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MODELING LONG-TERM PLUTONIUM TRANSPORT IN THE SAVANNAH RIVER SITE VADOSE ZONE

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MODELING LONG-TERM PLUTONIUM TRANSPORT IN THE SAVANNAH
RIVER SITE VADOSE ZONE

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Environmental Engineering and Science

by
Deniz Inci Demirkanli
December 2006

Accepted by:
Dr. Fred J. Molz, III, Committee Chair
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Dr. Daniel Kaplan
Dr. John T. Coates

ABSTRACT

Improved understanding of flow and radionuclide transport in vadose zone sediments is fundamental to future planning involving radioactive materials. To that end, long-term experiments were conducted at the Savannah River Site (SRS), where a series of lysimeters containing sources of different Pu oxidation states were placed in the shallow subsurface and exposed to the environment for 2 to 11 years. After the experiments, Pu activity concentrations were measured along vertical cores from the lysimeters. Pu distributions were anomalous in nature: transport from oxidized Pu sources was less than expected, and a small fraction of Pu from reduced sources moved farther below the source. Also, these measured distribution profiles exhibited unexpected upward migration regardless of the oxidation state of the source Pu. Studies conducted with these lysimeter sediments indicate that surface-mediated, oxidation/reduction (redox) reactions may be responsible for the anomalies. This hypothesis, for below source distributions, is tested by performing transient Pu transport simulations that include retardation and first-order redox reactions on mineral surfaces within a steady-state, net downward flow field. These simulations affirm the consistency of the surface-mediated, redox hypothesis with observed Pu activity profiles below the source. Such profiles, below the source, are captured well by a steady-state flow model, yet, as expected due to the presence of a net downward flow field in the soil, the observed upward migration was not captured with this model. The redox model explains how Pu(V/VI) sources release activity that moves downward more slowly than expected, and how Pu(III/IV) sources result in a small fraction of activity that moves downward farther

than expected. The calibrated parameter values were robust and well-defined throughout all simulations for the four independent data sets. Approximate retardation factors for Pu(V/VI) were 15, and for Pu(III/IV) were 10,000. For these values, oxidation rate constant (k_o) averaged $2.4 \times 10^{-7} \text{ hr}^{-1}$; reduction rate constant (k_r) averaged $7.1 \times 10^{-4} \text{ hr}^{-1}$ (standard deviations are $1.6 \times 10^{-7} \text{ hr}^{-1}$ and $1.6 \times 10^{-4} \text{ hr}^{-1}$ respectively).

The highly transient climatic nature of the environment, with numerous periods of rainfall alternating with evapotranspiration drying of the sediments and seasonal changes, created a very dynamic hydrologic system for the lysimeter experiments. Thus, for the purpose of evaluating the effects of this dynamic flow system on Pu migration and to further investigate the possible mechanisms causing the upward Pu movement, a variably saturated flow model with root water uptake (transpiration) was developed. The daily rainfall rates collected at the SRS throughout the entire experiment period were applied to the coupled reactive transport and variably saturated flow models. These simulations did not show any significant differences in the resulting Pu distributions compared to those from the steady-state flow simulations. A slight increase in the reduction rate constant was observed to counterbalance the effect of enhanced downward fluxes due to rainfall rates creating higher downward velocities than the steady-state, net downward velocity. Therefore, fully transient analyses of the data further supported the hypothesis of surface-mediated redox reactions with well-defined oxidation and reduction rate constants, but could not explain the observed upward migration of Pu.

Several tests conducted with the reactive transport model coupled to the variably saturated flow model with root water uptake, to evaluate possible mechanisms that might enhance the upward movement of Pu, were: addition of different root distributions,

addition of hysteresis, and modification of the oxidation rate constant to be a function of air. When a root distribution with 99% of the total density located within 5 cm from the surface was applied to the model, the upward migration was slightly increased in the oxidized Pu source case, but it had no effect on the distributions in the reduced Pu source case. Similarly, hysteresis, a phenomenon in which hydraulic conductivities in a soil are a function of the wetting history of the soil, also had a slight effect on the oxidized Pu source distributions, but the distributions from the reduced Pu source were the same. The modified oxidation rate constant was applied to the model to investigate the possible effect of having an oxidation process which can be enhanced due to availability of oxygen in the system, thus causing extra production of more mobile forms of Pu. Simulations with varying oxidation rates within two orders of magnitude showed no effect on Pu distributions regardless of the oxidation state of the source. Solutions show that upward water fluxes under drying conditions are very small because of a rapid decrease in hydraulic conductivity as the soil dries.

Very small amounts of Pu root/plant uptake and translocation within the transpiration system has been measured and reported in the literature. Therefore, a model was developed within this study for Pu root/plant uptake to test the possibility of such a mechanism in the lysimeter system which might cause the observed upward Pu movement. The developed Pu root uptake model was coupled to the reactive transport model through the aqueous activity concentration terms calculated in the lysimeter system, and it was coupled to the variably saturated flow model through the calculated water uptake term. The fraction of these aqueous activity concentrations transferred into the root system was defined by an uptake efficiency term. Pu transferred into the root

system was transported within this system by advection and diffusion in the root/shoot xylem, and retarded due to linear, reversible incorporation into the plant tissue. Simulations done with the reactive transport model with variably saturated flow and Pu root uptake/translocation showed a very small and realistic fraction of Pu migrating upward in the plant domain regardless of the oxidation state of the source.

The results of this research indicate that the hypothesis of surface-mediated redox reactions is consistent with the observed transport behavior of Pu from the lysimeter experiments. Upward migration of Pu might be due to an additional mechanism such as a root Pu uptake and translocation rather than the transport mechanisms and geochemistry of Pu within the lysimeter soil. This hypothesis deserves further study.

DEDICATION

I dedicate this work to my grandparents Hatice and Cemali Demirkanli. Without their support I wouldn't be here today.

ACKNOWLEDGEMENTS

Without the support and direction of my advisor Dr. Fred J. Molz, III, this work would not have been possible. I would like to express my sincere appreciation to him for giving me this chance to be here to pursue my career, and all of his guidance and support throughout this period of my life in Clemson, SC, which I grew to love and now call my second home. I also would like to thank to all my committee members for supporting this research and being a part of it. I would like to give my special thanks to Dr. Robert Fjeld and Dr. Daniel Kaplan, who continuously listened, supported, and discussed during this research. Without their suggestions, this work could not have been completed today. I gratefully appreciate former Ph.D. student Brian A. Powell's contributions to this project also.

I would like to acknowledge with thanks the support from the U.S. Department of Energy through the Savannah River National Laboratory (Task Order SC0194; Subcontract C001572-0), as well as fellowship support from Clemson University and the State of South Carolina.

Finally, I thank my sister, Teresa Demirkanli and my boyfriend, Patrick McLaughlin for their faith and continuous support, and my friends, Pinar Yolum, Ipek Arslan, Bob Martin and especially Devin Shippey for always listening to my worries over the years.

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ACRONYM DEFINITIONS

INL= Idaho National Laboratory

SRNL= Savannah River National Laboratory

SRS= Savannah River Site

CHAPTER 1

INTRODUCTION

Plutonium (Pu) is one of the transuranium elements of the actinide series. It was discovered by Glenn T. Seaborg in 1941 at the University of California Berkeley Laboratory during the atomic bomb project, the Manhattan Project (Choppin, 2004).

In the first several decades following the discovery of plutonium, the primary focus was on the research and development of the weapons programs (Choppin, 2004). During the early 1960's, the focus started to switch towards nuclear power driven chemical research as the interest in nuclear power increased. It also led to the idea of storing nuclear waste in facilities for permanent disposal in the late 1960's. However, by the late 1970's, large amounts of high-level waste stored in corroding waste tanks at Hanford, Savannah River, and other places in United States, as well as in the Soviet Union and other countries, became an increasing concern (Choppin, 2004).

By the late 1980's, surface testing of more than 420 nuclear weapons had released more than three metric tons of plutonium into the environment. Accidents, such as Chernobyl, and releases from weapons R&D in the former Soviet Union and the United States caused even more releases. At the Hanford Operation Site, 177 tanks below ground were used to store approximately 220,000 m³ of liquid waste from processing with a radioactivity of 11.8×10^9 GBq. It is estimated that more than 3800 m³ have now been released into the environment at the Hanford Site. Extensive ground contamination also has been detected at the Oak Ridge National Laboratory and other sites due to accidental

or deliberate releases of radionuclides during the operations of the Cold War (Choppin, 2004).

Plutonium in the environment is a major concern due to its high toxicity and very long half-life. Four of fifteen isotopes of plutonium are considered to be potentially dangerous for the environment and human health and they are listed in Table 1.1 below.

Table 1.1 Plutonium isotopes which are considered to be environmental concern (Smith and Amonette, 2006).

Isotope	Half-life (years)	Comments
Pu-238	87.7	Used to make radioisotope thermoelectric generators
Pu-239	24,100	Fissile material used in weapons
Pu-240	6,540	Decays by spontaneous fission releasing neutrons
Pu-241	14.4	Decays into Americium-241 (alpha emitter with 432 y half-life)

The main sources which contribute to the growing Pu inventory today are: (1) excess military Pu disposal worldwide from arms reduction agreements; (2) Pu generated in civilian commercial nuclear power reactors; and (3) a small amount of Pu from nuclear research reactors. Currently, only temporary storage areas exist for the waste produced from nuclear power plants and similar reactors. However, permanent deep geologic repositories are planned for storage and disposal such as the proposed Yucca Mountain

high-level radioactive waste repository. The main characteristic of such repositories is that they, with their engineered structures and location in the vadose zone, create a buffer between the disposed waste and a potential receptor. However, any accidental release or leaching above or below ground may result in radioactive contamination in the vadose zone. Thus, environmental risk assessments of Pu require models to predict its behavior in this zone. An improved understanding of flow and Pu transport in vadose zone sediments is fundamental to creating reliable Pu transport models and therefore is important for any kind of future planning involving waste disposal and environmental remediation of radioactive materials.

