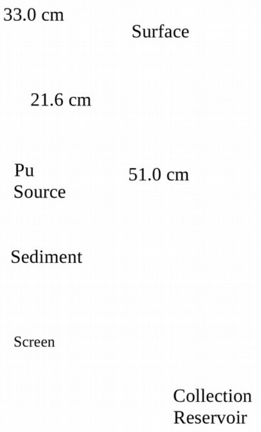
Final Report: Contract No. DE-FG02-07ER64401, “Biogeochemical Processes Responsible for the Enhanced Transport of Plutonium under Transient Unsaturated groundwater Conditions

Initial Mathematical Analysis

At or near-surface releases of Pu would typically move through the vadose zone before reaching groundwater. In order to better understand longer-term vadose zone transport in southeastern soils, field lysimeter experiments were conducted at the Savannah River Site (SRS) near Aiken, SC, in the 1980s (Kaplan et al., 2004, 2006, 2007). Each of the three lysimeters analyzed herein contained a filter paper spiked with different Pu solutions, and they were left exposed to the natural field environmental conditions (including the growth of annual weed grasses) for 11 years (Fig 1). The resulting Pu activity measurements from each lysimeter core showed anomalous activity distributions below the source, with significant migration of Pu above the source (Fig 2). A previously developed reactive transport model with surface-mediated redox reactions successfully simulated the lysimeter results below the source assuming a steady, net downward flow of soil water that yielded the volume discharge measured below the lysimeters (Demirkanli et al., 2007). However, little movement above the source occurred. This was attributed to the lack of upward soil water movement due to evapotranspiration with a steady, net downward flow model. (The constant vertical water flux was calculated as the difference between cumulative measured precipitation and measured lysimeter drainage.)

- Initiated: 1980s (11/25/1980)
- Purpose: To evaluate long-term Pu migration



Pu Source in the Experiment	Field Duration (yr)	Storage Duration (yr)	Initial Activity (μCi)
Pu(IV)(NO$_3$)$_4$	~11	~10	527
Pu(IV)(C$_2$O$_4$)$_2$	~11	~10	518
Pu(III)Cl$_3$	~11	~12.4	585

Figure 1. Experimental setting of the small field lysimeters used in plutonium migration studies at the SRS. The Pu source (filter paper) was initially placed 21.6 cm below the surface.

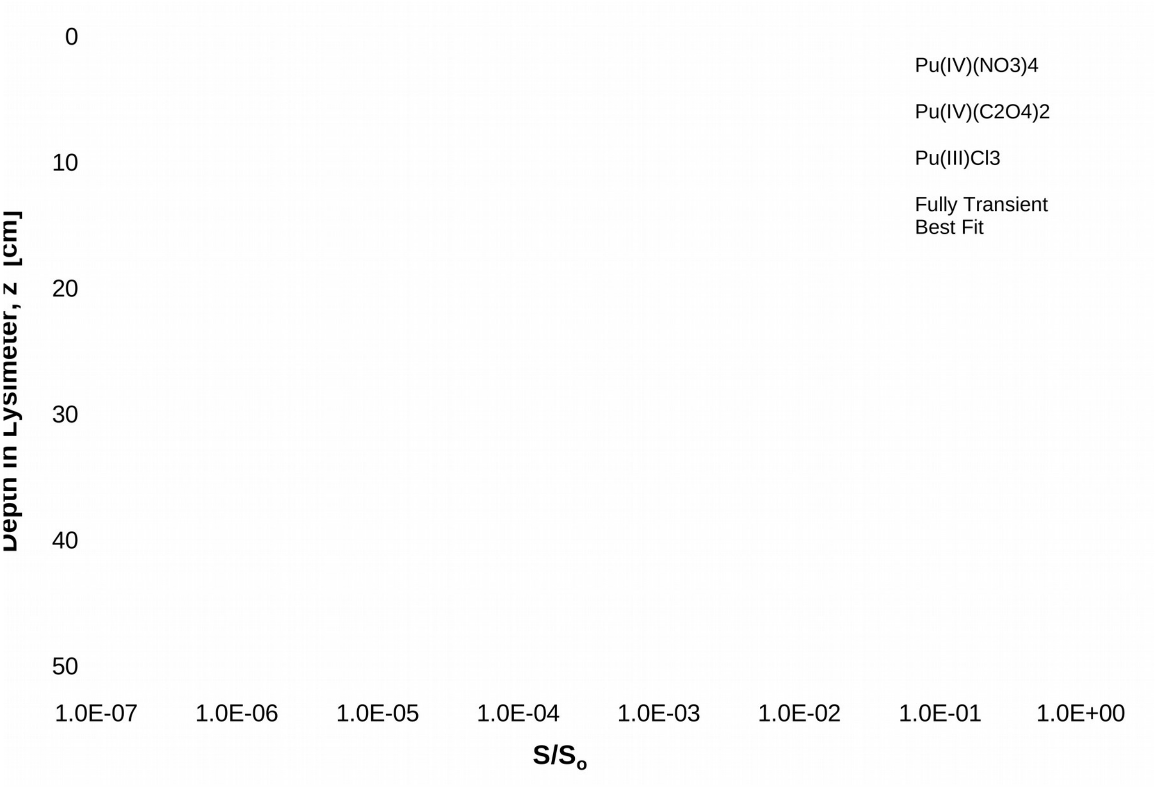


Figure 2. Measured Pu distributions with reduced sources superimposed by source location. The Pu activity migration above an elevation of 20 cm is irregular, but on average tends to be more uniform vertically.

This was the first result that motivated development of a more sophisticated mathematical model to serve as the basis for further analysis. To include additional phenomena that had to be occurring, a transient variably saturated flow model with root water uptake was developed and coupled to the reactive transport model (Demirkanli et al., 2008). Somewhat surprisingly, the fully transient analysis showed results nearly identical to those of the much simpler steady flow analysis, with little change in the calibrated oxidation/reduction rate constants (Fig 2). This seemed to at least partially validate the steady flow model, and the surface-mediated REDOX hypothesis as an explanation for the anomalous Pu transport remained consistent with the below source experimental data. However, all phenomena studied were unable to produce clear upward Pu transport observed in the data. The hydraulic and chemical mechanisms tested in the variably saturated model as potential enhancements for upward migration, included: 1) a root distribution maximizing upward movement of soil water, 2) hysteresis, which leads to larger hydraulic conductivities under drying conditions, and 3) air-content dependent oxidation, which yields more mobile Pu (oxidized forms) under drying conditions. None of these additional mechanisms yielded significant enhancement of the upward Pu transport (Demirkanli et al. 2008). While performing this exercise, we were careful not to over-calibrate our model by assigning unrealistic values to chemical/physical parameters. Such over-calibration results in hidden information by making the model fit better that it really is given the physical and chemical processes that are included.

