## Modeling Cesium Fate in the Rhizosphere

Lori Stern Siegel[1], Akram N. Alshawabkeh[1] and Melinda Hamilton[2]

[1]Department of Civil and Environmental Eng., Northeastern University, Boston, MA 02115
[2]Idaho National Engineering and Environmental Laboratory (INEEL), Idaho Falls, ID 83415

Radiocesium (Cs) is one of the most common contaminants found at Department of Energy (DOE) sites. Cs is either bound to soil solids, dissolved in pore water or, when plants are incorporated, phytoextracted. To engineer innovative remediation technologies, it is necessary to understand the solubilization of Cs from the bound phase in the rhizosphere, the zone where soil and plant roots interface. Researchers have investigated many mechanisms controlling the partitioning of Cs between the three phases in the rhizosphere, including geochemical, biological, and physical factors, but only as discrete subjects. Interactions between these components have not been comprehensively modeled as an ecological packet. A conceptual model is being developed that categorizes the processes into six sub-models: geochemistry, physical factors, root density, microorganisms, nutrients, and root exudates. A seventh sub-model (Cs fate) describes Cs movement between the three phases. Functional relationships and parametric values within and between the sub-models are being developed based on literature, field characterization, and on-going laboratory experiments. This approach allows for expertise in defining each sub-model, while simultaneously promoting the comprehensive nature of the system. This extended abstract describes the general foundation for the comprehensive model and focuses on the basic formulation for the Cs fate sub-model.

Remediation of Cs is challenging because Cs binds strongly within the soil matrix and its release may require breakdown of the soil minerals. Bringing the metal from the bound phase to the aqueous phase allows for several remedial approaches, such as phytoextraction, which address a number of regulatory and economic concerns. It is hypothesized that complex biogeochemical processes in the rhizosphere, the zone where soil and plant roots interface, can solubilize bound Cs. Once solubilized, Cs may be available for extraction by the root system. Many plants have the ability to accumulate metals, thereby potentially removing the Cs from the rhizosphere. Although the Cs accumulated in the plants still requires disposal, the volume is greatly reduced because the plants effectively concentrate the Cs. Solubilization and phytoextraction could also create an upward movement of contaminants into the top few inches of soil, thereby reducing leaching into the vadose zone and aquifer.

Evaluation of the Cs solubility within the rhizosphere is complex and involves many processes that are controlled by geochemical factors, such as pH and ionic strength; biological factors, such as exudates and microbial activity; and physical variables, such as soil water content and temperature. Although researchers have evaluated some of these variables and their effects on metal solubility, a "Systems Approach" that integrates the complex geochemical, biological, and physical processes is required to develop a comprehensive model for metals fate in the rhizosphere. This study focuses on Cs because of its high frequency at DOE sites.

A model rhizosphere system has been chosen such that the parameters of the model plant/soil system to be studied can be investigated with sufficient control. A crested wheatgrass system

with Cs contamination was selected. Three field sites were chosen for characterization. The data and relationships derived from field studies are available for inclusion in the model and have shaped laboratory conditions.

The modeling effort is being implemented using Systems Thinking, integrating the relationships between the many factors affecting Cs solubilization. Software (Stella/iThink, developed by High Performance Systems, Inc., Hanover, New Hampshire) based on this approach allows for these relationships to be set up in sectors, with each sector representing a sub-model. The sub-models are defined as Cs fate and the six categories of factors, i.e., geochemistry, physical factors, root density, microorganisms, nutrients, and root exudates. The basic relationships within each sub-model, as well as the interactions between sub-models have been established. This approach allows for expertise in defining each sector, while simultaneously promoting the ecological packet. Currently, this research focuses primarily on the specific effects of root exudates on Cs partitioning.

