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Modeling Cesium Partitioning In the Rhizosphere: A Focus on the Role of Root Exudates

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A conceptual model is being developed for the prediction of cesium partitioning between bound, aqueous, and phytoextracted phases in the rhizosphere. The model categorizes the processes that impact cesium partitioning into six submodels: geochemistry, physical factors, root density, microorganisms, nutrients, and root exudates. A seventh submodel (Cs fate) describes Cs movement between the three phases. Functional relationships and parametric values within and between the submodels are developed based on literature, field characterization, and laboratory experiments. Sensitivity analyses were first conducted to evaluate the effects of root exudates on Cs partitioning. The model was also used to test the sensitivity of root density, microbial population, potassium requirement and concentration, and moisture content on the concentration of root exudates and consequently on Cs partitioning. An increase in the concentration of root exudates results in a greater decrease in the bound concentration and greater increase in the aqueous and phytoextracted concentrations. In general, the other parameters affect Cs partitioning according to how they affect the fate of root exudates. However, the comprehensive nature of the system renders a complex overall effect on Cs partitioning. In summary, the model provides a framework for better understanding the complex interaction of processes that control Cs fate in the rhizosphere.

Key Words: *radiocesium, solubilization, phytoextraction.*

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INTRODUCTION

Radiocesium (particularly ^{137}Cs) is a common contaminant world-wide and one of the most common contaminants found at Department of Energy (DOE) sites (DART, 1999). Remediation of ^{137}Cs-contaminated soil is challenging because Cs binds strongly within the soil matrix and its release may require the breakdown of the soil minerals. Typical treatment approaches include soil excavation and capping to minimize surface exposure and leaching. However, such methods are expensive and do not extract the contaminants from the soil.

It is envisioned that the biological and chemical effects of the plant root system can promote release and capture of Cs. Many plants have the ability to accumulate metals, thereby providing a mechanism to effectively remove the Cs from the rhizosphere, the zone where soil and plant roots interface. Several investigations have demonstrated the ability of plants to accumulate radionuclides, including ^{137}Cs (e.g., Lasat *et al*., 1998). Research has included evaluations of the factors affecting Cs partitioning, such as plant type and growth stage (e.g., Broadley and Willey, 1997; Smolders and Shaw, 1995) and soil characteristics (e.g., Gerzabek *et al*., 1998).

The fate and bioavailability of Cs in the rhizosphere can be dramatically different from that of the bulk soil. In particular, three cesium pools, bound, aqueous, and phytoextracted, have to be considered for evaluation of Cs fate in the rhizosphere. Consistent with other ions with low hydration energies, inorganic complexes of Cs are generally weak. Precipitates of Cs under natural soil conditions are not expected. However, Cs^+ strongly binds to soils with high clay content (USEPA and USDOE, 1999).

Cs bound in the clay minerals is categorized further as either “fixed” or “exchangeable”. The “fixed” form is recalcitrant, because it is bound in the interlayers of the phyllosilicate minerals, such as mica, illite, vermiculite, and smectite. The “exchangeable” fraction includes the regular exchange sites (RES), located on the external surfaces of the mineral, and the frayed edge sites (FES) located in the wedge zones of the mineral. The FES specifically sorb low-hydration ions, particularly Cs, while other, more hydrated ions compete more effectively than Cs for the RES (Delvaux *et al.,* 2001). Although the FES accounts for a maximum of approximately 2% of the overall cation exchange capacity (CEC), these sites control the retention of Cs (Delvaux *et al*., 2000). Exchange reactions between aqueous and exchangeable fractions occur at a rate such that equilibrium can be established under typical environmental fluctuations. The release of ions with low-hydration energies, such as potassium (K^+) and Cs^+, from the recalcitrant pool occurs at low but measurable rates and appears to be driven by diffusion. Weathering of the minerals, however, may increase the rate of release (Kasimovsky, 1993; Palmer, 2000). This weathering is a function of root exudates and microorganisms in the rhizosphere.

Cesium fate and transport is clearly controlled by many interactive biological, geochemical, and physical processes. Thus, modeling Cs solubilization in the rhizosphere requires integrating these processes into a comprehensive model. Models have attempted to describe the fate and transport of radionuclides in the rhizosphere, including solubilization from the bound phase (e.g., Kasimovsky, 1993). However, these models only consider discrete subjects rather than incorporating the interactions between the processes as an ecological packet. The objective of the current work is to develop an integrated comprehensive model for Cs solubilization in the rhizosphere. This article presents the formulation and simulation of Cs partitioning and the factors affecting it in the rhizosphere, with particular focus on the role of root exudates.

FORMULATION

The conceptual model categorizes the processes into six submodels: geochemistry, physical factors, root density, microorganisms, nutrients, and root exudates. A seventh submodel relates the three specific forms of Cs: bound, aqueous, and phytoextracted and is the crux of the comprehensive model that is developed. Cs partitioning is modeled using functional relationships.

Cs Fate Submodel

The flows from the bound phase to the aqueous phase and from the aqueous phase to the phytoextracted phase ($\mathrm{Flow_{sol}}$ and $\mathrm{Flow_{phy}}$, respectively) reflect the principle that mass balance constrains the fate of Cs, such that in a given volume of interest (e.g., µmol Cs/L pore fluid):

$$\mathrm{Cs_{total}} = \mathrm{Cs_a} + \mathrm{Cs_b} + \mathrm{Cs_p} \tag{1}$$

where $\mathrm{Cs_{total}}$, $\mathrm{Cs_a}$, $\mathrm{Cs_b}$, and $\mathrm{Cs_p}$ are the total, aqueous, bound, and phytoextracted mass of Cs per volume of pore fluid, respectively. Precipitated Cs is ignored because the dominant aqueous Cs species is the free ion. The bound pool is the sum of exchangeable Cs ($\mathrm{Cs_e}$) and interlayer exchangeable Cs ($\mathrm{Cs_i}$). The phytoextracted pool is the sum of Cs in living plant tissue ($\mathrm{Cs_{pl}}$) and in decaying plant tissue ($\mathrm{Cs_{pd}}$). Therefore,

$$\mathrm{Cs_{total}} = \mathrm{Cs_a} + \mathrm{Cs_e} + \mathrm{Cs_i} + \mathrm{Cs_{pl}} + \mathrm{Cs_{pd}} \tag{2}$$

Assuming a batch system where the total mass in a control volume does not change with time and applying the chain rule,

$$\frac{\partial Cs_a}{\partial t}+\frac{\partial Cs_e}{\partial Cs_a}\frac{\partial Cs_a}{\partial t}+\frac{\partial Cs_i}{\partial t}+\frac{\partial Cs_{pl}}{\partial Cs_a}\frac{\partial Cs_a}{\partial t}+\frac{\partial Cs_{pd}}{\partial t}=0 \qquad (3)$$

Equation 3 can be rearranged to evaluate the change of aqueous Cs concentration with respect to time (Equation 4), which requires evaluation of the rates of solubilization and phytoextraction.

$$\frac{\partial Cs_a}{\partial t}=-\frac{\dfrac{\partial Cs_i}{\partial t}+\dfrac{\partial Cs_{pl}}{\partial Cs_a}\dfrac{\partial Cs_a}{\partial t}+\dfrac{\partial Cs_{pd}}{\partial t}}{\left(1+\dfrac{\partial Cs_e}{\partial Cs_a}\right)} \qquad (4)$$

The rate of change in aqueous Cs concentration is a function of the rate of change of interlayer Cs, the relationship between exchangeable and aqueous phases, the relationship between phytoextracted Cs in living plant tissue and aqueous phases, and the rate of release of phytoextracted Cs from decaying plant tissue.