This second result motivated another major change in the conceptual model. Essentially by process of elimination, it was concluded that a non-soil transport mechanism, such as Pu uptake by roots and upward advection in the xylem transpiration stream, had to be taking place. Initially, such a transport pathway was not thought to be relevant because of the huge retardation of reduced Pu in soil. There was therefore no obvious reason to think that the same Pu would be highly mobile in plant xylem. Nevertheless, the final change to the conceptual model used for data analysis was to extend the variably saturated flow and reactive transport model (Demirkanli et al., 2008) to include uptake and transport of Pu within the plant xylem. The plants simulated were native grasses that were allowed to grow on the lysimeter surfaces

Final Mathematical Analysis

The transient flow model and the reactive transport model for Pu migration in the soil remained essentially identical to those developed in Demirkanli et al. (2007; 2008), so these models will simply be listed here with a minimum of derivation detail. The model for Pu transport within plant xylem was new at the time of development, so this development will be presented in more detail. Transport in the plants is coupled to transport in the soil which is coupled to flow in the soil, but given values for daily transpiration based on climatological data, flow in the soil is independent of transport in the soil and plant. Thus annual plant growth is not considered in detail, only some type of "average" Pu uptake and transport in plants.

Fully Transient Transport Model

Based on the studies showing oxidation state transformations of Pu due to interaction with reactive mineral surfaces (i.e. iron and manganese oxides), a conceptual model was developed including equilibrium, reversible partitioning between aqueous and solid phases, and kinetic oxidation/reduction reactions in the sorbed phase to simulate activity concentration distributions from the lysimeter experiments (Demirkanli et al., 2007). As stated earlier, the model included two classes of Pu depending on their relative mobility in the environment: reduced Pu (Pur) (i.e., [Pu(III)] + [Pu(IV)] and oxidized Pu (Puo) (i.e., [Pu(V)] + [Pu(VI)]. One-dimensional advection and dispersion in the vertical direction were applied as the transport mechanisms for the field portion of the experiments, and only molecular diffusion was applied for the storage period. Equations (1) and (2) are the governing equations for Puo and Pur, respectively, and solved for aqueous activity concentrations of Puo (C_{Puo}) and Pur (C_{Pur}) in terms of activity per volume (sometimes called activity concentration).

$$\frac{\partial\left[C_{Puo}(z,t)\left(1+\frac{\rho}{\theta(z,t)}K_{do}\right)\right]}{\partial t} = -\frac{\partial\left[v(z,t)C_{Puo}(z,t) - D(z,t)\frac{\partial C_{Puo}(z,t)}{\partial z}\right]}{\partial z} + k_o C_{Pur}(z,t)\frac{\rho}{\theta(z,t)}K_{dr} - k_r C_{Puo}(z,t)\frac{\rho}{\theta(z,t)}K_{do} \quad (1)$$

$$\frac{\partial\left[C_{Pur}(z,t)\left(1+\frac{\rho}{\theta(z,t)}K_{dr}\right)\right]}{\partial t} = -\frac{\partial\left[v(z,t)C_{Pur}(z,t) - D(z,t)\frac{\partial C_{Pur}(z,t)}{\partial z}\right]}{\partial z} - k_o C_{Pur}(z,t)\frac{\rho}{\theta(z,t)}K_{dr} + k_r C_{Puo}(z,t)\frac{\rho}{\theta(z,t)}K_{do} \quad (2)$$

Values for the hydraulic functions in these equations [v(z,t), seepage velocity; D(z,t), hydrodynamic dispersion coefficient; θ(z,t), volumetric water content] are obtained by using the pressure head values calculated by the variably saturated flow model shown in Equation (3). The oxidation and reduction rate constants, k_o and k_r, respectively, are used as fitting parameters, since no attempt was made to measure these parameters in the natural system studied.

$$\frac{\theta(\psi)S_s}{\eta}\frac{\partial\psi(z,t)}{\partial t} + \frac{\partial\theta(\psi)}{\partial t} = \frac{\partial}{\partial z}\left[K(\psi)\frac{\partial\psi(z,t)}{\partial z}\right] + \frac{\partial K(\psi)}{\partial z} - S(z,\psi) \quad (3)$$

Values for soil hydraulic parameters in the variably saturated flow model, the unsaturated hydraulic conductivity function, K(ψ), and the volumetric water retention curve, θ(ψ), are calculated by using van Genuchten hydraulic functions (Demirkanli et al., 2008). The model also included root water uptake represented as a volumetric sink term, S(z,ψ).

Pu Root/xylem Uptake/Translocation Model

It has been found that some plants can absorb small amounts of Pu, usually quantified by a concentration ratio (CR) term determined by the ratio of activity concentration in the plant to activity concentration in the soil. As measured, this term is somewhat ill-defined, and it shows a wide range of values between 10^{-10} and 10^{-2}. About 12 years ago, Sanford et al. (1998) observed an unexpected upward migration of cesium (Cs) and strontium (Sr) as a result of a lysimeter study conducted at Oak Ridge National Laboratory. Although they could not determine definitively the mechanism causing this behavior, based on the distribution data of the radio nuclides in the lysimeter soil and a root later found in the lysimeter, they suggested that Cs and Sr migrated upward in the evapotranspiration stream of the root.

Based on these findings and the earlier results presented in Demirkanli et al. (2008), it appeared that upward migration of Pu observed in the data was likely due to Pu uptake by the plant roots and transport within the plants. To evaluate this hypothesis, a one-dimensional Pu root uptake and transport model was developed and coupled to the flow and reactive transport models in the soil. Since the possibility of this mechanism was not considered during the lysimeter experiment planning phase, the site specific plant data for validating this model are not available. However, there are other studies of the anatomy of many different species of grass roots (Hummel et al., 2007), so reasonable values for such things as root length per unit soil volume, xylem cross-sectional area per unit soil volume, xylem surface area, etc. can be identified from past studies. Thus, a model-based analysis can still be used to evaluate the general effect of a root uptake mechanism on the nature of the observed Pu distributions. For developing the model, the transport mechanisms within the root system were assumed to be advective and diffusive /dispersive movement of Pu within the evapotranspiration stream (in xylem). The potential effect of Pu exclusion by the root cortex is simulated by an uptake efficiency factor that can vary between 0 and 1, with a value of 1 indicating no exclusion. To date, the potential effect of chemical reactions between the Pu species within the xylem has not been considered, and these do not seem to be important.