Cs solubilization is modeled in the "Cs fate" sector. The flows from the bound phase to the aqueous phase and from the aqueous phase to the phytoextracted phase ($Flow_{sol}$ and $Flow_{phy}$, respectively) reflect the principle that mass balance controls the fate of Cs, such that in a given volume of interest (e.g., $\mu$mol Cs/L pore fluid):

$$Cs_{total} = Cs_a + Cs_w + Cs_i + Cs_p \qquad (1)$$

$Cs_{total}$, $Cs_a$, $Cs_w$, $Cs_i$, $Cs_p$ are the total, aqueous, weakly bound, interlayer tightly bound, and phytoextracted mass of Cs per volume of pore fluid, respectively. Precipitated Cs is ignored because the dominant aqueous Cs species is the uncomplexed ion. Both $Cs_w$ and $Cs_p$ depend on $Cs_a$. Assuming a batch system where the total mass does not change with time and applying the chain rule,

$$\frac{\partial Cs_a}{\partial t} + \frac{\partial Cs_w}{\partial Cs_a}\frac{\partial Cs_a}{\partial t} + \frac{\partial Cs_i}{\partial t} + \frac{\partial Cs_p}{\partial Cs_a}\frac{\partial Cs_a}{\partial t} = 0 \quad (2)$$

Therefore,

$$\frac{\partial Cs_a}{\partial t} = -\frac{1}{\left(1 + \frac{\partial Cs_w}{\partial Cs_a} + \frac{\partial Cs_p}{\partial Cs_a}\right)}\frac{\partial Cs_i}{\partial t} \qquad (3)$$

Equation 3 describes the change of $Cs_a$ with respect to time, which is dependent upon the rate of release of $Cs_i$, the relationship between $Cs_w$ and $Cs_a$, and the relationship between $Cs_p$ and $Cs_a$. Diffusion drives the release of $Cs_i$ to the weakly bound pool, but it is hypothesized that weathering of the minerals, enhanced in the rhizosphere, may increase the rate of release. The relationship between $Cs_w$ and $Cs_a$, which may also be affected in the rhizosphere, can be calculated assuming a Langmuir type adsorption isotherm, such that:

$$Cs_w = \frac{\rho_b}{\theta * conv}\frac{S_{max}KCs_a}{1 + KCs_a} \quad \text{and} \quad \frac{\partial Cs_w}{\partial Cs_a} = \frac{\rho_b}{\theta * conv}\frac{S_{max}K}{\left(1 + KCs_a\right)^2} \qquad (4)$$

$S_{max}$ is the maximum concentration of sites (e.g., $\mu$mol Cs/kg soil), K is the Langmuir adsorption parameter (1/aqueous concentration, e.g., L pore fluid/$\mu$mol Cs), $\rho_b$ is the dry bulk density of the soil (e.g., kg soil/m$^3$ bulk soil), $\theta$ is the volumetric water content (e.g., m$^3$ pore fluid/m$^3$ bulk soil,

determined in the physical factors sub-model) and *conv* is the volumetric conversion (e.g., 1000 L/m$^3$). The term $\rho_b/(\theta*conv)$ translates the units of $Cs_w$ from concentration per mass into a pore fluid volumetric concentration.

Each time step incorporates $Flow_{sol}$, i.e., the flow from the bound phase to the aqueous phase and $Flow_{phy}$, i.e., the flow from the aqueous phase to the phytoextracted phase. Looping back the resulting aqueous Cs concentration into the equation for $\partial Cs_w/\partial Cs_a$ (Equation 4) accounts for $\partial Cs_p/\partial Cs_a$ in Equation 3. The model code for $Flow_{sol}$ is thus:

$$Flow_{sol} = \frac{1}{\left(1 + \dfrac{\partial Cs_w}{\partial Cs_a}\right)} \frac{\partial Cs_i}{\partial t} \qquad (5)$$