The rate of release of Cs_i into the exchangeable pool is given by,

$$\frac{\partial Cs_i}{\partial t}=\left(\frac{\partial Cs_i}{\partial t}\right)_{[L]}+\left(\frac{\partial Cs_i}{\partial t}\right)_{[Ch]}+\left(\frac{\partial Cs_i}{\partial t}\right)_{pH}+\left(\frac{\partial Cs_i}{\partial t}\right)_{D} \qquad (5)$$

The terms on the right-hand side of Equation 5 are the release rates due to the concentration of exudate ligands ([L]), the concentration of microbial chelators ([Ch]), pH, and the diffusive rate (D), respectively. The promoted release rates due to exudate ligands and microbial chelators are based on their sorption with the soil matrix, thereby causing the dissolution of the mineral. It is assumed that these rates relate to [L] and [Ch], respectively, according to Langmuir isotherms. The relationship between pH and Cs_i is assumed to be relatively symmetrical, increasing exponentially as the pH moves from neutral in both directions. In the absence of any weathering effects, Cs_a may diffuse either into or out of the bound pool, depending on the concentration gradient. The evaluation of the ligand-promoted and pH-promoted release rates is the primary focus of current modeling effort.

The relationship between exchangeable and aqueous Cs can be calculated assuming a Langmuir-type adsorption isotherm,

$$Cs_w=\frac{\rho_b}{\theta\cdot \mathrm{conv}}\frac{S_{max}K_L Cs_a}{1+K_L Cs_a}\ \text{and}\ \frac{\partial Cs_e}{\partial Cs_a}=\frac{\rho_b}{\theta\cdot \mathrm{conv}}\frac{S_{max}K_L}{(1+K_L Cs_a)^2}=K_{ND}(Cs_a) \qquad (6)$$

where S_{max} is the maximum concentration of exchangeable sites (e.g., μmol Cs·kg^{-1} soil), K_L is the Langmuir adsorption parameter for exchangeable sites (aqueous concentration^{-1}, e.g., L pore fluid·μmol^{-1} Cs), ρ_b is the dry bulk density of the soil (e.g., kg soil·m^{-3} bulk soil), θ is the volumetric water content (e.g., m^3 pore fluid·m^{-3} bulk soil), and $conv_v$ is the volumetric conversion (e.g., L·m^{-3}). The term $\rho_b/(\theta^o conv_v)$ translates the units of Cs_e from concentration per mass of bulk soil into a pore fluid volumetric concentration. $K_{ND}(Cs_a)$, that is, K_{ND} as a function of Cs_a, is the nondimensional adsorption relationship between the concentrations in the exchangeable and aqueous phases. Exudate ligands, microbial chelators, and pH may increase or decrease the value of $K_{ND}(Cs_a)$, given in Equation 6, by multiplicative factors (F_L, F_{Ch}, and F_{pH}), and assumes that S_{max} and K_L were determined in the absence of complexing agents and at neutral pH, that is, effect of 1,

$$K'_{ND}(Cs_a) = K_{ND}(Cs_a) \cdot F_L \cdot F_{Ch} \cdot F_{pH} \tag{7}$$

Smolders *et al.* (1997) indicates that a linear relationship can be assumed between Cs_p and Cs_a,

$$Cs_p = CF \cdot Cs_a \text{ and } \frac{\partial Cs_p}{\partial Cs_a} = CF \tag{8}$$

where CF is a concentration factor. More accurately, it is the living plant tissue that is in equilibrium with the aqueous phase, as the decaying fraction releases Cs back into the aqueous pool at a kinetic rate. Therefore, this relationship is between Cs_{pl} and Cs_a.

$$\frac{\partial Cs_{pl}}{\partial Cs_a} = CF \tag{9}$$

where CF is the concentration factor defined by Smolders *et al.* (1997). They assumed that CF decreases logarithmically with a logarithmic increase in potassium concentration ($[K^+]$). Having examined Cs uptake by ryegrass in various soils as a function of $[K^+]$, they determined an empirical relationship (Equation 10), where b_0 and b_1 are regression coefficients.

$$\log(CF) = b_0 \exp(-b_1 \log[K^+]) \tag{10}$$

The CF described in Equation 10 applies only to the shoot concentration and is in L·kg^{-1} (Smolders *et al.*, 1997). It is made applicable for the total Cs_p and converted to a dimensionless CF_{ND} by,

$$CF_{ND} = CF \cdot \frac{1 + K_{sh\_rt}}{K_{sh\_rt}} \cdot \frac{BM_{shoot} \cdot \rho_p}{conv_m \cdot conv_v \cdot \theta} \tag{11}$$

where K_{sh_rt} is the Cs equilibrium transfer function between shoots and roots, BM_{shoot} is the shoot biomass (g·plant^{-1}), ρ_p is the volumetric plant density (plant·m^{-3}), $conv_m$ is a mass conversion (g·kg^{-1}), $conv_v$ (L·m^{-3}), and θ (m^3 pore fluid·m^{-3} bulk soil). The ρ_p is the aerial plant population density (plant·m^{-2}) divided by the depth that the plants extend (m). K_{sh_rt} is calculated as the ratio of the Cs pore fluid volumetric concentration in shoots (Cs_{p_sh}) to that in roots (Cs_{p_rt}), such that,

$$Cs_{p\_sh} = \frac{Cs_p \cdot K_{sh\_rt}}{1 + K_{sh\_rt}} \tag{12}$$

$$Cs_{p\_roots} = \frac{Cs_p}{1 + K_{shoot\_root}} \tag{13}$$

The relationship between Cs_a and Cs_p is affected by the release of phytoextracted Cs back into the aqueous pool due to the decay of plant biomass, that is, ($\partial Cs_{pd}/\partial t$) at the rate $k_{release}$, such that,

$$\frac{\partial Cs_{pd}}{\partial t} = -Cs_p \cdot k_{release} \tag{14}$$

Root Exudates and Other *Submodel*s

Solving for aqueous Cs concentration by Equation 4 requires evaluations of the release of interlayer cesium (Equation 5) and its relationship with exchangeable cesium (Equations 6 and 7) and phytoextracted cesium (Equations 8 to 14). This research focuses primarily on the effects of root exudates on Cs solubilization via the effects of [L] and pH, both determined in the geochemistry submodel as functions of the aqueous concentration of root exudates ([E]). The root exudate submodel defines the initial value of [E] and its rate of change (∂[E]/∂t) according to the influx ($\partial R_{Total}/\partial t$) and outflux ($\partial L_{Total}/\partial t$),

$$\frac{\partial [E]}{\partial t} = \frac{\partial R_{Total}}{\partial t} - \frac{\partial L_{Total}}{\partial t} \tag{15}$$

The influx is the rate per volume of pore solution that the roots release exudates into the rhizosphere,

$$\frac{\partial R_{\mathrm{Total}}}{\partial t} = \left(\frac{\partial R_S}{\partial t} + \frac{\partial R_{NS}}{\partial t}\right)\frac{\rho_r \rho_P}{\theta \cdot \mathrm{conv}_v} \qquad (16)$$

where $\partial R_{NS}/\partial t$ and $\partial R_S/\partial t$ are the release rates under nonstressed and stressed conditions, respectively, per unit weight of root dry matter. The factor $\rho_r\rho_p$/ $(\theta^{\underline{o}}\mathrm{conv}_v)$ converts the total release rate from units of flux per mass of bulk soil into a pore fluid volumetric flux, where ρ_r is the root density ($g \cdot plant^{-1}$). Root and volumetric plant density are defined in the root density submodel.