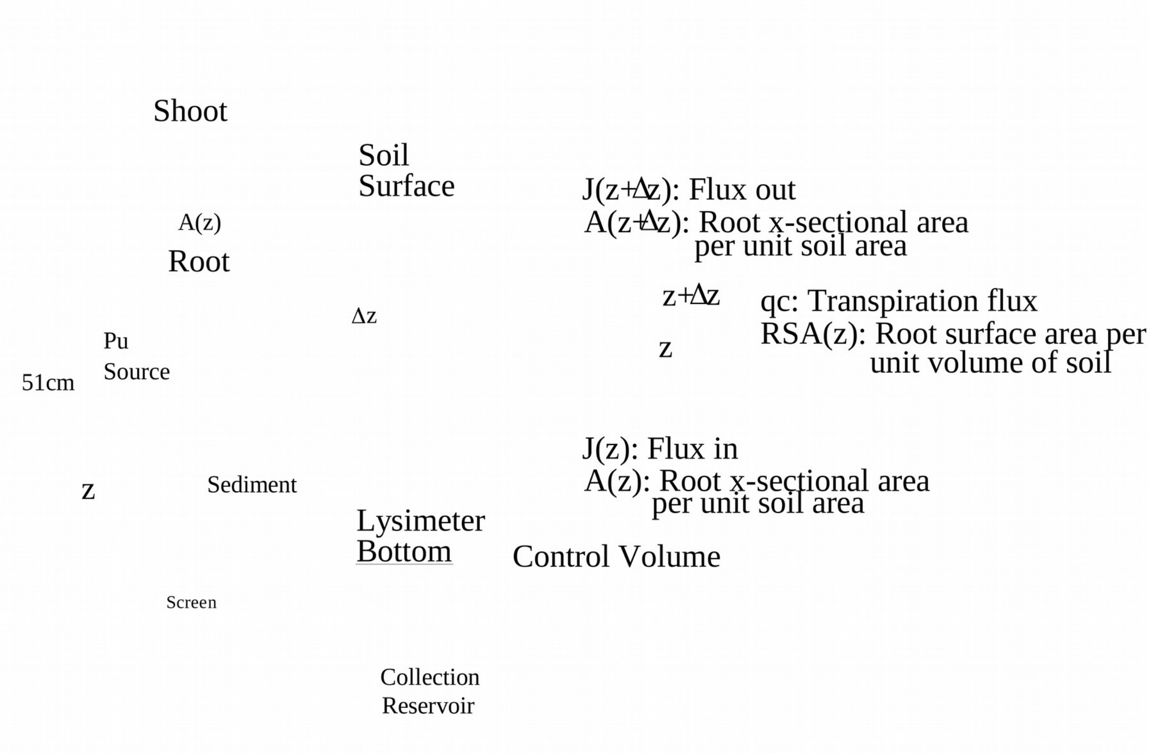


Figure 3. Schematic representation of the conceptual model for Pu uptake and transport by plant roots.

The relevant equations may be derived within the context of Figure 3, which shows a schematic representation of the root/shoot system in a lysimeter. Even though the roots in the soil grow irregularly, we can assume that the collective cross-sectional area of root xylems, the part of the root within which most Pu (normally > 90%) is transported upward, is proportional to root length density in the soil and the fraction of the root cross-sectional area that is xylem. This results in the simple conceptual visualization of the system for developing the Pu root uptake/translocation model shown in Figure 3. This can be quantified as Equation (6) where $A_r(z)$ is the ratio of total xylem area to the soil area at a given elevation, and RRD(z) represents the spatial distribution of the normalized root density (Demirkanli et al., 2008). β in this equation is a constant and can be calculated from a known A_r value at a specific location. For instance, Wahl and Ryser (2000) investigated several characteristics of root anatomy in an axile root of 19 perennial grass species from different habitats. Among the characteristics measured was total xylem cross-sectional area in a single root which averaged about 1567.53 μm^2. Based on this information, an average value of the ratio of total xylem cross sectional area to the soil area can be calculated as 3.19×10^{-6}. From the known value of RRD(z) at the top of the lysimeter, reported by Demirkanli et al. (2008), β can be calculated as 4.64×10^{-5} cm^3/cm^2.

$$A_r(z) = \beta \times RRD(z) \tag{4}$$

Similar to the sink term in the reactive transport model, a source term is needed in the root Pu uptake and translocation model to account for the Pu transferred from soil into the roots. This amount can be represented by a flux term, q_c in units of $\mu Ci/cm^2/h$ and calculated for Puo by Equation (5) (for Pur, $C_{Pur}(z,t)$ is used), where RSA(z) represents the root surface area per unit volume of soil at a given location in the lysimeter through which the activity is transferred. E_{puo} is the uptake efficiency.

$$q_c = \frac{E_{Puo} \times C_{Puo}(z,t) \times S(z,\psi)}{RSA(z)}$$

(5)

When a control volume approach is used as shown in Figure 3 and a mass/activity balance is applied to the control volume, the governing equation for the Pu root uptake and translocation can be derived as in Equation (6) and (7) for each Pu class:

$$\begin{aligned} R_{r\_Pur} \frac{\partial C_{r\_Pur}(z,t)}{\partial t} &= D_r \frac{\partial^2 C_{r\_Pur}(z,t)}{\partial z^2} - \frac{\partial}{\partial z}\left(v_r(z,t) C_{r\_Pur}(z,t)\right) \\ &- \frac{\partial\left(\ln A_r(z)\right)}{\partial z}\left[v_r(z,t) C_{r\_Pur}(z,t) - D_r \frac{\partial C_{r\_Pur}(z,t)}{\partial z}\right] + \frac{E_{Pur} C_{Pur}(z,t) S(z,\psi)}{\eta_r A_r(z)} \end{aligned} \tag{6}$$

$$\begin{aligned} R_{r\_Puo} \frac{\partial C_{r\_Puo}(z,t)}{\partial t} &= D_r \frac{\partial^2 C_{r\_Puo}(z,t)}{\partial z^2} - \frac{\partial}{\partial z}\left(v_r(z,t) C_{r\_Puo}(z,t)\right) \\ &- \frac{\partial\left(\ln A_r(z)\right)}{\partial z}\left[v_r(z,t) C_{r\_Puo}(z,t) - D_r \frac{\partial C_{r\_Puo}(z,t)}{\partial z}\right] + \frac{E_{Puo} C_{Puo}(z,t) S(z,\psi)}{\eta_r A_r(z)} \end{aligned} \tag{7}$$

In these governing equations, z is the elevation in the lysimeter and t is the time in terms of hours; C_{r_Pur} and C_{r_Puo} are the aqueous concentrations of indicated Pu classes in the roots in terms of µCi/cm^3; R_{r_Pur} and R_{r_Puo} are the retardation factors in root xylem for Pur and Puo respectively. η_r is the porosity of the root xylem, D_r is the diffusion coefficient and v_r is the water flux (velocity) in units of cm^2/h and cm/h, respectively. It is known that a very small percentage of water taken up by roots is used by plants; more than 90% of all water is simply lost by transpiration (Sutcliffe, 1968). Thus, the mean velocity at each depth can be approximated as the cumulative volume of water taken up by the roots divided by the xylem cross-sectional area, i.e:

$$Q_r(z,t) = \int_0^z S(z,\psi)\,dz \tag{8}$$

$$v_r(z,t) = \frac{Q_r(z,t)}{A_r(z)} \tag{9}$$

where, $Q_r(z,t)$ represents the vertical discharge through a unit area in the transpiration stream at a given elevation.

