韓國土壤環境學會誌 Vol.1, No.2 91 ~ 101, 1996
Journal of KoSES Vol.1, No.2 91 ~ 101, 1996

原著

녹지 토양내 탄화수소화합물의 분포변화에 관한 모델링 연구

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Model Study of the Fate of Hydrocarbons in the Soil-Plant Environment

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ABSTRACT

In recent years, phytoremediation, the use of plants to detoxify hydrocarbons, has been a promising new area of research, particularly in situ cleanup of large volumes of slightly contaminated soils. There is increasing need for a mathematical model that can be used as a predictive tool prior to actual field implementation of such a relatively new technique. Although a number of models exist for solute-plant interaction in the vegetated zone of soil, most of them have focused on ionic nutrients and some metals.In this study, we developed a mathematical model for simulation of bioremediation of hydrocarbons in soil, associated with plant root systems. The proposed model includes root interactions with soil-water and hydrocarbons in time and space, as well as advective and dispersive transport in unsaturated soil. The developed model considers gas phase diffusion and liquid-gas mass exchanges. For simulation of temporal and spatial changes in root behavior on soil-water and with hydrocarbons, time-specific distribution of root quantity through soil was incorporated into the simulation model. Hydrocarbon absorption and subsequent uptake into roots with water were simulated with empirical equations. In addition, microbial activity in the rhizosphere, a zone of unique interaction between roots and soil microorganisms, was modeled using a biofilm theory. This mathematical model for understanding and predicting fate and transport of compound in plant-aided remediation will assist effective application of plant-aided remediation to field contamination.

Key word: hydrocarbons, bioremediation, phytoremediation, unsaturated soil, solute transport

요 약 문

최근에 식물을 이용한 탄화수소화합물의 정화방법은 특히, 넓은 범위에 거쳐 저농도로 오염되어 있는 토양인 경우에 앞으로 각광을 받을 가능성이 높은 새로운 연구분야로 주목을 받아왔다 이의 기술을 실제 오염토양에 바로 적용하기전 적절한 설계에 필요한 예측모델링의 필요성이 함께 요구되고 있다. 현재 녹지토양내의 용질과 식물과의 상호작용에 관한 많은 모델들이 나와있지만 대부분이 이온상태의 무기영향물이나 금속류의 경우에만 한정되어 있다. 본연구에서는 토양내의 탄화수소화합물의 생물학적정화에 미치는 식물의 영향을 예측하기 위한 기본 수학적 모델식을 제안 하였다. 먼저 토양내의 식물뿌리가 토양수분과 오염물에게 미치는 영향과 비포화계층에서의 오염물의 이동현상 및 토양내 기/액상간의 물질전달을 수학적으로 나타내고자 하였으며 시간의 변화와 토양깊이별 식물의 오염물의 동태에 미치는 영향을 시뮬레이션하기 위하여 식물뿌리의 시간에 따른 양적성장과 깊이별 분포정도를 예측하기 위한 관계식도 아울러 모델링에 포함하였다. 오염물의 식물내의 흡수 및 생물막이론을 이용한 식물뿌리근처에서의 생물학적 분해에 관한 현상도 관계식을 이용 설명하고자 하였다. 본 연구에서 제시한 식물영향하의 탄화수소화합물의 토양내의 동태해석을 위한 모델식은 실제로 탄화수소화합물에 의해 오염된 토양을 식물을 이용하여 정화하고자 할때, 필요한 기본설계도구로서 유용하게 쓰여질 것으로 기대된다.