Unit release rates due to stresses on the plant system are caused by $[K^+]$, the concentration of ammonium ($[NH_4^+]$), θ, oxygen (O_2), and temperature (T) present in the soil system.

$$\frac{\partial R_S}{\partial t} = \frac{\partial R_{[K^+]}}{\partial t} + \frac{\partial R_{[NH_4^+]}}{\partial t} + \frac{\partial R_{\theta}}{\partial t} + \frac{\partial R_{O_2}}{\partial t} + \frac{\partial R_T}{\partial t} \qquad (17)$$

The nutrients submodel determines $[K^+]$ and $[NH_4^+]$, and the physical factors submodel determines θ, O_2, and T.

Outflux is the rate of total exudate loss per volume of pore solution. It is a function of miscellaneous exudate loss and microbial consumption of the exudates. The former is a product of a miscellaneous loss rate (k_{misc}) and [E]. Likewise, the latter is the product of a microbial consumption rate (k_{micro}) and [E]. The $\partial L_{Total}/\partial t$ is

$$\frac{\partial L_{\mathrm{Total}}}{\partial t} = [E]k_{\mathrm{misc}} + [E]k_{\mathrm{micro}} \qquad (18)$$

The parameter k_{micro} is a function of the size of the microbial population (MP) (g^{-1} soil) according to an assumed exponential relationship. MP and its change with time ($\partial MP/\partial t$) are defined in the microorganisms submodel. Microbial effects on [Ch] and pH are determined in the geochemistry submodel as functions of MP. The rate of pH change ($\partial pH/\partial t$) is calculated from [E] and MP and the buffer intensity of the soil, accounting for the time it takes to make the change.

The parameters θ, $[K^+]$, and ρ_r are determined in the submodels for physical factors, nutrients, and root density, respectively. The physical factors submodel defines the initial θ and its rate of change ($\partial\theta/\partial t$). The nutrients submodel defines the initial $[K^+]$ in units of mass per volume of pore fluid, and its rate of change ($\partial[K^+]/\partial t$) according to the nutrient input and uptake. This submodel largely depends on the $[K^+]$ required per day ($[K^+]_{reqd}$) and the fraction of nutrients needs met (FNNM), calculated as $[K^+]/[K^+]_{reqd}$ up to a maximum value of 1. The root density submodel defines the ρ_r and its rate of change ($\partial\rho_r/\partial t$). Root density also defines the plant biomass according to the specified shoot to root weight ratio.

SOLUTION PROCEDURE

The solution procedure is implemented using Systems Thinking, integrating the relationships between the factors affecting Cs fate. Submodels are defined as Cs fate and the six categories. The basic relationships within each submodel, as well as the interactions between submodels have been established. Finite difference methods are used in the Stella® Research 6.0 software package (High Performance Systems, Inc., Hanover, NH) to numerically solve the system of differential equations that comprise the model. The software performs numerical integration according to one of three explicit methods (Euler's method, second-order Runge-Kutta, and fourth-order Runge-Kutta). Although each method provides similar output, Euler's method requires the least computing time and therefore has been applied to this model.

Two critical functional relationships are Flow_{sol}, that is, the flow between the bound phase and the aqueous phase and Flow_{phy}, that is, the flow between the aqueous phase and the phytoextracted phase. Their derivation is based on the change in Cs_a with each time step, which is

$$\frac{\Delta \text{Cs}_a}{\Delta t} = \text{Flow}_{\text{sol}} - \text{Flow}_{\text{phy}} \tag{19}$$

where

$$\text{Flow}_{\text{sol}} = -\frac{1}{\left(1+\dfrac{\partial \text{Cs}_e}{\partial \text{Cs}_a}\right)}\frac{\Delta \text{Cs}_i}{\Delta t} \tag{20}$$

$$\text{Flow}_{\text{phy}} = \frac{\dfrac{\partial \text{Cs}_{pl}}{\partial \text{Cs}_a}\dfrac{\Delta \text{Cs}_a}{\Delta t} + \dfrac{\Delta \text{Cs}_{pd}}{\Delta t}}{\left(1+\dfrac{\partial \text{Cs}_e}{\partial \text{Cs}_a}\right)} \tag{21}$$

where Δ indicates that the changes are discrete approximations of the partial derivatives with time. Equation 20 indicates that Flow_{sol} is zero when there is no release of interlayer Cs. Equilibrium according to K'_{ND} between the total bound and aqueous pools suggests that 100% of the bound pool is exchangeable, thus indicating a depletion of interlayer Cs. The model code reflects this depletion as a multiplier (F_o), which ranges from 0 to 1 to prevent the model from overshooting equilibrium. If the ratio of the total bound concentration to the aqueous concentration is far from equilibrium, that is, greater than $2 \cdot K'_{ND}$, then the multiplier is 1 and the flow as given by Equation 20 will occur. Otherwise, as the ratio approaches equilibrium, the rate of flow is reduced until it is zero.

Substituting $K'_{ND}(Cs_a)$ according to Equations 6 and 7 for $\partial Cs_e/\partial Cs_a$, and accounting for F_o, Equation 20 becomes

$$\text{Flow}_{sol} = -F_o \cdot \frac{1}{1 + K'_{ND}(Cs_a)} \frac{\Delta Cs_i}{\Delta t} \tag{22}$$

There is an inherent circular connection, requiring convergence upon a solution, between K'_{ND} and Cs_a because they are functions of each other. However, due to limitations in the software, this convergence must be performed manually, and thus is performed only for the initial conditions. Subsequent time steps calculate $K'_{ND}(Cs_a)$ using Cs_a from the previous time step. This procedure assumes that the change in Cs_a between time steps is small enough that the sorption isotherm is linear in Δt. This assumption is reasonable in most cases for small Δt.