Pu geochemistry is the main factor that controls its behavior and transport characteristics in the subsurface. Complexation, precipitation, adsorption, colloid formation, and more importantly oxidation/reduction (redox) reactions not only determine what forms of Pu would be present in natural waters, but also how rapidly it would migrate in the environment (Powell et al., 2004; Choppin, 2004). Pu can exist in oxidation states III, IV, V, and VI in the environment, with two or three such oxidation state combinations commonly present at equilibrium (Choppin, 2003). The reduced states of plutonium (III, IV) are more stable in acidic media, while oxidized species (V, VI) are more stable at higher pH values (Choppin, 1997; Silva and Nitsche, 1995). The primary soluble species of plutonium in natural waters is the (V) oxidation state (Choppin, 2004). Once released into the environment, the movement of Pu is strongly related to its oxidation state. In porous media, it is generally observed that the Pu (III) and (IV) oxidation states are much less mobile, while the (V) and (VI) oxidation states are more mobile due to the differences in their partitioning characteristics; Pu(IV)

partitioning to sediment is generally 2 to 3 orders of magnitude greater than Pu(V) and Pu(VI) (Choppin, 2003; Powell et al., 2004; Kaplan et al., 2006).

Even though the primary redox state of Pu in the subsurface is commonly thought to be in the oxidation state of Pu(IV) (Keeney-Kennicutt and Morse 1985; Sanchez et al. 1985), and the migration is expected to be very restricted because of its high affinity for the solid phase, examples of greater than expected subsurface Pu transport have been reported. Some of the sites throughout the U.S. at which significant Pu transport was observed are the Mortandad Canyon at the Los Alamos National Laboratory, the 100K-Area at the U.S. Department of Energy's Hanford Site, the Nevada Test Site, and the Savannah River Site (SRS) (Penrose et al., 1990; Marty et al., 1997; Dai et al., 2002, 2005; Kersting et al., 1999). Several mechanisms have been proposed to explain enhanced migration, including acidic soil water, colloidal transport, oxidation state transformations due to microorganisms, organic complexation/chelation of free metal and soil-surface mediated oxidation of reduced, less mobile forms of Pu into more mobile forms.

It has been known for some time that reactive mineral surfaces, such as iron and manganese oxides, can oxidize or reduce Pu in environmental and laboratory systems. Researchers, such as Powell et al. (2004; 2005), Morgenstern and Choppin (2002), Keeney-Kennicutt and Morse (1985), and Sanchez et al. (1985) studied these reactions and some of them tried to develop rate expressions. A high-mobility fraction of Pu in column studies conducted with sediments from the Snake River Plain at the Idaho National Laboratory (INL) was also observed by Fjeld et al. (2001). In a separate column study conducted with soils from the SRS, two distinct physical/chemical forms of Pu

were observed, each with a different mobility (Fjeld et al., 2003). Formation of this high-mobility fraction was attributed to the redox speciation and mineral interactions of Pu in those systems. Their results indicated that a small high-mobility fraction of Pu can cause an enhanced transport behavior, and predicting Pu behavior in soil might be more complicated and problematic than the traditional, single-specie transport model in which species are subject only to linear reversible adsorption (Fjeld et al., 2003).

Reliable models that can simulate Pu behavior in the environment are essential for predicting doses and risks to human health and the environment from past, present, and future contamination (Whicker et al., 1999). Such predictions often become primary determinants in decision making processes on issues such as litigation, emergency response, waste management, and environmental remediation. The predictive accuracy of these models is directly related to how close their results are to the actual, real-life situations. Therefore, reactive transport modeling is an essential tool for the analysis of coupled physical, geochemical, and biological processes and to better integrate the results from the research (Steefel et al., 2005). The best, current scientific knowledge should be incorporated into these models, and they should be tested against actual data.

Long-term field experiments are often beneficial in understanding the chemistry-dependent Pu transport in complex natural systems. With this in mind, a series of field experiments were initiated at the SRS in the early 1980s. A group of lysimeters containing sources of known oxidation states of Pu were placed in the shallow subsurface. From 1981 until 1991 all lysimeters were left open to the environment except one, which was capped in 1983 and stored until it was analyzed. Aqueous leachate samples from these lysimeters were collected and analyzed for gross alpha and beta

activity during the field period. At the end of this period, a cover was put over these field lysimeters for an additional 5 years. Then these lysimeters were cored through the center and the cores were stored in a cooler for another 6 years. Plutonium activities in the cores were measured as a function of depth from the ground surface at the end of the storage period.

The main objective of this research is to develop a reactive transport model including surface-mediated redox chemistry for long-term Pu migration in the SRS vadose zone based on the lysimeter experiments and assess the model utility by comparing simulation results against the measured activity distributions obtained from the cores. The highly transient climatic nature of the environment, with numerous periods of rainfall alternating with evapotranspiration drying of the sediments and seasonal changes, created a very dynamic hydrologic system for the experiments. Therefore, the secondary aim of this research is to evaluate the effect of this dynamic hydrological system on migration of Pu. For this purpose, two different types of flow are applied to the transport model: steady-state flow and variably saturated flow with root water uptake. The final objective of the research is to use the model as a research tool to further investigate important processes that might significantly affect the transport of Pu in the system, such as volumetric moisture content dependent oxidation, hydrodynamic hysteresis, different root distributions, and Pu plant uptake.

CHAPTER 2

BACKGROUND

Plutonium Chemistry

Plutonium has multiple oxidation states with widely varying chemical properties. The oxidation state distribution of plutonium in natural waters controls its migration in the environment and it can be affected by E_H , hydrolysis, complexation, disproportionation, solubility, and redox interchange (Choppin, 1997).

Plutonium is known to exist in aqueous solutions in oxidation states (III), (IV), (V), and (VI), as Pu^{+3} , Pu^{+4} , PuO_2^+ , and PuO_2^{2+} , respectively. It is possible for all four of these oxidation states to co-exist in the same solution (Choppin, 2003). Such behavior is due to both the disproportionation tendency of Pu(IV) and Pu(V) and the kinetics of converting from one state to another (Cleveland, 1970). However, as seen in Table 2.1, while the redox potentials between these states are almost identical in a strong acid system, as pH increases to neutral and basic conditions, the III valent state is much less likely to be present, and the redox potentials between IV, V, and VI states stay similar (Choppin, 2003).

Table 2.1 Reduction potentials of plutonium (Choppin, 2003).

	pH=0	pH=8	pH=14
Pu(IV)/Pu(III)	0.98	-0.39	-1.04
$\text{Pu(V)O}_2^+/\text{Pu(IV)}$	1.17	0.70	0.52
$\text{Pu(VI)O}_2^{2+}/\text{Pu(V)O}_2^+$	0.92	0.60	0.16
$\text{Pu(VI)O}_2^{2+}/\text{Pu(IV)}$	1.04	0.65	0.34

As seen in Equations (2.1) and (2.2), oxidation or reduction reactions between Pu(III) and Pu(IV) and between Pu(V) and Pu(VI) consist of only electron transfer, and thus are rapid (Silva and Nitsche, 2002).

However, redox reactions between a dioxo cation and a simple ion, as shown in equation 2.3, are slow due to the disruption or formation of Pu-O bonds.

The fourth power dependency of the hydrogen ion concentration in equation (2.3) also indicates the need for higher hydrogen concentrations for this reduction reaction to occur. Therefore, the stability of the (V) and (VI) oxidations states increases with increasing pH (Choppin, 1997).

Another important factor which can affect the oxidation state distribution of plutonium in natural waters is complexation. The central plutonium atom in PuO_2^{+} has an effective charge of 2.2+ and an effective charge of 3.3+ in PuO_2^{2+} . As a result of this difference, the complexation behavior of plutonium varies as shown below (Choppin, 2003):

The strong complexation of the (IV) and (VI) oxidation states with the various ligands such as F^- , SO_4^{2-} , and CO_3^{2-} may alter the oxidation state distribution of plutonium by reducing Pu(V)O_2^+ to Pu(IV) (Choppin, 1997). The complexation strength of some ligands changes as shown below (Silva and Nitsche, 2002):

Oxidation states of III, IV, and VI are strongly hydrolyzed and sorbed to surfaces in natural waters. In oxic waters, PuO_2^+ is the major soluble form of plutonium (Choppin, 2003). The pH of the solution is very important for hydrolysis reactions. Pu(III) hydrolysis occurs around pH 5, whereas hydrolysis of Pu(IV) starts even when the pH is around 1. Pu(V)O_2^+ does not show very significant hydrolysis below pH 9, and Pu(VI)O_2^{2+} hydrolysis takes place in the pH range of 3-4 (Choppin, 1997).

Dissolved Pu may undergo oxidation by dissolved oxidants such as $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- or reduction by reductants such as Fe^{2+} and natural organic matter (Choppin, 1997).

The most common precipitated Pu in the environment is $\text{PuO}_2(\text{s})$ (Choppin, 2003). The low solubility of $\text{PuO}_2(\text{s})$ generally limits its subsurface mobility. Some researchers (Keeney-Kennicutt and Morse, 1985; Sanchez et al., 1985; Penrose et al., 1987) report (IV) as a stable solid phase oxidation state of plutonium. However, Haschke et al. (2000) has reported that in the presence of water, some of the plutonium dioxide

surface is oxidized to Pu(VI). Pu(IV) is generally 2-3 orders of magnitude less mobile than Pu(V/VI) in most environments due to its high affinity for the solid phase (Powell et al., 2006). Thus, this finding raises questions concerning the assumption of Pu(IV) as the thermodynamically stable form of Pu.

Plutonium Interactions with Minerals

Plutonium oxidation state transformations can be mediated by a solid phase. Reduced species at the mineral surfaces may provide a direct electron source, or the mineral phase may be a semiconductor, capable of providing a pathway for electron mobility (Powell et al., 2006). Oxidation of Pu(IV) on a manganese dioxide has been shown by Morgenstern and Choppin (2002). Similarly, reduction of Pu(V) on iron oxides has been reported by several researchers (Keeney-Kennicutt and Morse, 1985; Sanchez et al., 1985; Penrose et al., 1987).