$Flow_{phy}$ is not yet well developed and is being evaluated based on field characterization data and literature. However, based on literature, the relationship between phytoextracted and aqueous Cs can be quantified assuming linearity according to a concentration factor (CF), such that:

$$Cs_p = CF \cdot Cs_a \qquad \text{and} \qquad \frac{\partial Cs_p}{\partial Cs_a} = CF \qquad (6)$$

Substituting CF and $Flow_{sol}$ according to Equations 6 and 5 for $\partial Cs_p/\partial Cs_a$ and $\partial Cs_a/\partial t$, respectively, the model code for $Flow_{phy}$ is:

$$Flow_{phy} = CF \cdot Flow_{sol} \qquad (7)$$

Based on literature, it is assumed that CF decreases on a log-log scale with potassium concentration, determined in the nutrients sub-model. It is further assumed that CF increases nonlinearly with increasing root density, determined in the root density sub-model.

Figure 1 plots the three phases versus time for a one-year period for a hypothetical case, where initial $Cs_i + Cs_w$ = 1,000 µmol/L, initial $Cs_a$ = 0.1 µmol/L, initial $Cs_p$ = 0.025 µmol/L, $S_{max}$ = 5 µmol Cs/kg soil, K = 0.025 L pore fluid/µmol Cs, $\rho_b$ = 1,700 kg soil/m$^3$ bulk soil, conv = 1,000 L/m$^3$, [K] = 1.4 to 10 mM, $\rho_r$ = 0.02 to 0.339 mg root dry matter per plant, and $\theta$ = 0.06 to 0.25 m$^3$ pore fluid/m$^3$ bulk soil.
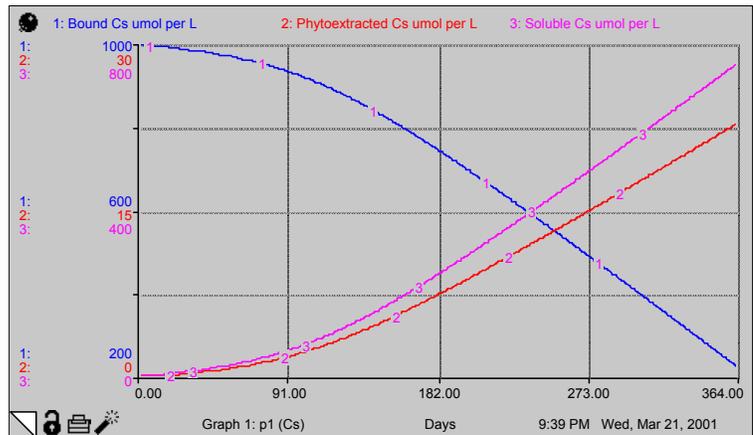


Figure 1: A simplified presentation of the Cs modeling results

In summary, the model provides a framework for better understanding the fundamental processes that control Cs fate in the rhizosphere. Modeling results will generate hypotheses for additional investigations to further elucidate these mechanisms. The ability to better understand, predict, and control Cs solubilization could be applied to other metals in the future. Ultimately, the model will be used as a tool for enhancing field implementation of *in situ* solubilization of metals for a variety of remedial activities.

## CONTACT INFORMATION

Lori Stern Siegel
Department of Civil and Environmental Engineering
Northeastern University, Boston, MA 02115
Mailing address:
33 Landing Road #2
Enfield, NH 03748
Tel:  603-632-7595
Fax:  603-632-7595
lsiegel@valley.net

Akram N. Alshawabkeh
Department of Civil and Environmental Engineering
Northeastern University
Huntington Avenue
Boston, MA 02115
Tel:  617-373-3994
Fax:  617-373-4419
aalsha@neu.edu

Melinda Hamilton
Idaho National Engineering and Environmental Laboratory (INEEL)
P.O. Box 1625
Idaho Falls, ID 83415-2203
Tel:  208-526-0948
Fax:  208-526-0828
hmn@inel.gov

Contact Author:  Lori Stern Siegel
Presenting Author:  Lori Stern Siegel

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