Substituting CF_{ND} for $\partial Cs_{pl}/\partial Cs_a$, $Cs_p \cdot k_{release}$ for $\partial Cs_{pd}/\partial t$, and ($\text{Flow}_{sol} - \text{Flow}_{phy}$) for $\Delta Cs_a/\Delta t$ according to Equations 8 and 11, Equation 14, and Equation 19, respectively, Flow_{phy} is rewritten as:

$$\text{Flow}_{phy} = \frac{CF_{ND}(\text{Flow}_{sol} - \text{Flow}_{phy}) - Cs_p \cdot k_{release}}{1 + K'_{ND}(Cs_a)} \tag{23}$$

The derivation of Flow_{phy} follows from rearranging the terms of Equation 23.

$$\text{Flow}_{phy} = \frac{CF_{ND} \cdot \text{Flow}_{sol} - Cs_p \cdot k_{release}}{1 + K'_{ND}(Cs_a) + CF_{ND}} \tag{24}$$

Equation 24 indicates that as CF_{ND} increases, Flow_{phy} approaches Flow_{sol}. Solving numerically, Cs_a, Cs_b, and Cs_p at time t are

$$Cs_a(t) = Cs_a(t - \Delta t) + (\text{Flow}_{sol} - \text{Flow}_{phy}) \cdot \Delta t \tag{25}$$

$$Cs_b(t) = Cs_b(t - \Delta t) - \text{Flow}_{sol} \cdot \Delta t \tag{26}$$

$$Cs_p(t) = Cs_p(t - \Delta t) + \text{Flow}_{phy} \cdot \Delta t \tag{27}$$

Similarly, each submodelapproximates the partial derivatives given in **Formulation**.

PARAMETER ESTIMATION AND CASE STUDY

Functional relationships within and between the submodels drive the comprehensive model. These relationships, which may be constants, equations, tabular input, or graphical interpretations of a relationship, define the required inputs of the model, including those presented in **Formulation**. Definitions of each functional relationship are based on field characterization and hypothesis-driven laboratory experimental data. Although the utility of this model is as a tool to guide effective management of soil contaminated with radiocesium, the laboratory experiments and much of the field characterization have been performed on stable Cs. Nevertheless, the model framework applies to both radiocesium and stable Cs. Hypothetical data, consistent with those presented in the literature, are used to define the relationships for which field characterization or experimental data are not available. Where practical, regression analysis on available data is used to determine the parametric values of each functional relationship. Parametric evaluations are limited to relationships that are well understood and for which the data are properly presented within the model framework.

Cs Fate Submodel

Initially, the model was used to evaluate a hypothetical case for which parametric values were assigned according to the literature and available field characterization. Parametric estimations were updated to reflect more current data, including that from initial laboratory experiments as they became available. According to field characterization data, a constant value was assigned to ρ_b (1000 kg soil·m^{-3} soil). Laboratory experimental data suggest a value of S_{max} of 107 μmol Cs·kg^{-1} soil and K_L of 0.78 L pore fluid·μmol^{-1} Cs at pH = 7. These values lead to an initial ratio of bound to aqueous of approximately 10,000 L pore fluid·kg^{-1} soil, which is reasonable considering literature suggests a linear adsorption constant for the total bound pool on the order of magnitude of 100 to 100,000 L, pore fluid·kg^{-1} soil (Smolders *et al*., 1997). Field characterization data support an initial estimate of stable Cs_b on the order of magnitude of 1000 μ*M* when converted according to estimated soil data. An estimated initial value for Cs_a was calculated according to the initial assumed K'_{ND} and initial fraction of exchangeable to total bound that was assumed to be 0.1. The initial value of K'_{ND} (1002) was reached by manually adjusting it until the solution converged within acceptable error (<0.5%). An initial estimate of Cs_p was calculated according to the initial CF_{ND}. The volumetric conversion factor $conv_v$ is a constant (1000 L·m^{-3}).

According to Smolders *et al*. (1997), the coefficients to determine CF (Equation 10) are $b_0 = 2.08 \pm 0.04$ and $b_1 = 0.59 \pm 0.03$ such that CF is in units of $L\cdot kg^{-1}$. CF_{ND} is calculated according to Equation 11 with $conv_m = 1000\ g\cdot kg^{-1}$ and $conv_v = 1000\ L\cdot m^{-3}$.

Consistent with values calculated from field characterization data, K_{sh_rt} is approximated to be 1. The relationship between the root decay rate and the release rate of Cs_p is assumed to be that 1 g root dry matter (DM)$\cdot$plant$^{-1}\cdot$day^{-1} yields a Cs release rate of 1 day^{-1}. The initial value of root decay in the root density submodelis adjusted to zero to eliminate any release of Cs_p.

Despite the fact that a quantitative assessment of the enhanced release rates from Cs_i into the exchangeable pool has not been completed, qualitative relationships are to some extent understood. As mentioned in **Formulation**, the promoted release rates due to exudate ligands and microbial chelators are assumed to relate to [L] and [Ch], respectively, according to Langmuir isotherms. As [L] increases from 0 to 1000 μM, the promoted release rate of Cs_i increases from 0 to 50 μM Cs$\cdot$day^{-1} (Figure 1a). The release rates caused by microbial chelators are assumed to be similar to those caused by the ligands. However, in this evaluation, [Ch] is assigned a value of 0 μM rendering $(\partial Cs_i/\partial t)_{[Ch]}$ to be 0 μM Cs$\cdot$day^{-1}. The promoted release rates due to pH are assumed to increases exponentially from 0 to 50 μM Cs$\cdot$day^{-1} as the pH moves away from neutral in both directions (Figure 1b). Diffusion of Cs between the bound and aqueous phases is hypothesized to be significantly less than the promoted release rates, and therefore is considered negligible ($(\Delta Cs_i/\Delta t)_D = 0\ \mu M$ Cs$\cdot$day^{-1}).

The effects on $\partial Cs_e/\partial Cs_a$ are assumed to be less significant than the effects due to weathering of the minerals. Linear regression analysis of laboratory experimental data suggests a relationship of $F_{pH} = 0.17\cdot pH\text{-}0.14$ for pH 6 to 10. Further experiments are required to test the effects of ligand and chelator concentrations on $\partial Cs_w/\partial Cs_a$. In the meantime, F_L and F_{Ch} are assigned to be 1, that is, no effect, for this initial evaluation of the model.

Root Exudates and Other Submodels

Currently, the root exudates submodelassigns an initial [E] of 0 μM. Equation 17 in **Formulation** presents the unit exudate release rate as a function of $[K^+]$, θ, $[NH_4^+]$, O_2, and T, present in the soil system. Preliminary experimental data suggest an average release rate of soluble organic carbon under nonstress conditions of approximately 0.14 mg$\cdot$plant^{-1} DM$\cdot$day (Bugbee, Bruce, 2002, personal communication), equivalent to approximately 15 μmol$\cdot$g^{-1} root DM$\cdot$day.