Numerical Modeling

The governing equations, Equations (6) and (7), were used to develop the numerical Pu root uptake and translocation model. Fully implicit, finite-difference approximations of these governing equations, shown as Equations (10) and (11), were solved for the activity concentration values by using a tri-diagonal algorithm for the one-dimensional, finite-difference grid system. In these equations, i represents the spatial node and j denotes the jth discrete time level for which the concentration values are solved. The one-dimensional root Pu uptake model domain was extended above the soil surface to cover the shoot section of the plants. Thus, the roots uptake Pu solution from the lysimeter soil and transfer it through their system to the plant shoots.

$$\begin{aligned}
&R_{r\_Pur}\frac{\left[C_{r\_Pur}(i,j)-C_{r\_Pur}(i,j-1)\right]}{\Delta t} = D_r\frac{\left[C_{r\_Pur}(i+1,j)-2C_{r\_Pur}(i,j)+C_{r\_Pur}(i-1,j)\right]}{(\Delta z)^2}\\
&-\left[\left(\frac{v_r(i+1,j)-v_r(i-1,j)}{2\Delta z}\right)C_{r\_Pur}(i,j)+v_r(i,j)\left(\frac{C_{r\_Pur}(i+1,j)-C_{r\_Pur}(i+1,j)}{2\Delta z}\right)\right]\\
&-\frac{1}{A_r(i)}\left(\frac{A_r(i+1)-A_r(i-1)}{2\Delta z}\right)\left[v_r(i,j)C_{r\_Pur}(i,j)-D_r\frac{\left[C_{r\_Pur}(i+1,j)-C_{r\_Pur}(i-1,j)\right]}{2\Delta z}\right]\\
&+\frac{E_{Pur}C_{Pur}(i,j)S(i,j)}{\eta_r A_r(i)}
\end{aligned} \tag{10}$$

$$
\begin{aligned}
R_{r\_Puo}\frac{\lfloor C_{r\_Puo}(i,j)-C_{r\_Puo}(i,j-1)\rfloor}{\Delta t} &= D_r\frac{\lfloor C_{r\_Puo}(i+1,j)-2C_{r\_Puo}(i,j)+C_{r\_Puo}(i-1,j)\rfloor}{(\Delta z)^2}\\
&-\left[\left(\frac{v_r(i+1,j)-v_r(i-1,j)}{2\Delta z}\right)C_{r\_Puo}(i,j)+v_r(i,j)\left(\frac{C_{r\_Puo}(i+1,j)-C_{r\_Puo}(i+1,j)}{2\Delta z}\right)\right]\\
&-\frac{1}{A_r(i)}\left(\frac{A_r(i+1)-A_r(i-1)}{2\Delta z}\right)\left[v_r(i,j)C_{r\_Puo}(i,j)-D_r\frac{\left[C_{r\_Puo}(i+1,j)-C_{r\_Puo}(i-1,j)\right]}{2\Delta z}\right]\\
&+\frac{E_{Pur}C_{Puo}(i,j)S(i,j)}{\eta_r A_r(i)}
\end{aligned}
\tag{11}
$$

The boundary condition for both classes of Pu at the bottom boundary was set as a zero flux (no flow) condition. Therefore no activity was taken up from the bottom into the lysimeter and root system. At the top boundary, advective flux is kept constant; the condition is then defined as $q_{Pu}(-\Delta z/2)=q_{Pu}(+\Delta z/2)$, which is equivalent to specifying an activity second derivative of zero. The amount of activity leaving the root system from the top boundary is calculated during the simulations for mass balance purposes. Thus one flow equation (Richards Equation) and four reactive transport equations (two in the soil and two in the plant xylem) were solved simultaneously. Flow velocity in the soil was driven by precipitation input along with transpiration and drainage output. The calculated velocity distribution drove the advection and dispersion of the 2 Pu species in the soil. Water uptake by the roots due to transpiration determined the flow velocity in the root xylem, and this along with uptake of Pu in the transpiration stream drove advection and dispersion of the two Pu species in the xylem. A numerical problem that resulted was due to the large mismatch of flow velocities in the soil and plant xylem. During wet periods with high potential transpiration, it was estimated that maximum flow velocities through the xylem, which has a relatively small cross-sectional area, would approach 600 cm/hr. This is many orders of magnitude larger than flow velocities in the soil. Thus xylem Pu transport would often have much larger Peclet numbers than soil Pu transport. In order to maintain numerical stability under all conditions, it was necessary to utilize a finer grid spacing for the xylem than for the soil when using the same numerical solution approach for both domains. Given modern computer speeds and capacities, this did not cause a problem.

Results and Initial Conclusions

Typical computational results are shown in Figure 4. With the inclusion of Pu uptake by grass roots and translocation in the transpiration stream, it is easy to simulate both the upward and downward movement of Pu activity that was observed in the experiments. However, the implied mobility in the plant xylem appeared to us to be too large, and given our conceptualization of the uptake and transport process, it was not easy to get a sufficient amount of Pu into the plant. Therefore, we typically used an uptake efficiency of 1, even though this seemed unreasonable. In order to employ something less than one, it was necessary to assume that for some reason, Pu was highly mobile in plants. This was at odds with it’s extremely low mobility in soil. Nevertheless, highly mobile and highly immobile conditions were considered mathematically, and the following initial conclusions were warranted.