주제어: 탄화수소화합물, 생물학적정화, 식물정화, 비포화토양, 물질이동

1. INTRODUCTION

The widespread spill of small volumes of hydrocarbons in the subsurface has led to contamination requiring expensive removal by conventional chemical, physical, and biological techniques. Hydrocarbons are known to be degraded as primary substrates under aerobic conditions by a mixed population of indigenous microorganisms. Recently, in situ bioremediation, which involves the use of indigenous microbes, has been applied for clean-up of soil slightly contaminated with hydrocarbons. However, there are some difficulties in implementation of in situ bioremediation, including requirement of continuous delivery of appropriate electron acceptors (e.g., oxygen) and substrates through the contaminated zone. Plants reportedly offer an alternative for the addition of organic amendments to increase microbial activity and improve the chemical and physical properties of soil[1]. A growing root system can be an effective means of increasing and distributing soil organic matter and soil microorganisms throughout the soil[2]. Therefore, use of plants to stimulate the remediation of a toxic and recalcitrant non-point hydrocarbon at low soil concentrations and with a wide distribution in soil may represent a potential low-cost and effective alternative for waste management.

Many phytoremediation projects are currently considered as polishing steps to follow emergent treatment of urgent situations. These projects are currently under way for remediation of more isolated and less contaminated sites over a long-term period in a field scale within the hazardous waste-cleanup industry[19].

Mathematical modeling associated with actual field implementation will present useful information for the assessment of availability and for prediction of duration of such remedial operations. Although there are a number of developed conceptual models, most have focused on the fate of ionic nutrients and metals in the root-soil zone[5),28]. Such models incorporate the transport mechanisms of nutrients and other solutes to the surface of roots and penetration of ions into the roots. Root-organic chemical interactions lack quantitative correlations and have therefore been ignored in most modeling efforts for chemically contaminated sites. Several recent theoretical models of the effect of vegetation on fate of organic chemicals at hazardous waste sites have been published[8), 11), 3]. Although the models show promise as predictive tools, they do not provide sufficient information about the degree of influence of each process or parameter on the performance of bioremediation.

This study examined the effect of plants on in situ bioremediation of large volumes of soil slightly contaminated with environmentally ubiquitous hydrocarbons found in hazardous waste sites.

2. MODEL DEVELOPMENT

Development of the Governing Equations for Soil-Water Flow in the Vegetated Unsaturated Zone : Assuming incompressible soil matrix and soil-water, a general macroscopic equation governing one-dimensional vertical water flow in unsaturated soil is

$$\frac{\partial \theta_w}{\partial t} = -\nabla q_w - S_w \cdots\cdots\cdots\cdots (1)$$

where θw is the volumetric water content of bulk soil [L^3L^{-3}], q_w is the Darcy velocity [$L^3 L^{-2} T^{-1}$], and Sw is the sink term which represents the root water uptake rate [$L^3L^{-3}T^{-1}$]. The general form of such a model for the one-dimensional vertical water flow in an unsaturated zone is

$$\frac{\partial \theta_w}{\partial t} - \frac{\partial}{\partial_z}\left[K_w\left(\frac{\partial h_w}{\partial_z} - 1\right)\right] + S_w = 0 \cdots (2)$$

where hw is the pressure head in bulk soil [L], related to θw by the soil-moisture characteristic curve and Kw is the unsaturated hydraulic conductivity [LT^{-1}].

Assuming constant root water uptake per unit length of the root above a critical soil-moisture content, below which the uptake decreases linearly with water content[15], the mean daily root water uptake rate per a unit volume of soil Sw in (2) is obtained

$$S_w = L_d \cdot q_{av} \cdots\cdots\cdots\cdots (3)$$

where L_d is the rooting density, defined as length of roots per unit volume of soil [LL^{-3}] and q_{av} *is the mean daily uptake rate* [$L^3L^{-1}T^{-1}$]. *Gerwitz and Page (1974)*[14] *found that under well watered conditions in a deep, uniform soil, a crop's root quantity normally declines exponentially with depth as:*

$$L_d = L_{md} e^{-fz} \cdots\cdots\cdots\cdots (4)$$

where f [L^{-1}] is a are constant over depth at a time period for plant growth and L_{md} [LL^{-3}] is the maximum value of L_d in topsoil. The expression of root distribution in equation (4) is similar to the uptake distribution function given by Raats (1976)[21]. Data of f for the majority of mature crop plants was summarized by Gerwitz and Page (1974) demonstrating adequate description of root distribution for approximately 70% of the cases quoted.