In the study conducted by Powell (2004), he focused on the Pu redox transformations occurring in suspensions of iron and manganese (oxyhydr)oxides. He found evidence to support the previous observation that Pu(V), usually the stable form in aqueous solution, is reduced following adsorption, regardless of the solid phase involved. In addition, he concluded that Pu(IV) appears to be the stable solid phase oxidation state regardless of the solid phase constitution.

Powell (2004) observed that Pu(V) is reduced by the iron oxides, magnetite (Fe_3O_4), hematite ($\alpha\text{-Fe}_2\text{O}_3$), and goethite ($\gamma\text{-FeOOH}$). One of the proposed mechanisms for the reduction of Pu(V) is existing Fe(II) in the mineral structure, particularly for magnetite. Another proposed explanation is the thermodynamic stability of Pu(IV) hydroxide species on the mineral surface and the added semi-conducting properties of the

iron minerals. He also observed oxidation and reduction with the manganese minerals hausmannite (Mn_3O_4), manganite ($\gamma\text{-MnOOH}$), and pyrolusite ($\beta\text{-MnO}_2(\text{s})$).

SRS Experiments

Lysimeter Experiments

There are numerous studies in the literature where lysimeters were used to obtain field information on radionuclide vertical distribution and migration. The common method used in these studies is to take a soil core sample and section it to determine the variation in radionuclide activity with depth, or the activity profile (Smith and Elder, 1999). One of the main advantages of such settings is that not only downward, but also upward migration can be observed and investigated through these systems. Among the radionuclides studied are ^{22}Na , ^{60}Co , ^{109}Cd , ^{36}Cl , ^{99}Tc , and especially ^{134}Cs , ^{137}Cs in connection with its use as a tracer for environmental processes (Smith and Elder, 1999; Burne et al., 1994; Wadey et al., 1994; 2001; Shaw et al., 2004). Some hydrological and transport modeling research has also been conducted using data from the above experiments (Butler and Wheeler, 1999a; 1999b; Butler et al., 1999).

As mentioned earlier, a set of lysimeter experiments was initiated at the SRS in the early 1980s to evaluate long-term plutonium migration both upward and downward from the source. As illustrated in Figure 1, lysimeters were constructed using 52 L inverted polyethylene carboys with the bottoms removed. The carboys were filled with remolded natural soil from the Burial Ground at the SRS. During the filling process, a small disc of filter paper spiked with Pu solutions of selected oxidation states and known total activity was placed near each lysimeter center, and the entire apparatus was buried with the top left open to the natural climate. The lysimeter bottoms were connected to a

reservoir so that any leachate exiting the containers could be collected and studied. Kaplan et al. (2004; 2006) provides physical and chemical details concerning preparation of the lysimeter experiments, obtaining the cores and subsequent measurements of Pu activity. Listed in Table 1 are the experiment durations, the oxidation states of the Pu source solutions, and the total activity released into the domain for the four experiments that were modeled in this research. The two different durations shown in the table are the “field experiment duration” or the time the lysimeters were in the field and open to the environmental conditions, and the “capped/storage duration” or the time after the lysimeters were capped until the cores were analyzed. Additional information on these lysimeters and measured activity concentrations can be found in Appendix A.

Figure 2.1 Experimental setting of the small field lysimeters used in plutonium migration studies at the SRS. The Pu source (spiked filter paper) was initially placed 21.6 cm below the surface.

Table 2.2 Data sets available from the lysimeter experiments.

Pu Source in the Experiment	Field Experiment Duration (yr)	Capped (Storage) Duration (yr)	Total Activity Released (μCi)
$\text{Pu(VI)O}_2(\text{NO}_3)_2$	2	0	29.6
$\text{Pu(IV)(NO}_3)_4$	11	10	152.98
$\text{Pu(IV)(C}_2\text{O}_4)_2$	11	10	89.75
Pu(III)Cl_3	11	12.4	165.28

During the first four years of the experiments, rainfall data were collected at the lysimeter site, along with leachate volumes, which were recorded for each lysimeter. For the entire duration of the experiments, rainfall data were collected at the nearby Area-200F weather station. At the soil surface, the lysimeters were open to natural conditions during the field periods. Thus, transpiration due to plants on the surface was a significant part of the water balance for these experiments, especially considering the southern, humid climate. The leachate volume (liter) data allowed us to calculate the average net downward water flow rates during the first four years of the experiments and then extrapolate these data to leachate generation periods where only rainfall data were available. Average net downward advective velocities calculated from the leachate volume data ranged from 0.016 to 0.028 cm/hr and will be discussed in more detail in a later section. Leachate Pu activity exiting the Pu-containing lysimeters did not exceed the natural activity leaving a set of control lysimeters at any time during the experiments. Drainage volume data for each lysimeter and monthly rainfall data collected at the Area-200F weather station are given in Appendix B.

Shown in Figures 2.2, 2.3, 2.4, and 2.5 are experimental data consisting of measured activity concentrations, normalized by the activity concentration, S_o , at the source location. As expected, there is a marked difference in mobility depending on whether the source was reduced, Pu(IV/III), or oxidized, Pu(V/VI). Distribution characteristics observed in data from the lysimeter experiments with the reduced sources, Pu(IV) and Pu(III), show the same anomalous shape with activity resulting from the source having a leading edge at low concentrations. This observation shows consistency with earlier findings by Fjeld et al. (2001, 2003), where they distinguished a very small, high-mobility, fraction of Pu and attributed this form to differences in redox state. Microscopic examination by synchrotron X-ray fluorescence spectroscopy of portions of the core samples did not provide any evidence for colloid transport (Kaplan et al. 2004). Thus, it is not likely that this observation is caused by a colloid facilitated transport mechanism. (This concern will be discussed further in a later section.)

Another significant observation in the data sets is that the amount of activity moving upward is comparable to the amount moving downward, even in the lysimeters with the reduced Pu sources. This finding indicates the possibility of a mechanism in the system which can transport Pu upward, such as a possible Pu plant uptake or transpiration-induced upward flow in the soil.

The most striking feature of the Pu profile for the lysimeters with the reduced Pu sources is the overall movement of Pu much deeper into the profile than expected. For Pu(IV) and (III) sources, the bulk Pu was retained within 2-4 cm below the filter, but, surprisingly, the overall migration was about 15 to 20 cm.

Figure 2.2 Measured sorbed activity concentrations for $\text{Pu(VI)O}_2(\text{NO}_3)_2$ lysimeter normalized by the sorbed activity concentration at the source location.

Figure 2.3 Measured sorbed activity concentrations for $\text{Pu(IV)(NO}_3)_4$ lysimeter normalized by the sorbed activity concentration at the source location.

Figure 2.4 Measured sorbed activity concentrations for $\text{Pu(IV)(C}_2\text{O}_4)_2$ lysimeter normalized by the sorbed activity concentration at the source location.

Figure 2.5 Measured sorbed activity concentrations for Pu(III)Cl_3 lysimeter normalized by the sorbed activity concentration at the source location.

Other Pu Geochemical Studies

Prout (1959) studied sorption of Pu(III), (IV), and (VI) as a function of pH with soils from the saturated zone at the SRS through a series of batch experiments. Resulting K_d values (partitioning coefficient between aqueous and solid phases) ranged from 10 mL/g to 10,000 mL/g for Pu(III), 100 mL/g to 10,000 mL/g for Pu(IV), and 10 mL/g to 300 mL/g for Pu(VI).

Kaplan et al. (2001) conducted column experiments to evaluate the effect of pH on plutonium transport through sandy coastal soil from the Savannah River Site. The soil was characterized as having reactive surface coatings of iron and aluminum. Long-term and short-term tests were conducted with the columns at three different pH values of 3, 5, and 8. In their results, two separate peaks were observed in the effluent profile, which indicated the presence of multiple plutonium species. It was concluded by Kaplan et al. (2001) that the resulting data from the experiments were consistent with a mechanism where multiple forms of Pu were developed by a surface mediated reduction reaction. First-order rate constants for reduction obtained from the study were in the range of 4.3×10^{-3} 1/s to 1.4×10^{-5} 1/s (Fjeld et al., 2003). Estimated retardation factors from the batch sorption experiments conducted to investigate Pu(V) sorption range from 1.3 to 1.5 for a pH value of 3, 7.9 to 8.8, for a pH value of 5, and 34 to 36 for a pH value of 8 (Kaplan et al., 2001)(Relationship between partitioning coefficients and retardation factors is described in Chapter 4). Kaplan et al. (2004) conducted laboratory experiments to monitor the oxidation state of Pu both in solution and on the solid phase after adding Pu(V) spike solution to the control lysimeter sediment. They observed that the sediment quickly reduced Pu(V) to Pu(IV) with a pseudo-first-order reduction rate constant of

0.112 1/h. They also investigated whether the sorbed Pu from the Pu(IV)-amended lysimeter sediment could be desorbed into the aqueous phase under natural oxidizing conditions. As a results of oxidizing wet/dry cycling, they observed a release of very small concentrations, presumably by oxidation of sorbed Pu(IV) to the more mobile Pu(V) species. They reported a pseudo-first-order oxidation rate constant value of 1.4×10^{-6} 1/h for this mechanism.

Fjeld et al. (2003) also reported results of column and batch sorption edge experiments with Pu(V) and Pu(IV) on the SRS Burial Ground sediments. Contrary to the previous findings, this work indicated the presence of only one peak in the column experiments. From the batch experiments, a shift of the sorption edge of Pu(V) to resemble that of Pu(IV) was observed, indicating a possible reduction of Pu(V) to Pu(IV). The estimated retardation factors for Pu(V) were around 38 for pH between 3 and 5, and for Pu(IV) they ranged from 150 at a pH value of 3 to 1500 at a pH value of 5. Kaplan et al. (2004) also summarized selected physical and chemical properties of the lysimeter sediment, which are reproduced in Table 2.3 below.

Table 2.3 Physical and chemical properties of the lysimeter sediment (Kaplan et al., 2004).

