrived at by combining each of the relationships we have previously given, is

$$\frac{\partial}{\partial t}(\theta + \theta_a H + \rho K_d + L_d A_{av}) C_w =$$
$$\frac{\partial}{\partial z}\left(\theta D_w \frac{\partial}{\partial z} C_w\right) - V \frac{\partial}{\partial z}(C_w) +$$
$$HD_a \frac{\partial}{\partial z}\left(\xi \frac{\partial C_w}{\partial z}\right) - \theta k C_w - RT_{scf} C_w \qquad (27)$$

where ξ, the inverse of the tortuosity factor for gaseous diffusion, is given by the relation shown below.

$$\xi = \frac{\theta_a^{10/3}}{\eta^2} \tag{28}$$

Boundary condition for the solute transport governing equation (27) at the soil-surface boundary is:

$$-\theta D_w \frac{\partial C_w}{\partial z}\Big|_L + VC_w\Big|_L - \xi H D_a \frac{\partial C_w}{\partial z}\Big|_L$$

$$= \frac{D_a}{d}\left(HC_w\big|_L - C_{air}\right) \text{ at surface} \tag{29}$$

The soil-surface boundary condition considers a 1-5 cm thick atmospheric boundary layer whose solute concentration is in equilibrium with the solute concentration in the soil water of the soil surface. This layer is relatively thick for a dense canopy of vegetation, while it is almost negligible for a well-mixed, windy, barren soil surface.

MODEL EXPECTATIONS

Due to the need for the model to interface with the graphical user interface as part of the decision support system, the model had a number of expectations. First, the model was to simulate the flow of soil water in vertical direction under the influence of soil type, vegetation, evaporation, and precipitation events. Second, the model was to simulate the transport and fate processes of solute in the vertical direction of soil environments under the influence of soil type, soil-water flow, solute type, plant uptake, and microbial degradation. Third, the model was to predict and study the movement of soil water due to seasonal variations and uptake of plants. Fourth, the model was to predict the fate processes of solutes released at the soil surface. Fifth, the model was to simulate to determine if infiltrating solute will eventually contaminate the groundwater table. Finally, the model was to determine if the growth of active vegetation on the soil surface would contain the infiltration of contaminated soil water, predict, and study over seasons, the extent of phytoremediation of solutes in the root zone.

NUMERICAL PROCEDURE

The numerical procedure used a combination of techniques. Governing equations (1) and (27), along with the constitutive relationships, are solved using weighted-residuals, Galerkin finite-element technique. Linear-shape functions are employed over the element for the Galerkin formulation of equations (1) and (27). For representing the time derivative, a Crank-Nicholson method was used with a weighting parameter equal to 0.5. The strategy at any given time step involved the following steps. First the governing equation (1) was solved to convergence along with top boundary condition in equation (11) and prescribed bottom boundary condition and initial condition for the soil domain. Next, the local Darcy soil-water fluxes were calculated based on current soil-water and pressure head conditions. Then the governing equation (27) was solved to convergence along with top boundary condition in Equation (29) and prescribed bottom boundary condition and initial condition for the