Literature suggests that the release rates increase nonlinearly with increasing stress (e.g., Rovira, 1969; Jones, 1998). Although actual release rates are not yet known, qualitative graphs based on hypothetical data are useful to illustrate the basic relationships between stress and release rate. Stress may cause up to an order

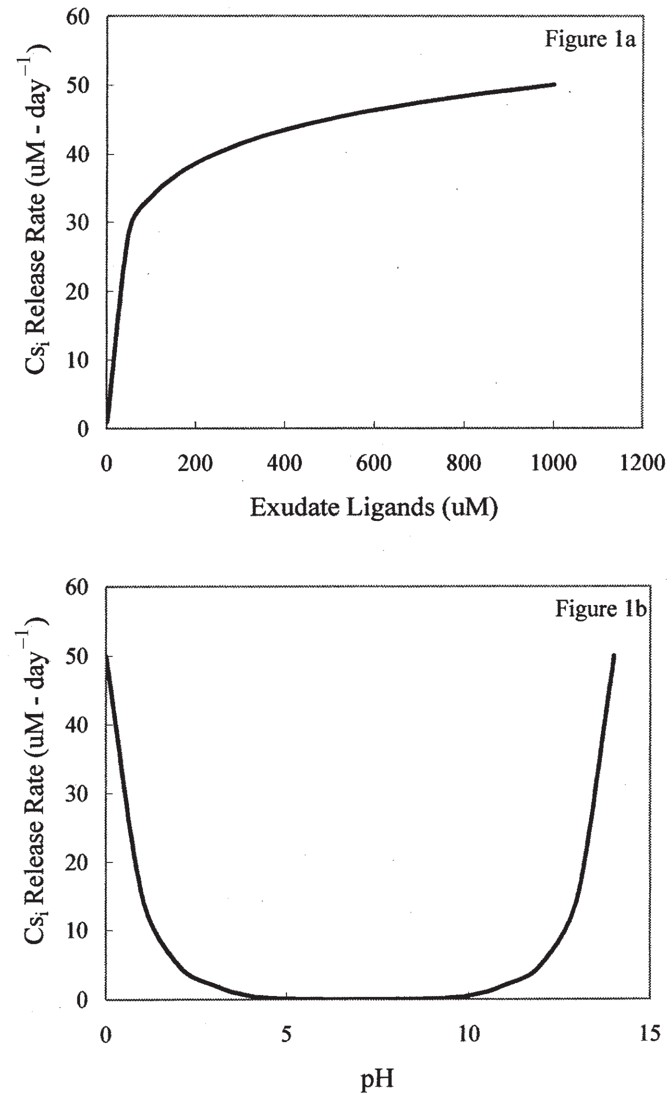

FIGURE 1

Promoted rates of release of Cs_i.

of magnitude increase in the release rate. However, such an increase is not likely to last for more than a few days (Bugbee, Bruce, 2002, personal communication). The initial evaluation of this model focuses only on stresses due to low $[K^+]$ and low θ, assigning the other stresses to be negligible. The model assumes that the FNNM ranges between 0 and 1, causing a respective release rate between an assumed maximum value of 150 and 0 μmol exudates·g^{-1} root DM·day^{-1}. Similarly, the release rate due to θ stress is 0 at saturation, that is, when θ equals the porosity n (assigned a value of 0.4 in the physical factors submodel), and increases to an assumed maximum value of 150 μmol exudates·g^{-1} root DM·day^{-1} when θ equals residual moisture (assigned a value of 0.05 in the physical factors submodel). The miscellaneous loss rate k_{misc} in Equation 18 is assigned a value of 0.2 day^{-1}. The microbial consumption loss rate k_{micro} is assumed to increase from 0 to 0.2 day^{-1} with a logarithmic increase in microbial population.

The geochemistry submodel relates [L] to [E] by a constant ratio of 0.1, that is, 10 μM of exudates yields 1 μM of exudate ligands. This ratio is based on preliminary experimental results, which suggest that approximately 10% of the exudates appear to be organic acid. Furthermore, the predominant organic acid is oxalic acid, which is present under nonstress conditions at approximately 5 mg·L^{-1} (Bugbee, Bruce, 2002, personal communication), equivalent to approximately 40 μM. The initial [Ch], $\partial[Ch]/\partial t$, and $\partial pH/\partial t$ due to microbial activity are all set to zero. Changes in pH with [E] ranging from 0 to 1000 μM are assumed to range from 8 to 6 pH units, respectively. Due to the buffer capacity of most soils and time lag to reach the adjusted pH, an estimate for the time required to change pH is 10 days.

Elements outside the root exudates, geochemistry, and Cs fate submodels are assumed constant. Field characterization results support a value of MP = 1E6 g^{-1} soil in the microorganism submodel. Likewise, for the root density submodel, field characterization results support an estimate of ρ_r = 10 g root DM·$plant^{-1}$, with a plant biomass to root weight ratio of 1.33, equivalent to a shoot to root biomass of 0.33. Such ratios are reasonable for desert grasses (Smith *et al*., 1997). The approximate density of plants is ρ_p = 10 plants·m^{-2} with a depth of roots extending 0.1 m. The nutrients submodel assumes a constant value of $[K^+]$ (0.1 mM), which is in line with such values presented by Smolders *et al*. (1997). The value for $[K^+]_{reqd}$ was assumed to be 0.01 mmol·g^{-1} plant·day^{-1} in order to bring the FNNM to a value such that significant stress would be imposed on the plants. Moisture content data, calculated as the difference between the fresh and dry weights of the soil samples, accounting for the water and soil densities, were averaged over the available field data, yielding a value of approximately 0.1.

Sensitivity Analyses

Sensitivity analyses were conducted to isolate the effects of the concentration of root exudates ([E]). Elements outside the geochemistry and Cs fate submodels are assumed constant. Figures 2a through 2c illustrate the influence that [E] (0, 1000, and 10,000 μ*M*) has on Cs fate. In particular, as [E] increases, [L] increases proportionally, resulting in a greater decrease of the bound concentration and a greater increase of the aqueous and phytoextracted concentrations. It is clear that the rates of release and phytoextraction are nonlinearly related to the concentration of root exudates. These results are consistent with the functional relationships defining the Cs_i promoted release caused by weathering of the minerals. With [E] = 10,000 μ*M* the release rate of Cs_i is so great that equilibrium according to the exchangeable K'_{ND} between the total bound and aqueous concentrations is reached. At that point, the concentration in each phase levels off because there is no more Cs_i to be released, forcing $Flow_{sol}$ and consequently $Flow_{phy}$ to become 0 μ*M* Cs·day^{-1}. Furthermore, as [E] increases, K'_L decreases due to the associated decrease in pH.

Sensitivity analyses were also conducted to isolate the effects of ρ_r, MP, $[K^+]_{reqd}$, and θ (Figures 3 through 6). For these analyses, the root exudates submodel is run with the geochemistry and Cs fate submodels. As the root density increases, the release of root exudates per liter of pore solution increases. Another effect of increasing ρ_r is an increase in the plant's nutrient needs, thus decreasing the FNNM, and consequently increasing [E]. To isolate the effects of ρ_r, θ stress was assigned a value of 0 for all values of θ. Furthermore, a denser root system allows for greater $Flow_{phy}$ and thus an increase in Cs_p. Figures 3a through 3c show the concentration of the three pools of Cs for ρ_r 0.01, 10, and 20 g root DM·plant^{-1}. With increasing ρ_r, the reduction of Cs_b and the increase of Cs_a and Cs_p are all greater. These results are similar to those for varying the initial [E] and holding it constant, because, with the other submodels held constant, the increase in [E] caused by an increase in ρ_r is qualitatively similar. Although an increase in ρ_r yields an increase in Cs_p per volume of pore solution, the mass of plant is also increased with increasing root density. Therefore, the concentration per mass of plant may be less with a greater root density. Nevertheless, the derivative of the phytoextraction curve increases with increasing root density.