Parameter	Value
pH	6.3
Sand/silt/clay	71%/10%/19%
Clay mineralogy	kaolinite>goethite>hematite>gibbsite
Total Fe, (mg/kg)	15,888
Total Mn, (mg/kg)	2,925

Plutonium Plant Uptake

Plutonium uptake by plants is potentially important for long-term transport and risk assessments. Most of the research relating Pu uptake and translocation by plants was conducted before the mid 1980s. The available information from those studies show wide variation in terms of parameter characterization and measurements (Sokolik et al., 2004; Lee et al., 2002a). Besides dose assessment purposes, another important reason for such research is to determine the effectiveness of phytoremediation as a technology to remediate contaminated sites in a cost-effective way (Lee et al., 2002a).

Quantitatively, plant uptake is usually determined by the ratio of activity concentration in the plant to activity concentration in the soil. Although there is not universal terminology for this ratio, some researchers use “concentration factor”, “transfer factor” or more commonly “concentration ratio” (CR) when discussing this parameter (Sokolik et al., 2004).

Values of concentration ratio are influenced by a number of factors including soil characteristics, particle size of Pu compounds, composition of the source material, chelation effects, and concentration of Pu in the soil (Lee et al., 2002b). The Pu concentration ratio values show a wide range between 10^{-10} and 10^{-2} in the literature (Sokolik et al., 2004; Lee et al., 2002b; Pinder et al., 1990; Adriano et al., 1986; Whicker et al., 1999b). Lee et al. (2002b) compared the uptake of Pu in *Brassica juncea* (Indian mustard) and *Helianthus annuus* (sunflower) from soils with varying chemical composition contaminated with two different Pu complexes: Pu-nitrate [$\text{Pu}(\text{NO}_3)_4$] and Pu-citrate [$\text{Pu}(\text{C}_6\text{H}_5\text{O}_7)^+$]. Table 2.4 summarizes the physical and chemical properties of the soil types that they used in their study. Without a chelating agent, there was an observed difference between the uptakes of the two different Pu complexes only in Indian

mustard in acidic Crowley soil. The CR values were higher with Pu-nitrate and ranged between $(1.73 \pm 0.17) \times 10^{-2}$ and $(19.45 \pm 4.34) \times 10^{-2}$. This range was between $(1.22 \pm 0.21) \times 10^{-2}$ and $(9.24 \pm 0.88) \times 10^{-2}$ with Pu-citrate. They also observed an increase in the uptake values as Pu activity concentrations in all the soils increased.

Similarly, Whicker et al. (1999b) also determined CR values of plutonium for three vegetable crops grown on exposed contaminated lake bed sediments of a former reactor cooling reservoir in South Carolina, USA. The crops used were turnips, beans, and sweet corn. In their results, turnip greens showed the highest uptake with a range of CR values of 2.3×10^{-3} and corn kernels showed the lowest uptake value of 2.1×10^{-5} .

Table 2.4 Chemical and physical properties of the soils used in Lee et al. (2002b).

Soil Type	Particle size distribution (%)			Moisture Content	pH	Oxalate Fe (mg/kg)
	Sand	Silt	Clay			
Weswood	67.6	25.6	6.8	0.149	7.55	58
Crockett	39.6	23.6	36.8	0.111	6.55	198
Crowley	56.8	19.7	23.5	0.179	4.80	798

Livens et al. (1994) questioned the meaning of CR measurements done using soil concentrations (solid plus aqueous concentrations). In his argument, he points out that although this approach yields results which are easily incorporated into predictive models, they are a gross oversimplification of many complex processes which govern soil-plant transfer. Therefore, they suggest that soil-plant transfer factors should be derived from soil solution analyses. The results of their experiments gave a range of

concentration ratio values which are consistent with the values reported in the literature when they used soil concentrations, but they observed inconsistent patterns in such data. In contrast, the parameters derived from solution concentrations displayed the consistent pattern that americium, with a higher affinity for the solid phase, was more readily translocated from solution into growing plants than plutonium. Transfer factors derived from the solution concentrations for Pu, in terms of the ratio of activity in the plant to that in solution, were in the range of 0.17 to 0.49.

Plutonium ReactiveTransport Modeling

The evaluation of risk due to subsurface contamination by Pu, development of remediation strategies, and the design of facilities for disposal of wastes require reliable models for predicting the behavior of Pu in the subsurface. An implicit assumption often used in predicting the transport behavior of Pu is that it exists in a single chemical/physical form in the subsurface environment (Fjeld et al., 2003). Based on its thermodynamic properties and chemistry, discussed earlier in this chapter, this form is usually assumed to be the oxidation state of (IV), which has a very low mobility compared to the other forms of Pu due to its high affinity for the solid phase. Therefore, traditional Pu transport modeling involves a single species advective and dispersive transport model with linear reversible adsorption (retardation) only. The retardation is usually obtained by batch sorption experiments and incorporated into the model through either K_d , the measured partitioning coefficient, or R , the retardation factor.

An analysis of the traditional modeling approach is shown in Figures 2.6 and 2.7 below, where the results of simulations using a single species transport model with only linear reversible adsorption are compared to the data obtained from the lysimeter

experiments conducted at the SRS. In Figure 2.6, the data are from a lysimeter with an oxidized plutonium source, $\text{Pu(VI)O}_2(\text{NO}_3)_2$, and, in Figure 2.7, it is from the lysimeter with a reduced plutonium source, $\text{Pu(IV)(NO}_3)_4$. R values in each figure are retardation factor values for Pu. As seen in the figures, apparent retardation factors are in the range of 25 to 100 for the Pu(VI) data and 3000 to 15000 for the Pu(IV) data. The pH of the system is about 6 (Table 2.3), so these values fall into the range measured experimentally for Pu(IV) given in the previous section. However, the values for Pu(VI) are high compared with the experimental measurements of retardation factors done for Pu(V), which are approximately 8 for a pH of 5 and 35 for a pH of 8 (Kaplan et al., 2001). None of the simulations with the traditional approach yielded the observed Pu distributions in both systems.

Figure 2.6 Measured activity distribution of the $\text{Pu(VI)O}_2(\text{NO}_3)_2$ lysimeter versus results of simulations with a single species transport model with adsorption only.

Figure 2.7 Measured activity distribution of the $\text{Pu(IV) (NO}_3)_4$ lysimeter versus results of simulations with a single species transport model with adsorption only.

The most striking feature of the Pu profile in Figure 2.7 for the $\text{Pu(IV)(NO}_3)_4$ lysimeter is the overall movement of Pu much deeper into the sediment than expected based on sorption phenomena alone ($R(\text{IV}) \cong 10,000$) while the overall movement shown in Figure 2.6 for the $\text{Pu(VI)O}_2(\text{NO}_3)_2$ lysimeter is less than expected ($R(\text{VI}) \cong 25$ or less). For the Pu(IV) experiment, penetration is expected to be about 3 or 4 cm for a retardation factor of 10,000, which is true for approximately 99.9% of the mass moving downward. However, actual penetration is observed approximately 10 cm beyond the expected penetration, albeit at low concentrations. For the Pu(VI) experiment, virtually the entire shape of the Pu activity profile is inconsistent with retardation alone.

Realistic and credible models that can better simulate the transport of Pu in the environment and are also consistent with experimental data are essential for predicting risk to human health. For this purpose, reactive transport modeling is an essential tool for the analysis of coupled physical, geochemical, and biological processes to better integrate the results from research (Steeffel et al., 2005). The major limitation of such models is the large amount of thermodynamic and kinetic data required to incorporate into the model for all possible geochemical processes. Therefore, the important processes which control contaminant migration should be determined well, and models should be kept as simple as possible to avoid the unnecessary addition of uncertainty. The model results should be tested against actual measured data whenever it is available` (Whicker et al., 1999a).

Numerous studies have sited development of reactive geochemical transport models and their applications in the literature. Yeh and Tripathi (1989) critically evaluate and discuss the development of hydrogeochemical transport models for multicomponent systems in terms of their ability to handle mixed kinetic and equilibrium reactions, computational efficiency, and equilibrium geochemical processes. Their results indicate that the sequential iteration approach (SIA) is computationally the most efficient to formulate the problem of a set of partial differential equations of hydrological transport and a set of nonlinear algebraic equations representing chemical equilibria. Their results also show that the same type of models and the mixed differential and algebraic approach are more flexible for treating mixed kinetic and equilibrium reactions. They recommend SIA models using the total analytical concentrations of aqueous components as the primary dependent variable for their practicality and flexibility. Later, Yeh and Tripathi (1991) present the development of a two-dimensional finite element hydrogeochemical

transport model, HYDROGEOCHEM. This model can simulate hydrologic processes in heterogeneous, anisotropic, saturated-unsaturated media under transient or steady state conditions. Chemically, it accounts for complexation, dissolution-precipitation, oxidation-reduction, adsorption, and ion exchange. Similarly, Chilakapati et al. (2000) presented the development and application of a coupled process model, RAFT. The primary use of this model is to predict the reactive flow and transport of dissolved contaminants in the saturated zone. Another research group that developed a reactive transport model is Walter et al. (1994). The model, MINTRAN, is for simulating transport of multiple thermodynamically reacting chemical substances in groundwater systems. It combines a transport module (PLUME 2D) with an equilibrium geochemistry module (MINTEQA2). The model is tested with respect to ion exchange and precipitation-dissolution chemistry involving multiple sharp fronts. Among other researchers who studied reactive transport modeling are Yeh et al. (2001), Cheng et al. (2000), Regnier et al. (2002), Wernberg (1998) and Tebes-Stevens et al. (1998). Tebes-Stevens et al. (1998) describe a reactive transport code (FEREACT) to examine the coupled effects of two-dimensional steady-state groundwater flow, equilibrium aqueous speciation reactions, and kinetically-controlled interphase reactions. The model uses an improved sequential iterative approach. Clement et al. (1998) give the details related to development of RT3D, a general purpose, multispecies, reactive transport code. Steefel et al. (2003) uses a multicomponent cation exchange model to describe enhanced Cs^+ migration in the Hanford vadose zone, where the migration was due to suppression of Cs^+ sorption as a result of the high concentrations of NaNO_3 in the HLW (High Level Waste) contaminant plume.