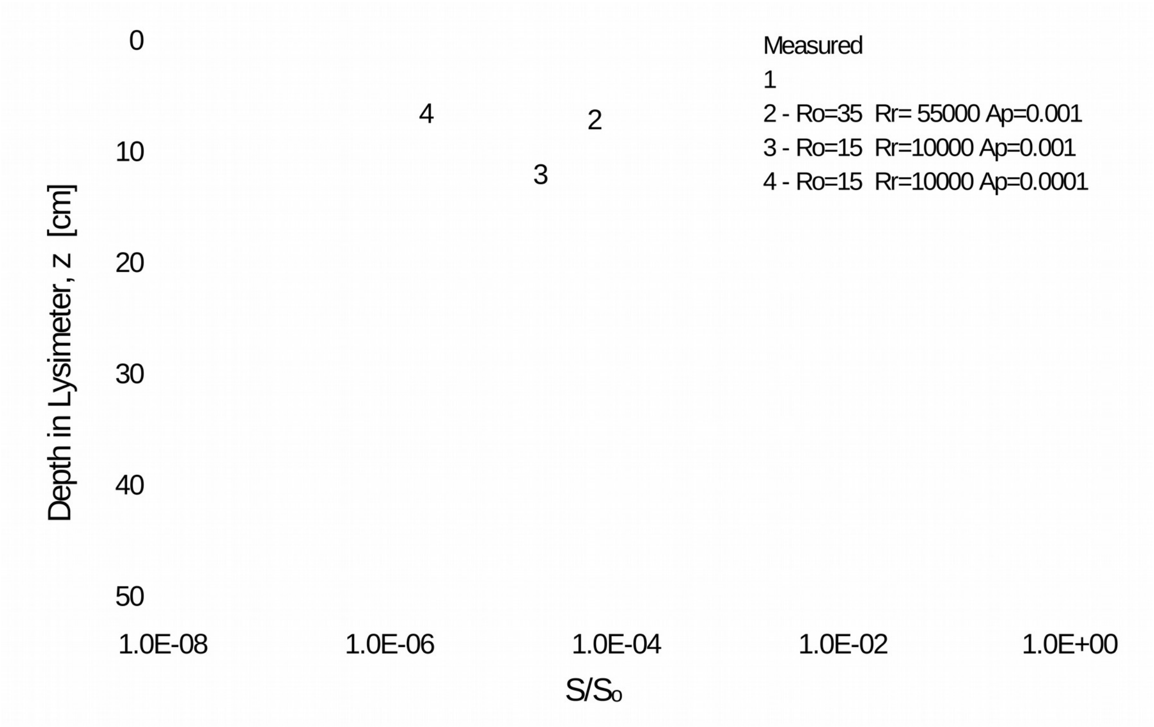


Figure 4. Typical Pu activity simulations that result when Pu uptake by grass roots and upward translocation in the root xylem is included, along with realistic values for the root anatomy/geometry.

1) Hysteresis, extreme root distribution functions, air-content dependent oxidation rate constants and large evaporation rates from the soil surface were not able to explain the observed upward migration characteristics of Pu.

2) Small amounts of Pu uptake by plant roots and translocation in the transpiration stream creates a realistic mechanism for upward Pu migration, and is also consistent with the previously simulated downward movement.

3) Realistic xylem cross-sectional areas imply high flow velocities (hundreds of cm/hr) under hot, wet conditions. Such flow velocities produce the correct shape for the observed activity distributions in the top 20 cm of the lysimeter soil provided consistent xylem Pu distribution coefficients are utilized.

4) Simulations imply that Pu should have moved into the above-ground grass tissue each year during the duration of the experiments. Presumably, when the plants died each winter this Pu residue would be deposited on the lysimeter surfaces. Consistent with this possibility, examination of Figure 2 indicates a tendency for Pu activity concentration to increase as one approaches the lysimeter surfaces.

Clearly, the upward movement, which we now attribute to Pu transport in the xylem of plant roots, has a more irregular nature than the downward transport in the soil. In the upward case, activities first drop fairly uniformly with elevation, and then become more constant, though scattered, above the upper 20 cm soil depth, where a distinct break in the distribution characteristics occurs. A little thought indicates that a more irregular activity distribution would be expected if transport were taking place in plant roots. Since the dominant species were annual grasses, roots would become inactive or die during the winter season. Then during each spring the root systems would regrow, with irregular growth depending on annual variations in climate, nutrients, insects, etc. Such an irregular pattern would occur each year. Thus, it would not be surprising if the resulting Pu activity distribution after 11 years was somewhat scattered, as the data in Figure 2 indicate.

New Measurements and Experiments motivated by the Simulations

The results described in the previous section resulted in paper number 3 (Demirkanli et al., 2009). However, the suggestion (prediction?) that Pu could have accumulated on the lysimeter surfaces could be tested with an isotope ratio measurement, and the uncertainty concerning Pu mobility in plant roots and xylem motivated basic laboratory experiments aimed at studying Pu uptake and translocation by plants. Even though these efforts went somewhat beyond the scope of the original proposal, they were pursued enthusiastically.

Isotope Ratio Measurements

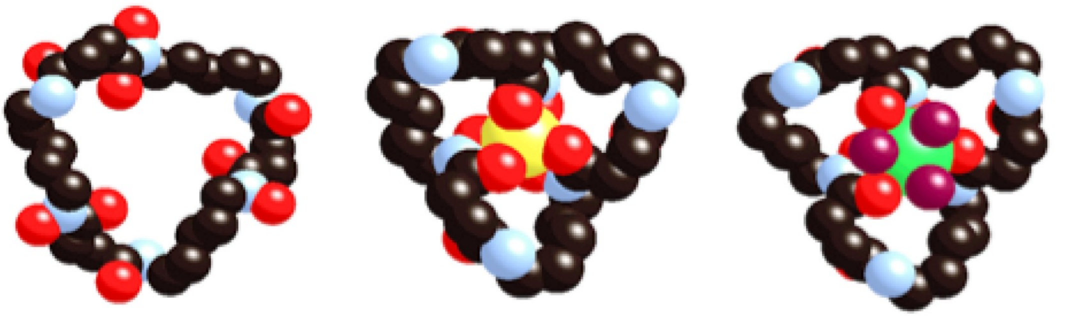
When activity measurements were made originally at the Savannah River site, it was noticed that a small activity concentration existed right at the surface. It seemed likely, however, that such an activity residue was simply due to atmospheric fallout, not transport upward from the buried Pu sources. But this could be determined with certainty by measuring the Pu isotope ratios of the surface residue and comparing them to the known values for atmospheric fallout measured at locations other than the lysimeter site, or the known isotope ratios of the buried sources. Such measurements were undertaken mainly by our colleagues at the SRS (Kaplan et al., 2010), and the results showed conclusively that the surface activity residue came from the buried sources. This was nearly conclusive evidence that the Pu was truly moving upward from the source mainly in plant xylem, and this provided further motivation to perform additional laboratory studies on real plants.

Uptake and Translocation of Pu in Corn

By this time, our simulation results and further study of the literature convinced us there had to be a special mechanism that facilitated Pu uptake by at least some plants and rapid transport in root and shoot xylem. But why would plants be interested in absorbing plutonium, essentially a man-made element? A thorough study of the plant physiology/biochemistry literature yielded a wealth of information. Iron is an essential nutrient required by plants, animals, fungi, and most microbes. It is commonly metabolized in activities that make use of its REDOX potential as an energy source. In green plants, a primary function of iron is in the development of chloroplasts which are essential for photosynthesis. Once the iron is metabolized in this process, it becomes incorporated in the leaf cell structure and cannot be recycled (Brown 1978). Due to its vital role in photosynthesis, plants have evolved physiological mechanisms to maintain a steady supply of iron from the soil. Importantly, while iron is an abundant element, it has a very low solubility at pH values favorable for plant growth. So plants must often perform two critical tasks to attain their required iron; first they must somehow obtain iron from the soil or soil solution (solubility) and second they must maintain high affinity transport pathways in order to rapidly incorporate iron when it is needed and available.

It is strongly believed that Fe chelating agents called siderophores function to address both the solubility issue and the incorporation of soluble metals into plants and microbes. Several studies have demonstrated that plant and fungal metal uptake is enhanced in the presence of bacterial siderophores (Bar-Ness et al. 1992, Ardon et al.1998) and plant siderophores (phytosiderophores) (Romheld and Marschner 1986). The synthesis of high molecular weight siderophore molecules has a high metabolic cost for plants, hence it is not efficient for plants to produce and exude siderophores unless they obtain iron in the process. Although questions remain about the mechanisms which siderophores use to increase metal solubility, research has demonstrated that once the metals are in solution, siderophores are very strong complexants and keep metals soluble under many conditions.