Another important relationship is that of the effect of the microbial population on the root exudates. A sensitivity analysis was performed for MP equals 1, 1E5, and 1E10 g^{-1} soil, the results of which are presented in Figures 4a through 4c. Stresses imposed on the system are eliminated. An increase in MP results in a decrease in [E] due to the microbial consumption of exudates, thus influencing Cs partitioning accordingly, that is, less of a decrease of Cs_b and less of an increase of Cs_a and Cs_p.

The model was also used to analyze the sensitivity of the system to the nutrient requirements per mass of plant (Figures 5a through 5c). To isolate the effects of potassium stress, θ stress was assigned a value of 0 for all values of θ. As the potassium requirement increases beyond the point where all needs are met, the fraction of nutrient needs met decreases, causing a stress on the system and consequently an increase in the release of exudates. However, a change in require-

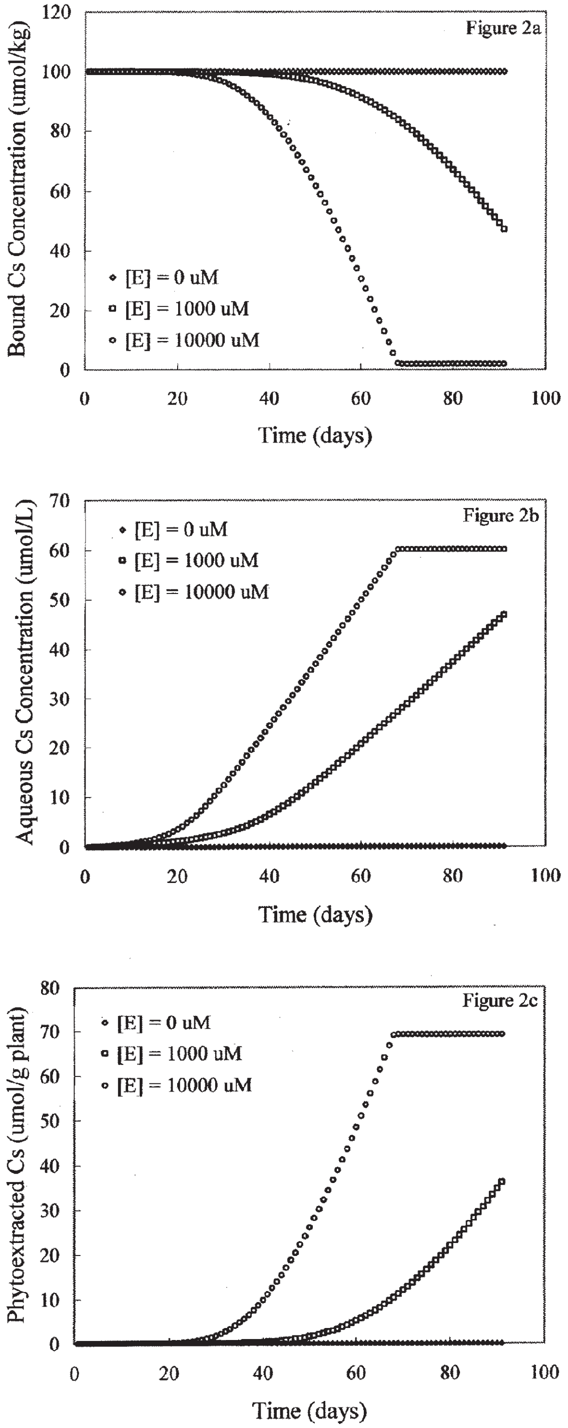

FIGURE 2

Effect of concentration of exudates [E] on Cs partitioning.

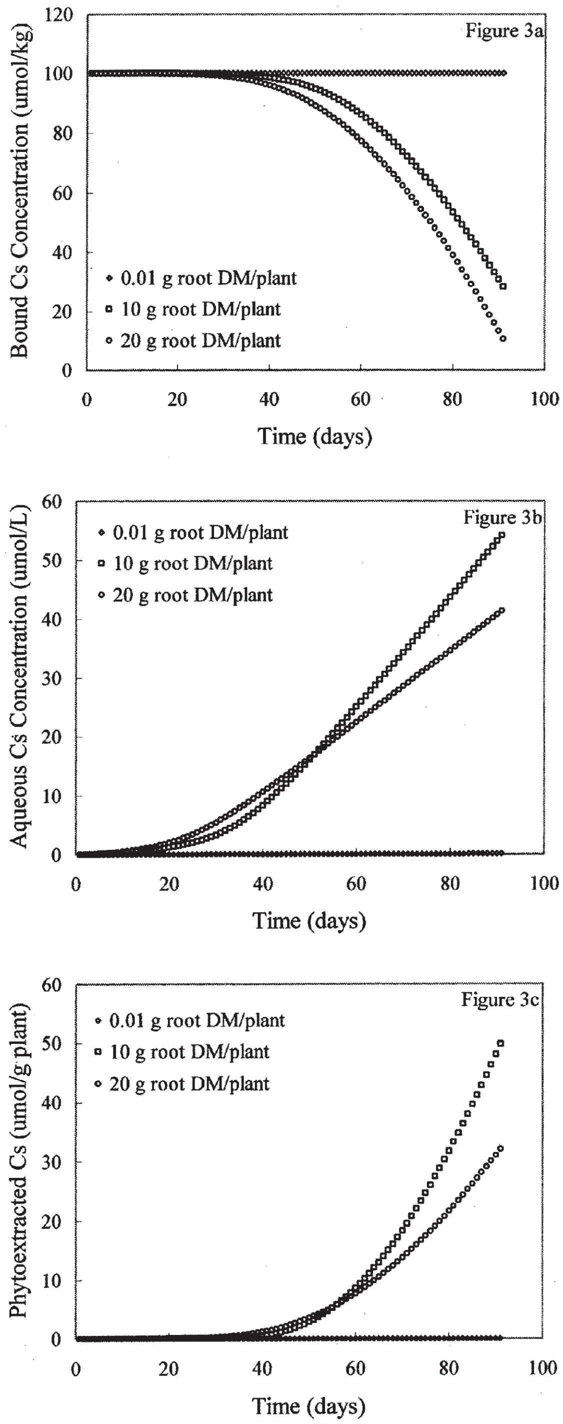

FIGURE 3

Effect of root density on Cs partitioning.