Most of the models based on the use of thermodynamic data neglect kinetic contributions, where these kinetic factors may lead to steady state conditions rather than the equilibrium conditions which are the common assumption in many modeling codes (Choppin, 2003; Kim, 2000; Nitzsche et al., 2000; Yeh et al., 2001).

For plutonium, the specifications for speciation must be able to include the possibility of redox change at different locations of the flow path (Choppin, 2003). Fjeld et al. (2003) and McGinnis (2000) studied modeling of plutonium migration at SRNL sediments. Previously, Fjeld et al. (2001) observed a high-mobility fraction of plutonium in column studies conducted with sediments from the Snake River Plain at the Idaho National Laboratory (INL). In a separate column study conducted with soils from the SRS, two distinct physical/chemical forms of Pu were also observed, each with a different mobility (Fjeld et al., 2003). Based on these findings, Fjeld et al. (2003) developed a conceptual model for the subsurface transport of plutonium involving surface-mediated reduction of Pu(V/VI) to Pu(III/IV) and equilibrium partitioning of Pu(V/VI) and Pu(III/IV) between aqueous and sorbed phases. Overall, their results were able to capture the features of the data better than a single specie adsorption approach.

CHAPTER 3

RESEARCH OBJECTIVES

As described in the previous chapter, Pu can exist in different oxidation states and has a very complex geochemistry. One fundamental reaction is that Pu can undergo oxidation state changes as a result of interactions with different mineral surfaces (Powel, 2004; Keeney-Kennicutt and Morse, 1985; Sanchez et al., 1985; Morgenstern and Choppin, 2002). Since plutonium mobility is strongly correlated to its oxidation state, these changes play an important role in terms of transport. Thus, it is important to understand surface-mediated redox reactions and determine to what extent they affect Pu migration in the subsurface. Therefore, the main objective of this research is to test the hypothesis of surface-mediated redox chemistry by developing a reactive transport model for long-term Pu migration both upward and downward in the SRS vadose zone based on the lysimeter experiments and to assess the model utility by comparing simulation results against the measured activity distributions obtained from these experiments. A highly transient climatic environment, with numerous periods of rainfall alternating with evapotranspiration drying of the sediments and seasonal changes, created a very dynamic hydrologic system for the experiments. Therefore, the secondary aim of this research is to evaluate the effect of this highly transient system on migration of Pu. Finally, the last objective of the research is to use the model as a research tool to further investigate important processes that might significantly affect the transport of Pu in the system, such as volumetric moisture content dependent oxidation, hysteresis, different root

distributions, and potential Pu plant uptake. The methodology used in this research proceeds as followed:

1. Development of the transient, one-dimensional reactive transport model:

Given the findings presented in the previous chapter, the transient reactive transport model is developed based on a conceptual model including equilibrium, reversible partitioning between aqueous and solid phases and kinetic oxidation/reduction reactions in the sorbed phase for two Pu classes, an oxidized class (Puo) (i.e., $[\text{Pu(V)}] + [\text{Pu(VI)}]$) and a reduced class (Pur) (i.e., $[\text{Pu(III)}] + [\text{Pu(IV)}]$).

2. Development of two different hydrological approaches and their application to the transport model:

- a. Steady-State Approach – Since it is computationally simpler and requires much less information than a full transient hydrological approach, a steady-state approach is developed including unsaturated net constant downward advection and one-dimensional hydrodynamic dispersion. This hydrological system is applied to the transport model by a constant velocity and a volumetric moisture content term.

- b. Transient Approach – Due to the dynamic nature of the system, a fully transient, one-dimensional variably saturated flow model with root water uptake is developed based on the available hydrological data. The variably saturated flow model is solved simultaneously with the reactive transport model and they are coupled to each other through the seepage velocity term.

3. Evaluation of possible mechanisms which might have a significant effect on migration of Pu:

a. Addition of different root distribution functions – Water uptake by roots creates upward fluxes in the vadose zone. Thus, when a root system is located more towards the soil surface, it would take up water from its vicinity and create more upward fluxes than a system distributed relatively more uniformly along the axis.

b. Addition of *hysteresis* phenomena – Hysteresis phenomenon affects the hydraulic conductivity properties of a soil system depending upon the wetting history of the soil. Thus, unsaturated hydraulic functions are modified to account for hysteresis in the lysimeter system due to wet and dry cycling.

c. A Moisture Content Dependent Oxidation Rate – Instead of a constant oxidation rate, the rate equation is modified to be a function of available oxygen, which depends on changing volumetric water content in the system. Thus, the new rate expression allows for an increase in oxidation rate when more oxygen is available.

d. Addition of Pu Plant Uptake – Due to very small amounts of Pu uptake by plants reported in the literature, an additional module to simulate this mechanism is added to the system with a capability of simulating vertical transport of Pu in a root system.

CHAPTER 4

REACTIVE TRANSPORT MODEL DEVELOPMENT: STEADY-STATE FLOW

Based on the findings given in chapter 2, a conceptual model is developed including equilibrium, reversible partitioning between aqueous and solid phases; kinetic oxidation/reduction reactions in the sorbed phase; steady-state, unsaturated net downward advection; and one-dimensional hydrodynamic dispersion along the vertical axis. For the purpose of testing the surface-mediated redox chemistry hypothesis, a steady-state flow assumption is made since such a model is computationally simpler and requires less information than a fully transient model. Because of the similar relatively low mobility of the reduced pair “Pu(III/IV),” compared to the higher mobility of the oxidized pair “Pu(V/VI),” we only consider two possible Pu classes: an oxidized class (Puo) (i.e., $[\text{Pu(V)}] + [\text{Pu(VI)}]$) and a reduced class (Pur) (i.e., $[\text{Pu(III)}] + [\text{Pu(IV)}]$). For each class of Pu, mass (activity) balance equations with constant velocity and moisture content due to the steady-state flow, equation (4.1) for Puo and (4.2) for Pur, state that the change of activity stored with respect to time in both the liquid and solid phases in a small control volume is equal to the net outflow rate due to advection plus the net outflow rate due to dispersion plus sources of activity, minus sinks of activity. Figure 4.1 shows a schematic representation of the control volume approach for developing the governing equations for the transport of each Pu class. It also shows the mass balance for each class in terms of the amount of activity going in and out of the control volume by the transport mechanisms of advection and dispersion and sources and sinks of activity in the control

volume. Thus, the resulting governing equations in $\mu\text{Ci}/\text{cm}^3/\text{hr}$ units may be written as shown below. Detailed derivation of these governing equations in a more generalized form in terms of variable velocity and hydraulic parameters is given in Appendix C.

$$R_o \frac{\partial C_{Puo}}{\partial t} = -v \frac{\partial C_{Puo}}{\partial z} + D \frac{\partial^2 C_{Puo}}{\partial z^2} + \frac{1}{\theta} (Sources_{Puo} - Sinks_{Puo}) \quad (4.1)$$

and

$$R_r \frac{\partial C_{Pur}}{\partial t} = -v \frac{\partial C_{Pur}}{\partial z} + D \frac{\partial^2 C_{Pur}}{\partial z^2} + \frac{1}{\theta} (Sources_{Pur} - Sinks_{Pur}) \quad (4.2)$$

In Equations (4.1) and (4.2), C is the activity concentration in terms of activity per unit volume for Pur and Puo as indicated by subscripts, t is time, z is the distance from the bottom of the lysimeter (positive upward), θ is the average volumetric water content (which in the assumed steady downward flow system plays a role similar to the porosity), R_r is the retardation factor for Pur and R_o is the retardation factor for Puo, v is the net downward advective velocity, and D is the hydrodynamic dispersion coefficient that includes molecular diffusion and mechanical dispersion. It is the source and sink terms that will be used to represent redox reactions in the adsorbed phase as seen in Figure 4.1.

Figure 4.1 Schematic representation of control volume approach and mass (activity) balance for both Pu classes, Puo and Pur.

It is hypothesized that on the surfaces, Pur can be oxidized to Puo, and Puo can be reduced to Pur. First order reaction rates based on Pu concentration were selected for both oxidation and reduction reactions. At any particular time, the activity on the surfaces is the sum of $\rho K_{dr} C_{Pur}$ and $\rho K_{do} C_{Puo}$, respectively, where K_{dr} and K_{do} are distribution coefficients and ρ is soil bulk density. If k_o is the oxidation rate constant and k_r is the reduction rate constant, then the oxidation and reduction rates in $\mu\text{Ci}/\text{cm}^3/\text{hr}$ are given by:

$$\frac{Source_{Puo}}{\theta} = \frac{Sink_{Pur}}{\theta} = \frac{k_o}{\theta} (\rho K_{dr} C_{Pur}) = k_o (R_r - 1) C_{Pur} \quad (4.3)$$

and

$$\frac{Source_{Pur}}{\theta} = \frac{Sink_{PuO}}{\theta} = \frac{k_r}{\theta} (\rho K_{do} C_{PuO}) = k_r (R_o - 1) C_{PuO} \quad (4.4)$$

When these expressions are substituted into Equations (4.1) and (4.2), the resulting governing equation for each Pu class is:

$$R_o \frac{\partial C_{PuO}}{\partial t} = -v \frac{\partial C_{PuO}}{\partial z} + D \frac{\partial^2 C_{PuO}}{\partial z^2} + k_o (R_r - 1) C_{Pur} - k_r (R_o - 1) C_{PuO} \quad (4.5)$$

and

$$R_r \frac{\partial C_{Pur}}{\partial t} = -v \frac{\partial C_{Pur}}{\partial z} + D \frac{\partial^2 C_{Pur}}{\partial z^2} - k_o (R_r - 1) C_{Pur} + k_r (R_o - 1) C_{PuO} \quad (4.6)$$

Transport Model Parameters

In order to begin simulations based on Equations (4.5) and (4.6), initial values are needed for the model parameters R_o , R_r , v , θ , D , k_o and k_r .