One fundamental reason Pu may be treated like Fe by plants and microbes is that the charge to ionic radius ratios for Fe(III) and Pu(IV) are both 0.47 nm^{-1}. Ruggiero et al. (2002) studied the structural properties and complexation of Fe and Pu with several siderophores including DFOB. Figure 5 is a reproduction of spatial models showing the metal free DFOE (denoted as DFE in John et al. (2001)) and DFOE complexed with Fe and with Pu. The Fe(III) and Pu(IV) complexation constants with DFOB are remarkably similar with Fe^{3+} LogK = 30.6 and Pu^{4+} LogK= 30.8.



Metal Free DFE Fe(III) DFE Complex Pu(IV) DFE Complex

Figure 5. Spatial models of the microbial siderophore DFOE: at left the tri-hydroxamate molecule is uncomplexed, at the center it is complexed with Fe(III), and at right it is complexed with Pu(IV). The Fe in the complex is 6-coordinate and the Pu is 9-coordinate (with 3 bound waters), so while the complex structures are approximately the same size, differences exist. (Figure from John et al. 2001)

The study of John et al. (2001) dealt specifically with the uptake amounts and rates of Fe and Pu complexed with DFOB with the bacterium (*Microbacter flavesence*). They tested the effects of competition between the complexes and demonstrated that both Fe and Pu are taken into the bacterium when added singly or together and that the complexed metals were recognized by the same proteins associated with transport channels and competed for the same sites of entry into bacteria. This result with a bacterium was clear motivation for similar experiments with plants from the grass family, such as corn, a common and easy to grow crop vegetable.

Shown in Figure 6 is the experimental set-up that was used to study the uptake of Pu and Fe in corn. Plants were started in wet paper wrapped around each corn seed. When the tap roots were sufficiently long, the seedlings were transplanted to a soil container with the tap root extending out the container bottom. The soil container was then placed over a nutrient solution container, and the solution served as an additional medium for hydroponic root growth (Thompson et al., 2009). The nutrient solution was aerated and changed periodically. To conduct an uptake study, the soil was allowed to dry so that virtually all water for transpiration came from the nutrient solution. Then a radioactive substance, such as Pu complexed with the bacterial siderophore DFOB, was added to the nutrient solution. After a suitable elapsed time, the corn plant was sacrificed, cut into 10 cm lengths, and the activity distribution measured. Many experiments aimed at different objectives were performed.

Figure 6. Corn plants growing in soil pots with the primary (tap) root inserted in nutrient solution. On the left, corn grown under plant lights; on the right, with the soil and nutrient pots removed, and the primary root shown. To initiate experiments, plants were exposed to new hydroponic solution containing complexed Pu or Fe.

<u>Results and Additional Conclusions</u>

1) The isotope ratio analysis showed that the observed surface Pu residue was from the buried sources, not atmospheric fallout.

2) The model with Pu root uptake and translocation produced simulations that captured the general behavior of the data above the source with no loss of ability to capture the below-source data. So the additional results still support the previous conclusion that a soil-surface-mediated REDOX process leads to the anomalous below-source Pu distribution.

3) The data shown in Figure 7 below indicate a Pu-DFOB velocity in the corn xylem of at least 174 cm/hr, much higher than ionic Pu in soil. Thus, Pu complexation with

chelating agents is probably what led to the enhanced uptake and mobility in grasses that was observed in the SRS lysimeter experiments.

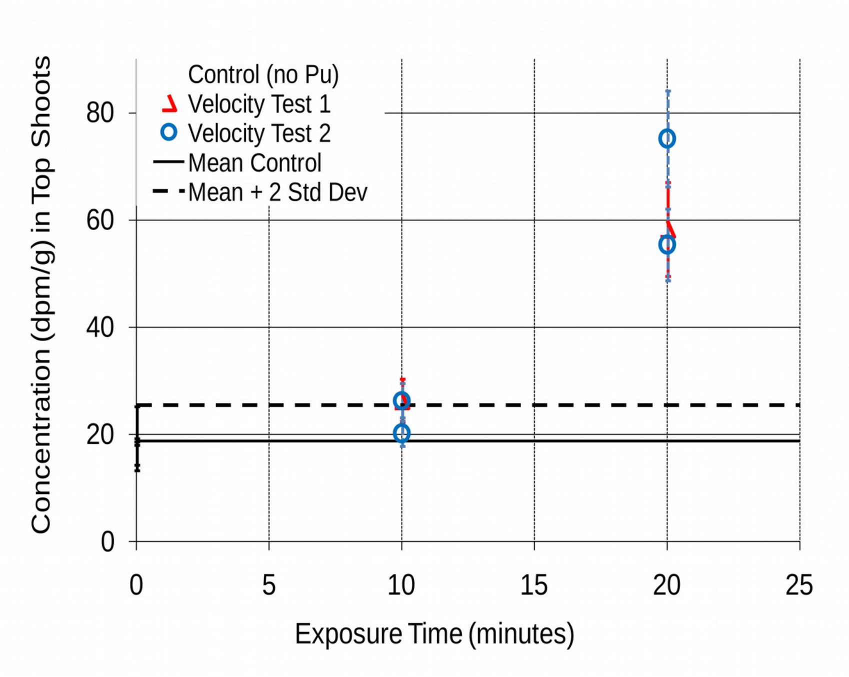


Figure 7. Exposure time versus activity concentration at a fixed location in the corn where the xylem travel distance is 58 cm. For this distance, the Pu-DFOB travel time is between 10 and 20 minutes, so the flow velocity is at least 174 cm/hr. In the SRS lysimeter experiments, most soil Pu moved only 2 or 3 cm in 11 years.

4) Results shown in Figure 8 indicate that the uptake of Fe-DFOB, Pu-DFOB and the resulting distributions are very similar. This supports the hypothesis that plant and bacterial iron-seeking chemistry mistakes Pu for Fe, allowing both to complex with siderophores, such as the bacterial siderophore DFOB, become more soluble in the soil solution and become highly mobile in the roots and xylem of some plants.