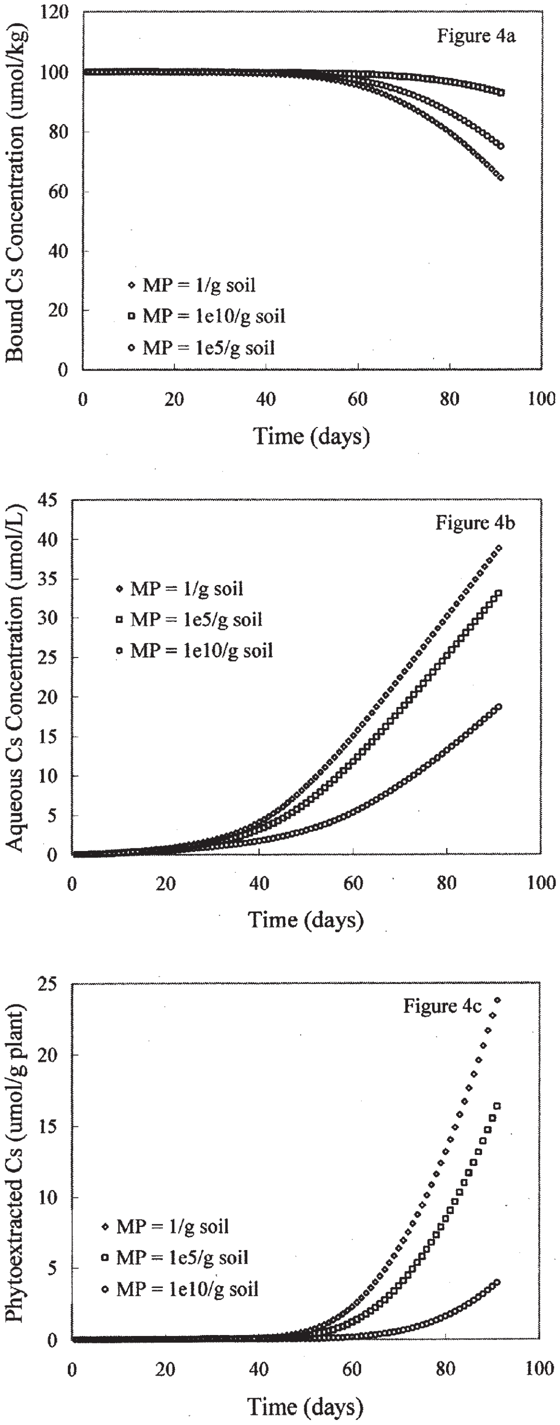

FIGURE 4

Effect of microbial population (MP) on Cs partitioning.

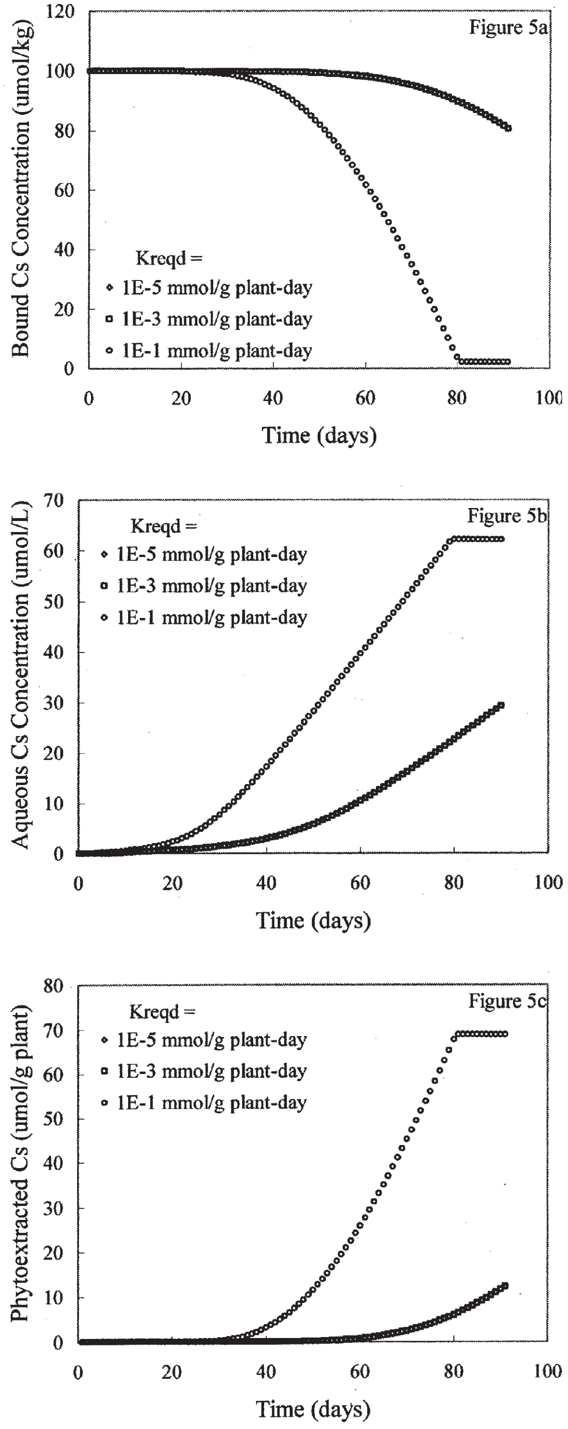

FIGURE 5

Effect of potassium required (K_{reqd}) on Cs partitioning.

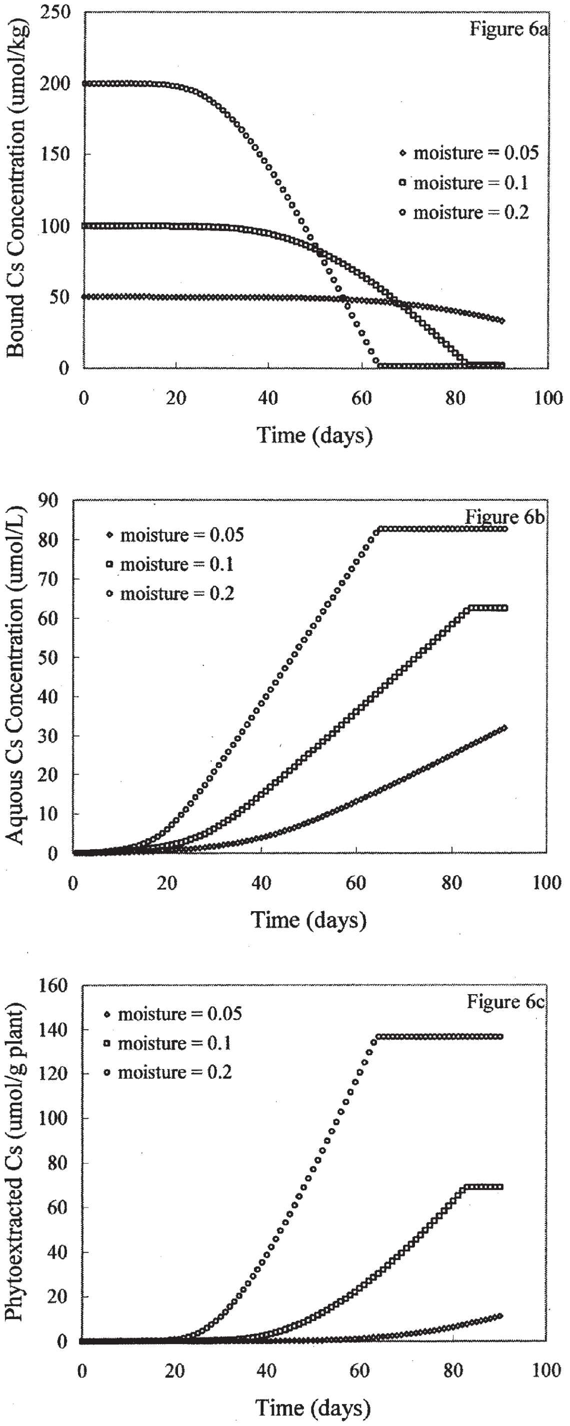

FIGURE 6

Effect of moisture content on Cs partitioning.