After a review of the depth development of roots of 48 crop species by analyzing 135 reported field observations under generally favorable environmental conditions for root growth, Borg and Grimes(1986)[14] found that the increase in rooting depth z_m with time delineates a sigmoidal curve which could be plotted by a single sine function, such that

$$z_m = z_T\left(0.5 + 0.5\sin\left[3.03 \cdot (t/t_T) - 1.49\right]\right) \cdots\cdots (5)$$

where t_T is the time to plant maturity [T], z_m is the current rooting depth [L], and z_T [L] is the maximum rooting depth to be achieved at $t = t_T$.

For evaluating the proportion of total active roots in depth increments and its change with time, the root growth model is coupled with the root distribution model of Gerwitz and Page (1974). The changes in L_{md} and $1/f$ with time are described in the same way as rooting depth z_m by the use of (5), that is

$$1/f = (1/f)_T\left\{0.5 + 0.5\sin\left[3.03(t/t_T) - 1.47\right]\right\} \cdots (6)$$

$$L_{md} = L_{Td}\left\{0.5 + 0.5\sin\left[3.03(t/t_T) - 1.47\right]\right\} \cdots\cdots (7)$$

where $(1/f)_T$ and L_{Td} are $1/f$ and L_{md} when z_m reaches the maximum rooting depth z_T. After fully grown, a plant assumably attains constants $(1/f)_T$ and L_{Td} for the values of 1/f and L_{md}.

Based on equation (4) coupled with (6) and (7) the rooting density profile, which is a function of depth and time, depends on the three parameters, t_T, L_{Td} and, $(1/f)_T$ to be found for various crops and soil conditions.

Hydrocarbon Transport in the Root-Soil Zone : In most modeling efforts, hydrocarbon transport in the vertical unsaturated water flow zone has been represented by the conventional advection-dispersion equation:

$$\frac{\partial \theta_w C_w}{\partial t} = -\frac{\partial}{\partial z}\left[q_w C_w - D_H \frac{\theta_w \partial C_w}{\partial_z}\right] - S_s \cdots (8)$$

where C_w is the hydrocarbon concentration in the aqueous phase [ML^{-3}], D_H is the hydrodynamic dispersion coefficient [L^2T^{-1}], S_s is the net rate of hydrocarbon losses in the aqueous phase [$ML^{-3}T^{-1}$], and θ_w and q_w are obtained from the solution of the soil-water flow equation (2). In this study, mechanisms for the hydrocarbon losses in the aqueous phase of the root-soil environment were included. The proposed processes are: 1) sorption onto a solid matrix and root surface; 2) uptake into the root transpiration stream; 3) biodegradation in bulk soil and the rhizosphere; and 4) mass transfer between air and water phases. Also:

$$S_s = S_{sd} + S_{rd} + S_{ru} + S_{sb} + S_{rb} + S_{aw} \cdots\cdots (9)$$

where S_{sd} is the rate of hydrocarbon sorption onto a solid matrix [$ML^{-3}T^{-1}$], S_{rd} is the rate of hydrocarbon partitioning to roots [$ML^{-3}T^{-1}$], S_{ru} is the rate of hydrocarbon uptake into the transpiration stream of the plant [$ML^{-3}T^{-1}$], S_{sb} is the rate of hydrocarbon biodegradation in bulk soil [$ML^{-3}T^{-1}$], S_{rb} is the rate of hydrocarbon biodegradation in the rhizosphere [$ML^{-3}T^{-1}$], and S_{aw} is the rate of loss of a hydrocarbon to the soil-air phase [$ML^{-3}T^{-1}$].