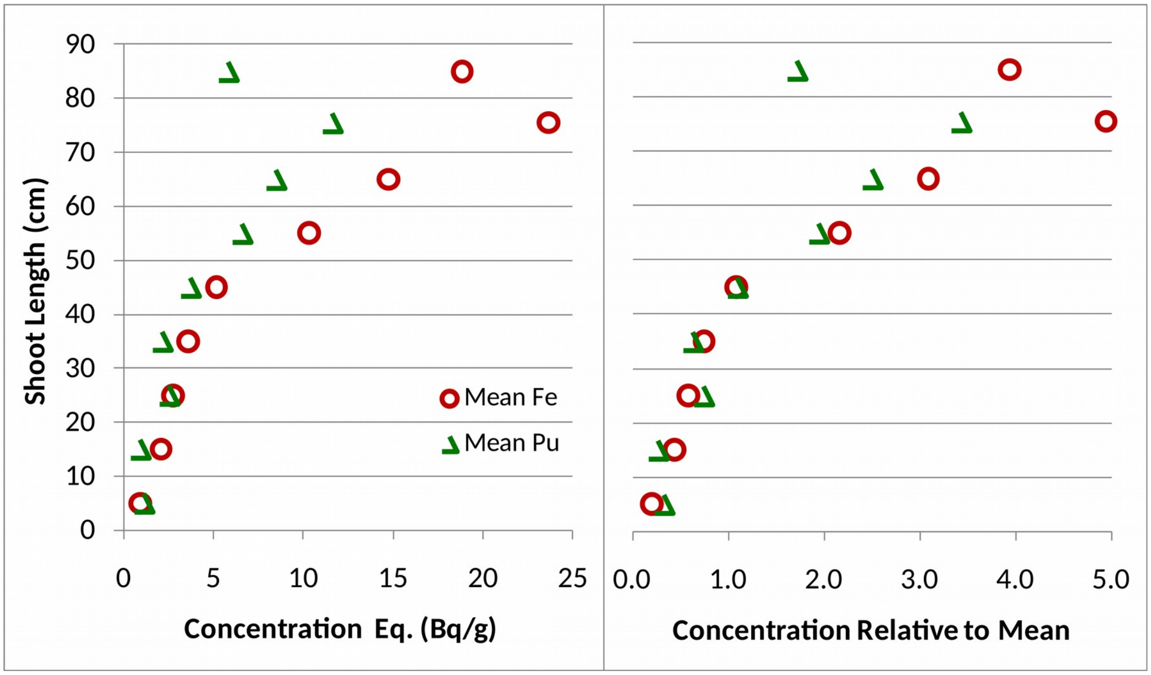


Figure 8. Combination plots of averaged (over 3 corn plants) and dimensionless ^{59}Fe and ^{238}Pu activity concentrations versus corn shoot position (zero at soil surface). Averaged data are shown on the left. On the right, averaged data are divided by the mean values, showing that relative to the mean, both Fe and Pu have very similar distributions.

Closing Discussion

Experiments aimed at further clarifying the relationship of chelated Fe and Pu, and the interaction of these two complexes when subjected to uptake by the roots of corn plants, are still on-going. In bacteria, chelated Pu and Fe compete with each other in order to get through the cell membrane, so different rates of uptake occur when both are present versus just one or the other (John et al., 2001). So far, we have not been able to show that similar interference occurs in corn roots, and it may not. To date, however, we are not completely confident of our results, so modifications to previous experiments are underway.

The research that resulted from the current project benefitted from a productive interaction between data, data analysis using computer simulation and follow-on experiments motivated in part by the results of the simulations. We have started to call this process “computer-aided thinking” to distinguish it from what might be called attempts at classical prediction using computer models. (A recent essay by Bredehoeft

(2010) discusses “computer-aided thinking from a slightly different viewpoint.) What are some of the characteristics of computer-aided thinking? First of all, significant knowledge of the main experimental parameters and conditions are needed. Simulations of the SRS lysimeter data were highly constrained by knowledge of the soil properties, recorded boundary conditions and collected data. So only a few parameters could be varied, and it was relatively easy to see what worked and what didn’t work in the models. Classical prediction is usually not well constrained by available data.

The simulations resulted in two main sets of inferences. It was concluded that longer distance upward transport could not have occurred in the soil alone, which implied that Pu uptake by plant roots and transport in the xylem was important. Follow-on isotope ratio analyses of surface residue showed that the activity observed was from the Pu source, not atmospheric fallout. In order to get sufficient Pu into plants to produce the observed activity distributions observed in the soil cores, Pu had to be much more mobile in plants than in soil. This result motivated laboratory experiments on Pu uptake and transport in corn plants. These experiments, along with data in the literature, strongly suggest that Pu adjacent to plant roots and in plant xylem exists in a chemically complexed form, probably involving chelating agents produced by plants and bacteria in order to obtain iron.

One final observation that is evident in Figures 2 and 4 is that the Pu distribution in the approximately 5 cm above the source is not simulated well by the model. Why might this be the case? It is known that many species of microbes are highly active in root zones and that many of these microbes produce iron chelating agents (siderophores) and also can adsorb metals. Microbes might also slowly migrate upward by various mechanisms in order to stay in the root zone where nourishment is relatively abundant. Thus there is a real possibility that that portion of the data is being dominated by microbe-facilitated transport, something that we hope to study in future research.

REFERENCES

1. Ardon, O., Nudelman, R., Caris, C., Libman, J., Shanzer, A., Chen, Y. N. Hadar, Y. (1998). "Iron uptake in Ustilago maydis: Tracking the iron path." Journal of Bacteriology 180(8): 2021-2026.

2. Bar-Ness, E., Hadar, Y., Chen, Y., Shanzer, A., Libman, J. (1992). "Iron uptake by plants from microbial siderophores." Plant Physiology 99: 1329-1335.

3. Bredehoeft, J.D (2010). Models and model analysis. Ground Water, 48(3): 328.

4. Brown, J. C. (1978). "Mechanism of iron uptake by plants." Plant, Cell and Environment 1: 249-257.

5. Demirkanli, D. I., Molz, F. J., Kaplan, D. I., Fjeld, R. A. (2009). "Soil-root interactions controlling upward plutonium transport in variably saturated soils." Vadose Zone Journal 8(3): 574-585.

6. Demirkanli, D. I., Molz, F. J., Kaplan, D. I., Fjeld, R. A. (2008). "A fully transient model for long-term plutonium transport in the Savannah River Site vadose zone: Root water uptake." Vadose Zone Journal 7(3): 1099-1109.

7. Demirkanli, D. I., Molz, F. J., Kaplan, D. I., Fjeld, R. A., Serkiz, S. M. (2007). "Modeling long-term plutonium transport in the Savannah River Site vadose zone." Vadose Zone Journal 6(2): 344-353.

8. Garland, T. R., Cataldo, D. A., Wildung, R. E. (1981). "Absorption, Transport, and Chemical Fate of Plutonium in Soybean Plants." Journal of Agricultural and Food Chemistry 29(5): 915-920.

9. Kaplan, D. I., Demirkanli, D. I., Gumapas, L., Powell, B. A., Fjeld, R. A., Molz, F. J., Serkiz, S. M. (2006). "Eleven-year field study of Pu migration from PuIII, IV, and VI sources." Environmental Science & Technology 40(2): 443-448.

10. Kaplan, D. I., Powell, B. A., Demirkanli, D. I., Fjeld, R. A., Molz, F. J., Serkiz, S. M., Coates, J. T. (2004). "Influence of oxidation states on plutonium mobility during long-term transport through an unsaturated subsurface environment." Environmental Science & Technology 38(19): 5053-5058.