Retardation Factors

The retardation factor is a bulk property that describes the overall migration of the chemical with respect to water. It quantifies the amount of retardation that the chemical undergoes due to interactions with solid surfaces. It is quantified by Equation (4.7) shown below.

$$R = 1 + \frac{\rho K_d}{\theta} \quad (4.7)$$

R_o is the retardation factor for Puo calculated by using the distribution (partitioning) coefficient for Puo, K_{do} , and R_r is the retardation factor for Pur calculated by using the distribution coefficient for Pur, K_{dr} . Values of retardation factors are taken from the range which was experimentally measured for each class as described in chapter 2 and also from the apparent values observed in Figures 2.6 and 2.7.

Volumetric Water Content

Average volumetric water content in the assumed steady downward flow system plays a role similar to the porosity. This average is estimated by using unsaturated hydraulic conductivity (K) measurements and particle size distribution measurements that were determined using the lysimeter study location. A particle size distribution analysis was performed by using a standard sieve analysis refined by the hydrometer method and the results are given in Appendix D. The results match well to an independent measurement done by Kaplan et al. (2004). The unsaturated hydraulic conductivity measurements were made using an unsaturated flow apparatus (UFA Ventures Inc., Richland, WA) based on open-flow centrifugation (Nimmo et al., 1991; Conca and Wright, 1992). Soil bulk density was estimated to be 1.55 g/cm^3 based on the particle size distribution (Dragun, 1998). A soil particle size distribution measurement independent than the reported in Table 2.3 was conducted and the result was approximately 70% sand, 7.8% silt, and 22.2% clay. These data were used as inputs to Rosetta, a program developed by Schaap et al. (2001) to estimate the Van Genuchten soil hydraulic parameters. When the measured particle size distributions are modified slightly, the resulting function agrees well with the first three centrifuge-measured unsaturated

hydraulic conductivity values as shown in Figure 4.2. Below these measured values, the unsaturated hydraulic conductivity drops very quickly about one or two orders of magnitude; this slows the moisture movement in the field significantly. Thus, the agreement with the higher measured conductivity values is more important to be able to have a realistic estimation of the field conditions.

Figure 4.2 Measured and estimated unsaturated hydraulic conductivity as a function of volumetric water content.

Estimated Van Genuchten functions (saturation (S_e), hydraulic conductivity (K), and volumetric water content (θ)) as functions of pressure head (Ψ) are given by:

$$S_e = \left[1 + (0.027816|\Psi|)^{1.48013} \right]^{-0.32438}$$

$$K(\psi) = K_{sat} S_e^{-1.0633} \left\{ 1 - \left[1 - S_e^{3.08277} \right]^{0.32438} \right\}^2 \quad (4.8)$$

and

$$\theta(\psi) = \theta_r + \frac{\theta_{sat} - \theta_r}{\left[1 + (0.027816\psi)^{1.48013} \right]^{0.3244}} \quad (4.9)$$

In the above equations, K_{sat} represents the saturated hydraulic conductivity, which is estimated as 15.984 cm/d by Rosetta. θ_{sat} and θ_r are the saturated and residual water contents, and their values are estimated as 0.392 and 0.0589 respectively.

Obtaining the $K(\psi)$ and $\theta(\psi)$ functions enables one to estimate a water content value consistent with the measured net downward flow, assumed to be due to gravity. In such a situation, the hydraulic gradient is one, and K is flux per unit gradient. Using four separate lysimeters, the measured Darcy velocities range between 4.01×10^{-3} cm/h and 6.98×10^{-3} cm/h (Appendix E; Table 4.1). The corresponding water contents for these fluxes, treated as K values in Figure 4.2, fall between 0.243 and 0.264. As a result, the average steady-state volumetric water content consistent with the net downward flow is selected as 0.25 for the simulations.

Seepage Velocities

In a steady-state unsaturated flow system, a constant net downward velocity is applied to the transport model along with constant hydraulic properties such as moisture content, as described in the previous section. Therefore, an average Darcy velocity for each lysimeter is calculated from the measured leachate volumes, shown as in Appendix

B and E, and averaged over the four-year collection period. For the experiments in which the duration exceeded four years, a percolation percentage of the leachate volumes out of the total rainfall calculated from the available four year data for each lysimeter is assumed to be maintained. The average Darcy velocity for each of those lysimeters is calculated from the estimated leachate volumes for the whole experimental period by using the surface area of the lysimeter. In order to change Darcy velocities to seepage velocities, average water content, θ , is used as determined in the previous section, which is 0.25. Thus, seepage velocities are calculated for each data set by dividing the Darcy velocities with the average steady-state volumetric water content and are shown in Table 4.1 for each lysimeter.

Table 4.1 Estimated Darcy and seepage velocities for the calculated average lysimeter water content of 0.25.

Lysimeter	Darcy Velocity (cm/h)	Seepage Velocity (cm/h)
Pu(VI)O ₂ (NO ₃) ₂	4.01.10 ⁻³	0.016
Pu(IV)(NO ₃) ₄	6.98.10 ⁻³	0.028
Pu(IV)(C ₂ O ₄) ₂	6.53.10 ⁻³	0.026
Pu(III)Cl ₃	4.84.10 ⁻³	0.019

Dispersion Coefficients

The hydrodynamic dispersion coefficient is defined by Equation (4.10). The molecular diffusion coefficient (D_d) estimated using the Nernst equation is 3.16×10^{-6} cm²/s at 0°C, and 6.82×10^{-6} cm²/s at 25°C as shown in Figure 4.3. An average value of 5×10^{-6} cm²/s is used for the calculations.

$$D_L = \omega.D_d + \alpha_L.v \quad (4.10)$$

Based on high levels of sand content of the sediment determined by mean particle size data, tortuosity (ω) is estimated as 0.4, knowing that clean uniform sand would yield a tortuosity value of about 0.7 (Fetter, 1999).

Figure 4.3 Regression of calculated molecular diffusivity for PuO_2^+ in water with temperature (Calc-Note X-CLC-A-000016, Rev. 0)

Dispersivity (α_L) is estimated based on a combination of column experiments reported in McGinnis (2000) and curves relating dimensionless dispersion coefficients to

Peclet number presented in Fetter (1999, p. 58). The direct measurements from columns 8 cm in length resulted in an average dispersivity of 0.33 cm. Fetter's (1999) dimensionless curves with a mean particle diameter (D_{50}) of 0.029 cm resulted in a dispersivity of 0.3 cm. This results in an overall mean value of about 0.3 cm. At a mean net downward seepage velocity of 0.02 cm/hr (5.6×10^{-6} cm/s) and a mean annual temperature of 10 C°, the resulting dispersion coefficient is about 0.013 cm²/h (3.7×10^{-6} cm²/s), essentially the same as molecular Pu diffusion in free water. Since the overall results were dominated by advective transport during the field portion of the lysimeter experiments, simulations were not sensitive to ω , D_d or α_L . During the storage period for each experiment, the seepage velocity was set to zero, which reduces the transport process to effective molecular diffusion only, adjusted for the storage temperature.

Oxidation and Reduction Rate Constants

Surface mediated oxidation and reduction reactions on different mineral surfaces have been reported in the literature, as stated previously. Kaplan et al. (2004) reported a pseudo-first-order reduction rate as 0.112 1/h and an oxidation rate as 1.4×10^{-6} 1/h. Powell (2004) reported no oxidation or reduction of Pu(IV) or Pu(V) in circum-neutral solution when no solids (minerals) were present. For this reason, the oxidation/reduction reactions in the model are assumed to occur in the sorbed phase only due to a surface reaction of plutonium with the sediments. The rate constants k_o and k_r are fitted to the data resulting from the lysimeter experiments and compared with the measured values.

Activity Release into the Domain (Core)

The total activity released into the domain is calculated as a constant release rate for each data set by using equation (4.11), where ($\text{Area}_{\text{filter}} \Delta z$) represents the volume

where the activity is released and $t_{\text{experiment}}$ is the release period. A_{released} is the amount of activity found in the core at the end of the experiment. It is assumed that all activity is released during the field portion of the experiments, when there is an assumed constant net downward flow through the domain. Furthermore, it was assumed that no Pu leached out of the lysimeters, consistent with monthly and quarterly monitoring data of the lysimeter leachate. Thus, for simulation purposes, the release activity is the total amount of activity found in the lysimeter cores at the end of the experiments.

$$q_o = \frac{A_{\text{released}}}{\text{Area}_{\text{filter}} \Delta z t_{\text{experiment}}} \quad (4.11)$$

The release term for the source is applied as shown in equations (4.12) and (4.13). Depending on the source Pu class, either $q_{o, \text{Pu}o}$ or $q_{o, \text{Pu}r}$ is applied to the system at the point where the filter was located, z_{source} .

$$\begin{aligned} R_o \frac{\partial C_{\text{Pu}o}}{\partial t} = & -v \frac{\partial C_{\text{Pu}o}}{\partial z} + D \frac{\partial^2 C_{\text{Pu}o}}{\partial z^2} + k_o (R_r - 1) C_{\text{Pu}r} - k_r (R_o - 1) C_{\text{Pu}o} \\ & + \frac{q_{o, \text{Pu}o}}{\theta} \delta(z_{\text{source}} - z) \end{aligned} \quad (4.12)$$

and

$$\begin{aligned} R_r \frac{\partial C_{\text{Pu}r}}{\partial t} = & -v \frac{\partial C_{\text{Pu}r}}{\partial z} + D \frac{\partial^2 C_{\text{Pu}r}}{\partial z^2} - k_o (R_r - 1) C_{\text{Pu}r} + k_r (R_o - 1) C_{\text{Pu}o} \\ & + \frac{q_{o, \text{Pu}r}}{\theta} \delta(z_{\text{source}} - z) \end{aligned} \quad (4.13)$$

Besides a constant release rate scenario, an exponentially decreasing rate of release can also be assumed, which would presumably account for decreasing Pu activity on the source. Equation (4.14) releases an exponentially decreasing amount of the initial total activity on the filter disk (A_o) into the domain for each time step (Δt).

$$q_o = \frac{A_o \left[e^{-k_{\text{release}}(t-\Delta t)} - e^{-k_{\text{release}}t} \right]}{\text{Area}_{\text{filter}} \Delta z \Delta t} \quad (4.14)$$

where, k_{release} represents the release rate constant for the source in units of 1/h. It can be calculated by using the initial activity amount on the filter (A_o), the activity found on the sediment at the end of the experiment which is assumed as the released activity (A_{released}), and the experiment duration ($t_{\text{experiment}}$), as shown below:

$$k_{\text{release}} = -\frac{1}{t_{\text{experiment}}} \ln\left(\frac{A_o - A_{\text{released}}}{A_o}\right) \quad (4.15)$$

Over the duration of the experiments, both release rates, constant and exponentially decreasing, were adjusted so that the same amount of activity was released. An example of activity release rates versus time for one of the Pu(IV) lysimeters is shown in Figure 4.4 below. A sensitivity analysis was performed using both release scenarios to evaluate the effect of release rate on the distribution of Pu at the end of the simulations. There was little effect, and results will be presented in Chapter 5.