Hydrocarbon Sorption onto the Solid Matrix : The rate of hydrocarbon sorption from the aqueous phase onto the solid surface is described as

$$S_{sd} = \frac{\partial}{\partial t}\left[\rho_s(1-n)\ C_{sd}\right] \cdots\cdots\cdots\cdots (10)$$

where ρs is the mass density of solid matrix [ML^{-3}], and n is the porosity of bulk soil [L^3L^{-3}], and Csd is the hydrocarbon mass sorbed onto solid per unit weight of solid [MM^{-1}]. It is anticipated that a plant remediation strategy would be used solely for low levels of ground water and soil contamination at a slow rate of ground water flow in the vadose zone. This enables the use of a linear isotherm equilibrium model to simulate the adsorption of the hydrocarbon to the solid matrix[12]. The resulting expression for Csd is described by the equation

$$C_{sd}=K_d C_w \cdots\cdots\cdots\cdots (11)$$

where K_d is the distribution coefficient [L^3M^{-1}].

Sorption and Uptake of Hydrocarbons by Roots: Organic solute absorption by plants from soil can be regarded as a series of consecutive partitions of solute between soil particles and solution, between root and soil solution, and between the transpiration stream and tissues of a plant root[3]. Among the chemical properties, lipophilicity of the solute has been found to be the main factor determining partition[7], [18], [3]. Paterson and coworkers (1990) compiled a review of 150 references addressing uptake mechanisms of 70 organic chemicals from soil and the atmosphere by 88 species of plants and trees[20]. S_{rd} in (9) can be expressed as S_{sd} in (10).

$$S_{rd} = \frac{\partial \sigma_r C_r}{\partial_t} \cdots\cdots\cdots\cdots (12)$$

where C_r is the organic concentration sorbed onto root [ML^{-3}], σ_r is the volumetric root content in soil [L^3L^{-3}], calculated with radius of root r_r [L] and rooting density Ld in (4) as:

$$\sigma_r = \pi r_r^2 L_d \cdots\cdots\cdots\cdots (13)$$

For non-ionic organic chemicals, absorbed organic concentrations in roots are found to have a linear relationship with the concentration in external solution at an equilibrium state. Briggs and coworkers (1982) expressed this relationship with an empirical equation:

$$C_r = R_{cf} C_w \cdots\cdots\cdots\cdots (14)$$

where R_{cf} is the root concentration factor of the plant and is a function of the organic octanol-water partition coefficient K_{ow}[6].

Briggs and coworkers (1983) also demonstrated the second process in absorption of the organic solute by roots, which is the translocation of solute into shoots, as a linear function of root water uptake rate for diluted solutions. This is described using transpiration stream concentration factor T_{scf} [-], which was first introduced by Shone and Wood (1974)[26)]

$$C_{ts}=T_{scf}C_w \cdots\cdots(15)$$

where C_{ts} is the organic concentration in the transpiration stream [ML^{-3}]. T_{scf}, which is independent of concentration in the external solution and is usually less than unity, is maximum at an optimum lipophilicity. Translocation to the shoots was most efficient for compounds of intermediate polarity. The uptake rate of organic solute into the transpiration stream then can be described as a linear function of the root water uptake rate S_w such that:

$$S_{ru}=C_{ts}S_w \cdots\cdots(16)$$

Although the models of Briggs and coworkers (1982) were developed for barley, several subsequent experiment results showed the validity of the models for a wide range of plant species and organic chemicals[3), 18)]. The models of Briggs and coworkers have been used by several modelers for the simulation of organic solute uptake by roots[25), 3)].

Biodegradation of Hydrocarbons: The vast majority of microorganisms, bacteria, are within 1 to 2 meters of the vadose zone in which most biological activity occurs due to its proximity to vegetation at the ground surface. The bacterial population, which decreases with increasing depth, is typically 10^6 to 10^7 cells per gram of dry sediment in subsurface under natural conditions[13)]. Biodegradation of a hazardous organic compound at low levels can be accomplished in the presence of bacteria by either one or both of the following metabolisms: 1) cometabolism, biodegradation of a cometabolite by the same enzymes generated by micro-organisms to degrade a primary substrate, and 2) secondary utilization, the metabolism of a compound in the presence of other substrates that supply the microorganism's primary growth needs[17), 24)]. The utilization of a compound by either cometabolism or secondary utilization is known to be inconsequential to biomass growth [17)]. The kinetics of biodegradation for low level concentrations of hydrocarbons in bulk soil have been expressed by a modified or original Monod type expression by a number of researchers with good prediction of experimental data[17), 19), 24)].