11. Kaplan, D. I., Powell, B. A., Duff, M. C., Demirkanli, D. I., Denham, M., Fjeld, R. A., Molz, F. J. (2007). "Influence of sources on plutonium mobility and oxidation state transformations in vadose zone sediments." Environmental Science & Technology 41(21): 7417-7423.

12. Kaplan, D.I., D.I. Demirkanli, F.J. Molz, D.M. Beals, J.R. Cadieux and J.E. Halverson. (2010). Upward movement of plutonium to surface sediments during an 11-year field study. Journal of Environmental Radioactivity, 101: 338-344.

13. Romheld, V., Marschner, H. (1986). "Evidence of specific uptake system for iron phytosiderophores in roots of grasses." Plant Physiology 80: 175-180.

14. Ruggiero, C. E., Matonic, J. H., Reilly, S. D., Neu, M. P. (2002). "Dissolution of plutonium(IV) hydroxide by desferrioxamine siderophores and simple organic chelators." Inorganic Chemistry 41(14): 3593-3595.

15. Sanford, W. E., Larsen, I. L., McConnell, J. W., Rogers, R. D. (1998). "Upward migration of radio-cesium and strontium in a sand-filled lysimeter." Journal of Environmental Radioactivity 41(2): 147-162.

16. Sperry, J. S., Stiller, V., Hacke, U. G. (2003). "Xylem hydraulics and the soil-plant-atmosphere continuum: Opportunities and unresolved issues." Agronomy Journal 95(6): 1362-1370.

17. Steudle, E. (2000). "Water uptake by roots: effects of water deficit." Journal of Experimental Botany 51(350): 1531-1542.

18. Sutcliffe, J. (1968). Plants and Water. St. Martin’s Press, New York.

19. Thompson, S. W.; Molz, F. J.; Fjeld, R. A.; Kaplan, D. I. (2009). “Plutonium uptake velocity in *Zea mays* (corn) and implications for plant uptake of Pu in the root zone.” J. Radioanal. Nucl. Ch. 282, 439-442.

20. Walker, F. W., Parrington, J. R., Feiner, F. (1989). Nuclides and Isotopes. San Jose, CA, General Electric Company.

21. Wahl, S. and P. Ryser. (2000). Root tissue structure is linked to ecological strategies of grasses. New Phytologist, 148: 459-471.

Executive Summary: Contract No. DE-FG02-07ER64401, “Biogeochemical Processes Responsible for the Enhanced Transport of Plutonium under Transient Unsaturated groundwater Conditions

To better understand longer-term vadose zone transport in southeastern soils, field lysimeter experiments were conducted at the Savannah River Site (SRS) near Aiken, SC, in the 1980s. Each of the three lysimeters analyzed herein contained a filter paper spiked with different Pu solutions, and they were left exposed to natural environmental conditions (including the growth of annual weed grasses) for 11 years. The resulting Pu activity measurements from each lysimeter core showed anomalous activity distributions below the source, with significant migration of Pu above the source. Such results are not explainable by adsorption phenomena alone.

A transient variably saturated flow model with root water uptake was developed and coupled to a soil reactive transport model. Somewhat surprisingly, the fully transient analysis showed results nearly identical to those of a much simpler steady flow analysis performed previously. However, all phenomena studied were unable to produce the upward Pu transport observed in the data. This result suggests another transport mechanism such as Pu uptake by roots and upward transport due to transpiration. Thus, the variably saturated flow and reactive transport model was extended to include uptake and transport of Pu within the root xylem, along with computational methodology and results. In the extended model, flow velocity in the soil was driven by precipitation input along with transpiration and drainage output. The calculated velocity distribution drove the advection and dispersion of the 2 Pu species in the soil. Water uptake by the roots due to transpiration determined the flow velocity in the root xylem, and this along with uptake of Pu in the transpiration stream drove advection and dispersion of the two Pu species (to date non-reactive) in the xylem. During wet periods with high potential evapotranspiration, it was estimated that maximum flow velocities through the xylem would approach 600 cm/hr. This is many orders of magnitude larger that flow velocities in the soil.

Values for parameters and the correct conceptual viewpoint for Pu transport in plant xylem was uncertain. This motivated further experiments devoted to Pu uptake by corn roots and xylem transport. (Corn is a member of the grass family.) Plants were started in wet paper wrapped around each corn seed. When the tap roots were sufficiently long, the seedlings were transplanted to a soil container with the tap root extending out the container bottom. The soil container was then placed over a nutrient solution container, and the solution served as an additional medium for hydroponic root The nutrient solution was aerated and changed periodically. To conduct an uptake study, the soil was allowed to dry so that virtually all water for transpiration came from the nutrient solution. Then a radioactive substance, such as Pu complexed with the bacterial siderophore DFOB, was added to the nutrient solution. After a suitable elapsed time, the corn plant was sacrificed, cut into 10 cm lengths, and the activity distribution measured. Many experiments aimed at different objectives were performed. The results of these experiments clarified the basic nature of Pu uptake and transport in corn plants, and resulting simulations suggested that each growing season Pu in the SRS lysimeters would move into the plant shoots and be deposited on the soil surface during the Fall dieback. Subsequent isotope ratio analyses showed that this did happen.

OVERALL RESULTS AND CONCLUSIONS

1) Pu transport downward from the source is controlled by advection, dispersion and adsorption, along with surface-mediated REDOX reactions between oxidized and reduced forms of Pu..

2) Hysteresis, extreme root distribution functions, air-content dependent oxidation rate constants, and large evaporation rates from the soil surface were not able to explain the observed upward migration of Pu.

3) Small amounts of Pu uptake by plant roots and translocation in the transpiration stream creates a realistic mechanism for upward Pu migration, and is also consistent with the previously simulated downward movement in the soil.

4) Realistic xylem cross-sectional areas imply high flow velocities (hundreds of cm/hr) under hot, wet conditions. Such flow velocities produce the correct shape for the observed activity distributions in the top 20 cm of the lysimeter soil.

5) Simulations imply that Pu should have moved into the above-ground grass tissue each year during the duration of the experiments, resulting in an activity residual accumulating on the soil surface. An isotope ratio analysis showed that the observed surface Pu residue was from the buried sources, not atmospheric fallout.

7) The plant experiments indicate a Pu-DFOB velocity in the corn xylem of at least 174 cm/hr, much higher than ionic Pu in soil. Thus, Pu complexation with chelating agents is probably what led to the enhanced uptake and mobility in grasses that was observed in the SRS lysimeter experiments.

8) Plant experiments show that the uptake of Fe-DFOB, Pu-DFOB and the resulting distributions are very similar. This supports the hypothesis that plant and bacterial iron-seeking chemistry mistakes Pu for Fe, allowing both to complex with siderophores, such as the bacterial siderophore DFOB, become more soluble in the soil solution and become highly mobile in the roots and xylem of some plants.