ments that does not reduce the nutrient needs met does not stress the system, and thus does not impart an influence on [E] or on Cs partitioning, which is why the lines for $[K^+]_{reqd}$ = 1E-5 and 1E-3 mmol·g^{-1} plant·day^{-1} overlap. Beyond the threshold requirement, the affects are qualitatively similar to those for increasing [E]. Similar results are observed for varying $[K^+]$ in solution instead of $[K^+]_{reqd}$ because it qualitatively has the same effect on the fraction of nutrient needs met that drives the release of [E] (figure not shown). However, CF is also a function of $[K^+]$ according to Equation 5, rendering the effect to be not as straightforward. In that case, a decrease in $[K^+]$, which causes stress on the system and thus an increase in the release of exudates, also causes an exponential increase in CF. As CF increases $Flow_{phy}$ approaches $Flow_{sol}$, so that the flux into the aqueous pool equals the flux into the phytoextracted pool. Such a scenario allows for a decrease in Cs_b without an increase in Cs_a, thereby allowing for greater reduction in Cs_b before reaching equilibrium. Conversely, a decrease in CF, which would result from an increase in $[K^+]$, would cause a decrease in $Flow_{phy}$ and consequently equilibrium to be reached at a greater Cs_b.

Finally, the model tested the sensitivity of the system to changes in θ. With FNNM assigned a value of 1, the stress due to potassium stress was eliminated to isolate the effects of θ stress. The overall effect of θ on Cs partitioning is complicated by the fact that there are several individual effects. An increase in θ yields a decrease in K'_{ND}, and consequently an increase in $Flow_{sol}$. Accordingly, the initial value of K'_{ND} must be adjusted for each θ (initial $K'_{ND} = 2021$ for $\theta = 0.05$; initial $K'_{ND} = 1002$ for $\theta = 0.1$; initial $K'_{ND} = 494$ for $\theta = 0.2$). Likewise, an increase in θ yields a decrease in CF_{ND}, resulting in a decrease in $Flow_{phy}$. However, dilution with increasing θ reduces [E]. An increase in θ may also reduce the level of stress, thereby further decreasing [E]. As [E] decreases, so do their effects on Cs fate. Figures 6a through 6c illustrate the overall influence of θ on the three pools of Cs, suggesting that the increase in [E] outweighs the shifts in equilibrium.

SUMMARY AND CONCLUSIONS

A conceptual model is presented as a framework for better understanding the complex interactions of processes that control Cs fate in the rhizosphere. The model is based on seven integrated submodels for the prediction of processes controlling cesium solubility and partitioning in the rhizosphere. Analyses tested the sensitivity of root exudates on Cs partitioning. Analyses also tested the sensitivity of root density, microbial population, potassium requirement and concentration, and moisture content on the fate of root exudates and consequently on Cs partitioning. The following conclusions were derived based on the results.

1. An increase in [E] results in a greater decrease in Cs_b and a greater increase in Cs_a and Cs_p.

2. Increasing root density results in an increase in [E], thus influencing Cs partitioning accordingly. However, the mass of plant also increases with increasing root density, potentially decreasing the phytoextracted concentration per mass of plant. Additionally, increasing root density increases the ability of the roots to intercept Cs_a.
3. Increasing the microbial population causes a decrease in [E] due to the microbial consumption of exudates, thus influencing Cs partitioning accordingly.
4. Increasing the potassium requirement above the threshold that decreases the FNNM causes a stress on the system, increasing [E], thus influencing Cs partitioning accordingly.
5. Several individual effects of water content on Cs partitioning complicate its overall effect. Increasing θ shifts the equilibria between Cs phases. Dilution with increasing θ reduces [E], thus reducing the effects of exudates. However, θ stress may cause the release of exudates, thus influencing Cs partitioning accordingly.

Modeling the interacting processes affecting cesium partitioning in the rhizosphere will help to generate hypotheses concerning the behavior of cesium in actual complex field soils. Ultimately, the model will be a tool to effectively manage radiocesium contamination in vegetated, shallow soil systems. The future inclusion of other processes in the model will expand its utility and make the model applicable for other metals.

REFERENCES

Broadley, M.R. and Willey, N.J. 1997. Differences in root uptake of radiocaesium by 30 plant taxa. *Environ. Pollut.* **97**, 11–15.

Bugbee, B. 2002. Personal communication, May.

Delvaux, B., Kruyts, N., Maes, E., and Cremers, A. 2001. Fate of radiocesium in soil and rhizosphere. In: *Trace Elements in the Rhizosphere*. (Gobran, G.R., Wenzel, W.W., and Lombi, E., Eds). Boca Raton, CRC Press.

Delvaux, B., Kruyts, N., and Cremers, A. 2000. Rhizosphere mobilization of radiocesium in soils. *Environ. Sci. Technol.* **34**, 1489–1493.

DART. 1999. Decision Analysis for Remediation Technology (DART) Report Generator, Ver. 1.4b. INEEL/SCFA. 1999.

Gerzabek, M.H., Strebl, F., and Temmel, B. 1998. Plant uptake of radionuclides in lysimeter expeimeriments. *Environ. Pollut.* **99**, 93–103.

Kasimovsky, A.A. 1993. Analytical solution for the model of soil radionuclide migration with fixation-leaching reaction. *Ecol. Model.* **66**, 217–229.

Jones, D.L. 1998. Organic acids in the rhizosphere — a critical review. *Plant Soil* **205**, 25–44.

Lasat, M.M., Fuhrmann, M., Ebbs, S.D., Cornish, J.E., and Kochian, L.V. 1998. Phytoremediation of a radiocaesium-contaminated soil: evaluation of cesium-137 bioaccumulation in the shoots of three plant species. *J. Environ. Qual.* **27**, 165–169.

Palmer, C.D. 2000. Cesium Uptake and Release from Phyllosilicates. Draft Scope of Work to INEEL. August 30, 2000.

Rovira, A.D. 1969. Plant root exudates. *Bot. Rev.* **35**, 35–57.

Smith, S.D., Monson, R.K., and Anderson, J.E. 1997. Physiological Ecology of North American Desert Plants. In: *Adaptations of Desert Organisms (*Cloudsley-Thompson, J.L., Eds). Berlin, Springer.

Smolders, E., Van De Brande, K., and Merckx, R. 1997. Concentrations of Cs-137 and K in soil solution predict the plant availability of Cs-137 in soils. *Environ. Sci. Technol.* **31**(12), 3432–3438.

Smolders, E. and Shaw, G. 1995. Changes in radiocaesium uptake and distribution in wheat during plant development: a solution culture study. Plant Soil **176**, 1–6.

United States Environmental Protection Agency (USEPA) and United States Department of Energy (USDOE). 1999. Understanding Variation in Partition Coefficient, K_d Values: Volume II: Review of Geochemistry and Available K_d Values for Cadmium, Cesium, Chromium, Lead, Plutonium, Radon, Strontium, Thorium, Tritium (3H), and Uranium. August 1999.