Most of the bacteria in natural subsurface have tendency to be attached to solid particles and form a biofilm. The biofilm, in general, is fully penetrated by substrates for all reasonable values of groundwater flow velocity and substrate utilization[22)]. Therefore, the chemical concentrations in the biofilm can be assumed to be the same as the average bulk fluid concentration. This provides an expression for the rate of utilization of a hydrocarbon at low levels in a bulk soil, by the use of the Monod type expression.

$$S_{sb} = \frac{k_b X_b C_w}{K_{bs} + C_w} \cdots\cdots(17)$$

where k_b is the maximum substrate utilization rate in the bulk soil [$MM^{-1}T^{-1}$], K_{bs} is the half-saturation coefficient in the bulk soil [ML^{-3}], and X_b is the microbial concentration in the bulk soil [ML^{-3}].

Due to different characteristics, the rhizosphere, which is the volume of the soil that surrounds the root tissues, shows different influence on the metabolism of soil contaminants compared to surrounding bulk soil. Because of abundant root releases as exudates, lysates, and mucilages (50-100 mg/g of root per day) and the low microbial maintenance coefficient (0.03 mg $g^{-1}d^{-1}$), there is a rapid buildup of a biofilm around root surface[13]. Most of the microorganisms, which are 50-100 times as many per unit volume of soil as in the bulk soil, occur within 50 m of the root surface. However, some of them are detected as far as 1-2 mm from the root surface with counts of 10^9 bacteria, 10^7 actinomycetes, 10^6 fungi, 10^3 protozoa, and 10^3 algae per gram of rhizosphere soil[13]. If the biomass becomes sufficiently thick, there may be diffusion resistance within the biomass and development of nonlinear concentration profile due to biodegradation in the biofilm[23]. When the concentration profile within the biofilm changes rapidly with respect to the biofilm thickness, the rate of utilization of substrates in the biofilm can be described with a steady state biofilm model. Corapcioglu (1992) simulated the microbial activity on the root surface by the use of the biofilm model. The mass balance for the organic solute concentration in a unit thickness of biofilm around root results in a second order, nonlinear differential equation.

$$D_f\left(\frac{\partial^2 C_f}{\partial r^2}+\frac{\partial C_f}{r\,\partial r}\right)=\frac{k_f X_f C_f}{K_{fs}+C_f}\; r_r \le r \le r_r + L_f \cdots \quad (18)$$

weher D_f is the diffusion coefficient within biofilm $[L^2T^{-1}]$, C_f is the organic solute concentration in the biofilm $[MM^{-1}T^{-1}]$, r is the film depth [L], k_f is the maximum substrate utilization rate in the biofilm $[MM^{-1}T^{-1}]$, K_{fs} is the half-saturation coefficient in the biofilm $[ML^{-3}]$, X_f is the microbial concentration in the biofilm $[ML^{-3}]$, L_f is the biofilm thickness [L], and r_r is the radius of root [L]. The equation was solved with the boundary conditions of

$$C_f = C_{Lf} \text{ at} r = r_r + L_f \text{ and } \frac{\partial C_f}{\partial_r} = 0 \text{ at } r = r_r$$

where $C_{Lf}[ML^{-3}]$ is the substrate concentration at the interface between the biofilm and aqueous phases. The substrate flux into the biofilm, neglecting the diffusion resistance in liquid phase, is then expressed mathematically as

$$J_f = \int_{r_r}^{r_r+L_f} \frac{k_f X_f C_f}{K_{fs}+C_f}\, d\,\pi r^2 \cdots\cdots\cdots\cdots (19)$$

where J_f is the substrate flux into the biofilm $[ML^{-1}T^{-1}]$. Multiplying the substrate flux into the biofilm by rooting density in soil, the rate of utilization of a hydrocarbon in rhizosphere is expressed as

$$S_{rb} = L_d \cdot J_f \cdots\cdots\cdots\cdots (20)$$

In this study, indigenous sources for primary substrate utilization were assumed to be enough to maintain constant microbial concentration in soil. Since the utilization of secondary substrate is inconsequential to biomass growth, biomass yield as well as endogenous decay with the secondary substrate were not included in the biodegradation modeling.