Figure 4.4 Constant and exponentially decreasing release rate functions for the $\text{Pu(IV)(NO}_3)_4$ data set with a total released activity of 152.98 μCi , calculated for $\Delta t=1\text{d}$.

Numerical Transport Modeling

Numerical modeling consists of three fundamental components: (1) a theoretical basis for translating physical and chemical phenomena into governing partial differential equations (PDEs), (2) a numerical method to develop an approximate solution to the governing equations, and (3) a computer implementation (Mansell et al., 2002). Finite difference method (FDM) is one of the most common approach used for transforming a set of PDEs into a set of algebraic equations that would be solved by a computer code (Wang and Anderson, 1982). In this study, transport in the cored portions of the lysimeters, which were analyzed at the end of the experiments for the sorbed plutonium

distribution profiles, is simulated using the governing equations, Equations (4.12) and (4.13). Fully-implicit, finite-difference approximations of these governing equations for P_{uo} and P_{ur} may be written as:

$$\begin{aligned}
 R_o \frac{[C_{P_{uo}}^{m+1}(i, j) - C_{P_{uo}}^m(i, j-1)]}{\Delta t} = \\
 -v \frac{[C_{P_{uo}}^m(i+1, j) - C_{P_{uo}}^{m+1}(i-1, j)]}{2\Delta z} + D \frac{[C_{P_{uo}}^m(i+1, j) - 2C_{P_{uo}}^{m+1}(i, j) + C_{P_{uo}}^{m+1}(i-1, j)]}{\Delta z^2} \quad (4.16) \\
 + k_o(R_r - 1)C_{P_{ur}}^m(i, j-1) - k_r(R_o - 1)C_{P_{uo}}^{m+1}(i, j) + \frac{q_{o,P_{uo}}}{\theta} \delta(i - i_{source})
 \end{aligned}$$

and

$$\begin{aligned}
 R_r \frac{[C_{P_{ur}}^{m+1}(i, j) - C_{P_{ur}}^m(i, j-1)]}{\Delta t} = \\
 -v \frac{[C_{P_{ur}}^m(i+1, j) - C_{P_{ur}}^{m+1}(i-1, j)]}{2\Delta z} + D \frac{[C_{P_{ur}}^m(i+1, j) - 2C_{P_{ur}}^{m+1}(i, j) + C_{P_{ur}}^{m+1}(i-1, j)]}{\Delta z^2} \quad (4.17) \\
 -k_o(R_r - 1)C_{P_{ur}}^{m+1}(i, j) + k_r(R_o - 1)C_{P_{uo}}^{m+1}(i, j) + \frac{q_{o,P_{ur}}}{\theta} \delta(i - i_{source})
 \end{aligned}$$

where i represents the node, j denotes the j^{th} discrete time level, when the solution is unknown (thus, $\Delta t = t(j) - t(j-1)$ is the time step) and m is the iteration level. The source terms are denoted by $q_{o,P_{uo}}$ and $q_{o,P_{ur}}$ and added to the governing equation at the node where the filter was located (i_{source}). Implicit finite difference approximations to the coupled governing equations are solved simultaneously using Picard iteration for the coupling and the Gauss-Siedel iterative method to solve the difference equations. The upper boundary condition in the model is defined as a Dirichlet boundary condition where

zero activity concentrations are set at the node $i=N$ ($z=51$) for both Pu_r and Pu_o . To define the lower boundary, Neumann boundary condition is used at $i=1$ ($z=0$), where the Pu flux is a function of constant advective water flux (q_w). Thus, the Pu flux out of the system (either oxidized or reduced forms) is given by:

$$q_{Pu} = q_w C_{Pu} - D \frac{\partial C_{Pu}}{\partial z} \quad (4.18)$$

Then the boundary condition is defined by $q_{Pu}(-\Delta z/2) = q_{Pu}(+\Delta z/2)$. In finite-difference form, this condition allows the Pu to simply disperse and drain out with the water flux at the bottom boundary, as illustrated in more detail in Figure 4.5. At the end of each simulation, the total activity remaining in the domain is calculated for mass balance purposes.

Figure 4.5 below schematically represents the model domain in terms of the nodal system. The release rate term (source term) for the activity into the domain is located at the node where the filter disk was found at the time when the data were collected (Figure 4.5). Thus, the distance from the top to the source term varies for each data set.

Figure 4.5 One dimensional finite difference approximation of the domain.

CHAPTER 5

RESULTS OF THE REACTIVE TRANSPORT MODELING

WITH STEADY-STATE FLOW AND DISCUSSIONS

Pu(VI)O₂(NO₃)₂ Simulation Results

During this 118 week experiment, a total of 29.6 μCi of activity was released to the domain from the Pu(VI) source at a constant rate of $1.4115 \times 10^{-3} \mu\text{Ci}/\text{cm}^3/\text{h}$, with the released amount being calculated from initial activity and recovered activity on the sediment before and after the experiment. Based on the previously measured retardation factor values for oxidized Pu on the SRS sediments given in Chapter 2, a range of retardation factors for Pu(VI) (treated as Pu_o in the model) was applied, and the results are presented in Figure 5.1 as three different simulations sets, with the retardation factor for Pu(IV) held constant at 10,000. In the figure legend, total activity (TA) represents total amount of activity in the domain at the end of the simulations. For all three of the sets, Simulation 1, where both oxidation (k_o) and reduction (k_r) rate constants were set to zero, showed the single species transport front with retardation only. Since no oxidation or reduction was allowed during these initial simulations, the oxidation state of the plutonium species transported was the same oxidation state as that of the plutonium source, which is Pu_o. As discussed previously (Figure 2.6), single species retarded transport is not able to capture the overall Pu distribution characteristics. As shown in Figure 5.1 for Pu_o, Simulation 1 always indicates the maximum migration possible for the particular retardation factor, since the plutonium stayed in the more mobile form

throughout the simulation. The addition of surface mediated redox reactions always decreases the overall migration for a PuO source. A PuO retardation factor of 50 is clearly too large, because the front did not migrate sufficiently far as seen in Figure 5.1a. When the retardation factor decreases to 25, the total distance of the migration was captured with a zero or a very small reduction rate constant, but the bulk movement of the plutonium was overestimated for most of the Pu (Figure 5.1b). Therefore, the PuO retardation factor was chosen as 15 for the last set of simulations, and the results as shown in Figure 5.1c, were able to match the data reasonably well with a fitted rate constants of 1.0×10^{-8} 1/h for oxidation and 3.3×10^{-4} 1/h for reduction. This leads us to infer that the mobility of the PuO was decreased by being converted to a less mobile form of Pu. Thus the reduction mechanism becomes the source for the additional non-adsorptive retardation. So, even though the actual adsorptive retardation of the PuO during the experiments is not known exactly, one can infer, based on the simulations, that the retardation factor for Pu(VI) was about 15.

Figure 5.1c also shows the effect of including surface mediated redox reactions on the migration of plutonium. When a high reduction rate (k_r) relative to the oxidation rate (k_o) is applied to the system, the migration was excessively retarded as seen in Simulation 2, since the released Pu converts into a less mobile form very quickly and stays in that form for the rest of the simulations. The simulations did not show any significant change due to the oxidation rate constant, as shown by Simulations 2, 3, and 4. Since oxidation is a very slow process, this result is attributed to the relatively short duration of this particular experiment, which is about 2 years.

(a)

(b)

(c)

Figure 5.1 Comparison of activity distribution measurements with modeling results for the $\text{Pu(VI)O}_2(\text{NO}_3)_2$ data set for different oxidation (k_o) and reduction (k_r) rate constants, and retardation factors, R_o and R_r . (a) $R_o=50$, $R_r=10,000$; (b) $R_o=25$, $R_r=10,000$; (c) $R_o=15$, $R_r=10,000$ ($TA=\text{Total Activity}$).

The response of the system to the reduction rate constant can be seen through Simulations 3, 5, 6, and 7, with 7 giving the best fit to the experimental data with a coefficient of determination (R^2) value of 0.978. As the reduction rate increased, the retardation of Pu also increased. As expected, due to the assumption of constant net downward velocity in the system, none of the simulations resulted in the upward migration of Pu which is observed in the data set.

A set of simulations was done with the Pu_o retardation factor kept at 15, and the oxidation and reduction rate constants chosen from Simulation 7 of Figure 5.1c to evaluate the model sensitivity to retardation factor for Pu_r (R_r). The Pu_r retardation factor

was then varied from 50 through 15,000. As can be seen in Figure 5.2, the Pur retardation factor had almost no effect on the simulation results when the values range between 50 and 15,000. Therefore, the important factors in simulating Pu(VI) transport in the SRS lysimeter were the Puo retardation (R_o), and how fast Puo reduced to Pur (k_r). It is not possible to use this data set to infer detailed information on either the oxidation rate constant (k_o) or the reduced retardation factor (R_r). Due to its low mobility and the relatively short duration of the experiment, once Puo became reduced it essentially remained in place in the Pur form. A summary of the best fit oxidation and reduction rate constants for different Puo retardation factor values around 15 is presented in Table 5.1 and plots resulting from simulation are given in Appendix F.