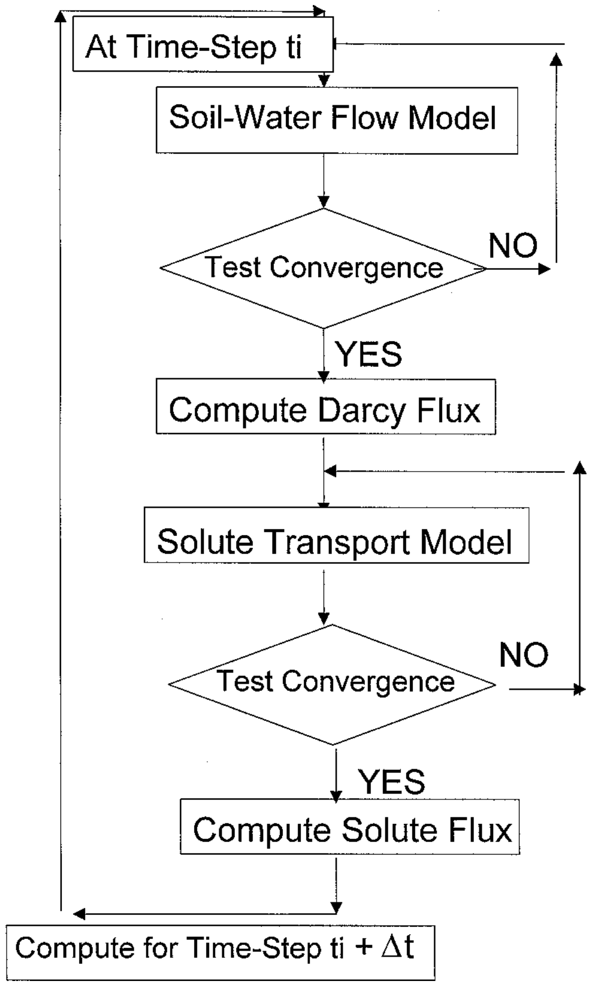

Figure 1. Schematic of the Solution Methodology.

problem domain. This entire procedure was repeated for each time step. Figure 1 shows a schematic of this solution strategy.

CONCLUSIONS

For the phytoremediation treatment-design decision support system, a special model was necessary to meet the needs of the system. The derived model used standard representations for soil-water flow, the various phase interactions, and the solute transport. Root water uptake was taken into account as well as microbial degradation of the solute. Results from this model will be used to predict the time needed to reach a given regulatory limit for cleanup of a contaminated site and the extent to which solute will be transported to the groundwater table.

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NOMENCLATURE

A_{av}	average cross-section area of the roots (m^2)
C_a	concentration of solute in soil air (g/m^3)
C_{air}	concentration of solute in air (g/m^3)
C_r	concentration of solute in roots (g/m^3)
C_s	concentration of solute in soil solids (g/m^3)
C_T	total solute concentration in a soil element (g/m^3)
C_w	concentration of solute in soil water (g/m^3)
D_{eff}	effective gas-phase diffusion coefficient (m^2/hr)
D_w	hydrodynamic dispersion coefficient (m^2/hr)
E	evapotranspiration rate (m/hr)
H	dimensionless Henry's law constant of solute
k	decay constant (1/hr)
K	hydraulic conductivity (m/hr)
K_s	unsaturated hydraulic conductivity (m/hr)
K_{oc}	carbon-water partition coefficient ($g/m^3/g/m^3$)
K_d	sorption coefficient of solute onto soil solids (m^3/g)
k_{ow}	octanol-water partition coefficient ($g/m^3/g/m^3$)
L_d	root-length density ($m/(m^3)$)
$L_{d,s}$	soil-surface root-length density ($m/(m^3)$)
m	van Genuchten parameter
n	van Genuchten parameter
q_{max}	maximum rate of uptake per unit root length ($m^3/(m.\ hr)$)
q_r	rate of uptake per unit root length ($m^3/(m.\ hr)$)
q_T	total solute flux ($g/(m^2.hr)$)
R	rate of soil-water uptake by roots ($m^3/(m^3.\ hr)$)
R_{cf}	root concentration factor ($g/m^3/g/m^3$)
S	sink term for the solute in soil ($g/(m^3.hr)$)
S_e	effective saturation (m^3/m^3)
S_w	degree of saturation (m^3/m^3)
S_s	specific storativity (1/m)
S_s	specific yield of soil (m^3/m^3)
t	time (hr)

T_{scf} transpiration stream concentration factor of solute (g/m^3/g/m^3)

V Darcy soil-water flux (m/hr)

z Cartesian coordinate in vertical direction (m)

α van Genuchten parameter

α_w dispersivity factor (m)

β = 0 if $\psi_s \leq 0$ and = 1 if $\psi_s > 0$

η soil porosity (m^3/m^3)

θ volumetric soil-water content (m^3/m^3)

θ_a volumetric gas porosity (m^3/m^3)

θ_r residual volumetric soil-water content (m^3/m^3)

θ_s saturated volumetric soil-water content (m^3/m^3)

ρ bulk density of soil (g/m^3)

ξ reciprocal of tortuosity factor for gaseous diffusion

ψ_s soil-water pressure head (m)

ψ_r root-water pressure head (m)