Mass Transfer between Water and Gas Phases: In the shallow depth of unsaturated subsurface, transport of volatile hydrocarbons as vapor in the gas phase as well as solute in the water phase can occur. Interphase mass transfer of organic occurs by partitioning of the organic between the gas and water phases. In order to account for the gas-water mass exchanges, two approaches, in general, are used in transport equations. The first approach is to describe the partitioning of the organic between phases with equilibrium model. This approach presumes that the organic reaches equilibrium rapidly between the volatilized and dissolved phases at all locations, then the relationship can be described by a linear isotherm, which is called Henry's law. This law states that there is a linear relationship between the partial pressure of a gas above the water and the mole fraction of the gas dissolved in the water as

$$P_g = H \cdot C_w \cdots\cdots (21)$$

where P_g is the partial pressure of gas [atm] and H is the Henry's constant [atm/mol/m^3 water]. Henry's law is obeyed well for sparingly soluble, reasonably ideal, and nonreactive gases [9]. The greater the Henry's law constant, the greater is the rate of volatilization from soil or water. Under the ideal gas assumptions, one obtains

$$C_g = \frac{H}{R_o T} C_w \cdots\cdots (22)$$

where C_g is the concentration in gas phase [mol/m^3 gas], R_o is the ideal gas constant [= 8.2 atm m^3 gas/mol/K], and T is the temperature [K]. The dimensionless parameter $\frac{H}{R_o T}$, which is a measure of the preference of a constituent for the gas or water phase, is defined as the gas-water partitioning coefficient by McAulitte (1971)[9] and termed as H' in this study. The partitioning coefficient well represents the equilibrium relations between mole fractions in different phases when temperatures and pressures are moderate and organic solubility in the water phase are small[27]. The advantages of the equilibrium assumption results in substantial simplification of the models. In that case, the rate of loss of a hydrocarbon to gas phase S_{aw} in (9) is described by the equilibrium model as

$$S_w = \frac{\partial \theta_g C_g}{\partial t} = \frac{\partial (n - \theta_w) H' C_w}{\partial t} \cdots\cdots (23)$$

where H' is the gas-water partitioning coefficient [-] and θ_g is the volumetric gas content [L^3L^{-3}].

The water may infiltrate at such a fast rate that aqueous phase concentration may not attain an equilibrium with gas phase concentration. The water-gas mass exchanges in nonequilibrium conditions are described by a kinetic model, which is the second approach. In the kinetic model, the rate of mass loss due to gas-water phase mass transfer is described by a first-order linear function:

$$\frac{\partial \theta_g C_g}{\partial t} = a_{gw} k_{gw} \theta_g (H' C_w - C_g) \cdots\cdots (24)$$

where a_{gw} is the specific interfacial area between the gas and mobile water [L^2L^{-3}], k_{gw} is the mass transfer coefficient [LT^{-1}]. Since the product of these parameters, a_{gw} and k_{gw} is typically measured by experiments, an effective mass transfer coefficient $K_{gw} (= a_{gw} k_{gw}) [T^{-1}]$, is generally used for the product of a_{gw} and k_{gw} [16]. The rate of losses of a hydrocarbon to gas phase S_{aw} in (9) is described by the nonequilibrium model as

$$S_{aw} = \frac{\partial \theta_g C_g}{\partial t} = K_{gw} \theta_g (H' C_w - C_g) \cdots\cdots (25)$$

In addition to solute transport in aqueous phase, vapor solute transport subsequent to mass exchanges between water and gas may play a significant role in controlling the fate of volatile contaminant in the unsaturated soil. Vapor diffusion of the volatile contaminant, especially in upper soil of the unsaturated zone may be significant. A general governing equation for the fate of a component in the gas phase in the unsaturated soil may be written using equilibrium approach:

$$\frac{\partial \theta_g C_g}{\partial t} = \frac{\partial}{\partial z}\left(D_g \theta_g \tau_g \frac{\partial C_g}{\partial z}\right) \cdots\cdots (26)$$

where τ_g is the tortuosity for the gas phase, $[LL^{-1}]$ and D_g is diffusion coefficient in the gas phase $[L^2T^{-1}]$. The equilibrium relationships given by (23) are substituted into (26) to obtain the conservation of mass equation for the equilibrium model. The equation for the kinetic model is :

$$\frac{\partial \theta_g C_g}{\partial t} = \frac{\partial}{\partial z}\left(D_g \theta_g \tau_g \frac{\partial C_g}{\partial z}\right) + K_{gw} \theta_g (H' C_w - C_g) \cdots\cdots (27)$$

Corapcioglu (1987) termed $D_g \theta_g \tau_g$ as the effective soil diffusion coefficient for gas phase.

In this study, we assumed immobile gas to be at atmospheric pressure, and neglected density gradients for simplicity of model. Water is assumed to act as the wetting fluid in the aquifer system, which implies that there is no direct contacts between the gas and solid phase, biomass or roots.

While using the equilibrium model for gas-water mass transfer, the substitution of (10), (12), (16), (17), (20), and (23) coupled with (11), (13), (14), (15), and (19) into (9) gives the mass balance equation for the aqueous phase hydrocarbon in vegetated unsaturated soils

$$\frac{\partial}{\partial t}\left[1 + \frac{\rho_{s(1-n)} K_d}{\theta_w} + \frac{\pi_r^2 L_d R_{cf}}{\theta_w} + \frac{H'(n-\theta_w) C_w}{\theta_w}\right] \theta_w C_w \cdots\cdots (28)$$

$$= -\frac{\partial}{\partial z}\left[q_w C_w - D_H \frac{\theta_w \partial C_w}{\partial z}\right] - \frac{k_b X_b C_w}{K_{bs} + C_w} - L_d \int_{r_r}^{r_r + L_r} \frac{k_f X_f C_f}{K_{fs} + C_f}\, d\pi r^2 - T_{scf} C_w L_d q_{av}$$

The conservation of mass equation in aqueous phase for nonequilibrium mass transfer model is by substituting (25) instead of (23) into (9).

$$\frac{\partial}{\partial t}\left[1 + \frac{\rho_s (1-n) K_d}{\theta_w} + \frac{\pi_r^2 L_d R_{cf}}{\theta_w}\right] \theta_w C_w \cdots (29)$$

$$= -\frac{\partial}{\partial z}\left[q_w C_w - D_H \frac{\theta_w \partial C_w}{\partial z}\right] - \frac{k_b X_b C_w}{K_{bs} + C_w} - L_d \int_{r_r}^{r_r + L_r} \frac{k_f X_f C_f}{K_{fs} + C_f}\, d\pi r^2 - T_{scf} C_w L_d q_{av} - K_g \theta_g (H' C_w - C_g)$$

A set of equations (26) coupled with (28) and a set of equations (29) coupled with (27), respectively, constitute governing equations for the fate and transport of a volatile hydrocarbon in vegetated unsaturated soils where vapor solute diffusion occurs with equilibrium and nonequilibrium mass transfer between water and gas phases.

3. SUMMARY

In this study, we developed a one-dimensional mathematical model to investigate the effect of the use of vegetation in situ to decontaminate soils containing a volatile hydrocarbon. This model needs more information on microbial behavior such as microbial transport and microbial population changes in the root-soil zone, as well as on the volatilization affects of plants. Changes of oxygen concentration available for aerobic biological reactions in the planted soil, which were assumed to be negligible in this study, may be significant enough to be considered. Lateral diffusive transport was not taken into account in this simulation by assuming large volumes of contaminated soil, but it may be great in small volumes of hydrocarbon-contaminated soils.

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