Figure 5.2 Comparison of simulated and measured activity distributions for the $\text{Pu(VI)O}_2(\text{NO}_3)_2$ source as a function of the reduced retardation factor R_r , when $R_o=15$, $k_o=1.0 \times 10^{-8}$ 1/h and $k_r=3.3 \times 10^{-4}$ 1/h.

Table 5.1 Best fit values of oxidation and reduction rate constants for the Pu(VI) data set simulations as a function of R_o .

Plutonium Source	Retardation Factors		Rate Constants (1/h)	
	For Pur	For Puo	Oxidation	Reduction
	R_r	R_o	k_o	k_r
Pu(VI)O ₂ (NO ₃) ₂ (Modeled as Puo)	10,000	10	1.0×10^{-8}	6.0×10^{-4}
		15	1.0×10^{-8}	3.3×10^{-4}
		20	1.0×10^{-8}	2.0×10^{-4}
		25	1.0×10^{-8}	5.0×10^{-5}

Sensitivity Analysis for Different Activity Release Functions

In terms of activity release rate, the second possible scenario is to assume an exponentially decreasing release as shown in Equation (4.14) and Figure 4.4. From the data available, released rate (k_{release}) is calculated from Equation (4.15) as 2.996×10^{-6} 1/h and resulting exponentially decreasing release rate function is given in Equation (5.1) below.

$$q_o = \frac{477 \left[e^{-2.996 \cdot 10^{-6} (t - \Delta t)} - e^{-2.996 \cdot 10^{-6} t} \right]}{Area_{filter} \Delta z \Delta t} \quad (5.1)$$

As seen in Figure 5.4, no significant differences were observed in the resulting simulated activity distributions using the two different release rate scenarios

An additional release scenario where the total activity is released into the domain during first hour of the simulation period is also tested. The results indicated that the distribution characteristics are independent from the release function.

Figure 5.3 Comparison of two different activity release scenarios, exponentially decreasing and constant rate for the retardation factors of $R_r=10,000$ and $R_o=15$, oxidation and reduction rate constants of $k_o=1.0\times 10^{-8}$ 1/h and $k_r=3.3\times 10^{-4}$ 1/h.

Pu(IV)(NO₃)₄, Pu(IV)(C₂O₄)₂, and Pu(III)Cl₃ Simulation Results

As stated earlier, Pu(III) and Pu(IV) are the less mobile forms of plutonium having similar transport characteristics, they are therefore both modeled as Pur. This is also consistent with the observation that the data presented in Figures 2.3, 2.4 and 2.5 which are similar for sources containing different reduced states. The Pu(III) and Pu(IV) activity distributions showed significant differences compared to the Pu(VI) distributions. During the 11-year Pu(III) and Pu(IV) experiments, the bulk of the plutonium migration was retained in the first few centimeters below the filter. (The corresponding distance for the 2-year Pu(VI) experiment was about 15 cm). Previously, the Pur retardation factor was determined to be between 5000 and 15,000 as a result of the single species retarded

transport analysis. For the simulations presented here in Figures 5.5, 5.6, and 5.7, the Pur retardation factor was 10,000, and the Puo retardation factor was 15.

Shown in Figures 5.5, 5.6, and 5.7 are results of the model simulations for different oxidation and reduction rate constants, compared to the measured data for the Pu(IV)(NO₃)₄, Pu(IV)(C₂O₄)₂, and Pu(III)Cl₃ data sets respectively. For each data set, the release rate is assumed to be constant, and released activity is calculated from the differences between initial and the recovered activities on the filter, as given in Table 5.2.

Table 5.2 Amount of total activity released and constant release rates for each lysimeter, for a filter radius of 2.5 cm and thickness of 0.2 cm.

Pu Source in the Experiment	Total Activity Released (μCi) (A_{sediment})	Constant Activity Release Rate (μCi/cm³/h)
Pu(IV)(NO ₃) ₄	152.98	1.658×10 ⁻³
Pu(IV)(C ₂ O ₄) ₂	89.75	9.729×10 ⁻⁴
Pu(III)Cl ₃	165.28	1.792×10 ⁻³

When oxidation and reduction were eliminated by setting the values of the rate constants to zero, as shown in Simulation 1 for each data set, the model simulated single species transport with only Pur in the domain and retarded by the applicable Pur retardation factor. Without any oxidation and reduction occurring, the plutonium stayed in the reduced, less mobile form throughout the simulation, and the mobility of the leading edges was highly underestimated. This also shows that modeling Pu transport in the environment assuming that it stays in the reduced form may not be a good approximation for migration evaluations.

Figure 5.4 Comparison of simulated and measured activity distributions for $\text{Pu(IV)(NO}_3)_4$ source as a function of oxidation and reduction rate constants. The retardation factors are held constant at $R_0=15$, $R_r=10,000$.

Figure 5.5 Comparison of simulated and measured activity distributions for $\text{Pu(IV)(C}_2\text{O}_4)_2$ source as a function of oxidation and reduction rate constants. The retardation factors are held constant at $R_0=15$, $R_r=10,000$.

Figure 5.6 Comparison of simulated and measured activity distributions for Pu(III)Cl_3 source as a function of oxidation and reduction rate constants. The retardation factors are held constant at $R_o=15$, $R_r=10,000$.

The oxidation rate constant in the Pur data sets had a very significant effect on the Pu activity distributions due to the longer durations of the experiments. As seen in Simulations 2, 3, 4, 5, and 6 in Figure 5.5, the value of this rate constant (k_o) determines the fraction of plutonium which moves farthest into the domain (high-mobility fraction). Even though the bulk of the Pur activity distributions are consistent with single species retarded transport, the oxidation process produces the small, high-mobility fraction that is observed in all the Pur data sets, as shown in Figures 5.4 through Figure 5.6.

If we assume there is only oxidation in the system with no reduction, as seen in simulations 2 and 3 in the graphs for each data set in Figure 5.4, 5.5, and 5.6, a poor fit to the data results. In fact, with a high enough oxidation rate in the system, Pu converts into the more mobile form and migrates through the bottom boundary (Simulation 2).

Simulations 6, 7, and 8 in Figure 5.5 show that the reduction rate constant (k_r) determines how fast the high-mobility fraction moves; in other words, it determines the amount of retardation that fraction undergoes, since it converts more mobile forms of plutonium (Puo) to less mobile forms (Pur) following contact with mineral surfaces. After adsorption of Puo, as the reduction rate increases, the amount of Puo converted to Pur in a given time also increases. So, in simulation 6 with a higher reduction rate, the high-mobility fraction was retarded more, whereas in simulation 8 with a lower reduction rate, the high-mobility fraction moved more quickly in the domain, in some cases exiting the lower model boundary, which was not observed in the field experiments. Similar behavior is shown in Figure 5.4 and Figure 5.6. Thus, both oxidation and reduction are needed in the Pur simulations in order to match the data. The oxidation and reduction rate constants in simulation 6 in Figure 5.4, Figure 5.5, and Figure 5.6 for each data set gave the best fit to the data with coefficient of determination (R^2) values of 0.929, 0.997, and 0.940 respectively. Also, a summary of the best fit oxidation and reduction rate constants is presented for different Pur and Puo retardation factors in Table 5.3, and simulations results for those cases are presented in Appendix F.

The significant upward migration observed in each data set can not be predicted with this model, since there is no upward transport mechanism except for molecular diffusion. Upward movement of plutonium in simulations 2 and 3 for each data set is due to this molecular diffusion when there is no reduction in the system. The below filter portion of these simulations show that this is not a realistic upward migration, and diffusion itself can not be the mechanism which carries Pu upward.

Table 5.3 Resulting best fit values of oxidation and reduction rate constants for Pu(IV) and Pu(III) data set simulations.

Plutonium Source		Retardation Factors		Rate Constants [1/h]	
		For Pu _o	For Pu _r	Oxidation	Reduction
		R_o	R_r	k_o	k_r
(Modeled as Pu _r)	Pu(IV)(NO ₃) ₄	10	5000	2.0×10 ⁻⁸	1.5×10 ⁻³
			10000	3.5×10 ⁻⁸	1.5×10 ⁻³
			15000	5.0×10 ⁻⁸	1.5×10 ⁻³
		15	5000	2.0×10 ⁻⁸	1.0×10 ⁻³
			10000	5.0×10 ⁻⁸	1.0×10 ⁻³
			15000	6.0×10 ⁻⁸	1.0×10 ⁻³
		20	5000	2.0×10 ⁻⁸	7.0×10 ⁻⁴
			10000	5.0×10 ⁻⁸	7.0×10 ⁻⁴
			15000	6.0×10 ⁻⁸	7.0×10 ⁻⁴
	Pu(IV)(C ₂ O ₄) ₂	10	5000	8.0×10 ⁻⁸	8.0×10 ⁻⁴
			10000	3.0×10 ⁻⁷	1.0×10 ⁻³
			15000	3.0×10 ⁻⁷	1.0×10 ⁻³
		15	5000	8.0×10 ⁻⁸	5.0×10 ⁻⁴
			10000	3.0×10 ⁻⁷	7.0×10 ⁻⁴
			15000	3.0×10 ⁻⁷	7.0×10 ⁻⁴
		20	5000	9.0×10 ⁻⁸	4.0×10 ⁻⁴
			10000	3.0×10 ⁻⁷	5.0×10 ⁻⁴
			15000	3.0×10 ⁻⁷	5.0×10 ⁻⁴
	Pu(III)Cl ₃	10	5000	4.0×10 ⁻⁷	1.5×10 ⁻³
			10000	5.0×10 ⁻⁷	1.3×10 ⁻³
			15000	6.0×10 ⁻⁷	1.2×10 ⁻³
		15	5000	3.0×10 ⁻⁷	8.0×10 ⁻⁴
			10000	5.0×10 ⁻⁷	7.5×10 ⁻⁴
			15000	6.0×10 ⁻⁷	7.0×10 ⁻⁴
		20	5000	6.0×10 ⁻⁷	7.0×10 ⁻⁴
			10000	6.0×10 ⁻⁷	6.0×10 ⁻⁴
			15000	6.0×10 ⁻⁷	5.5×10 ⁻⁴

Sensitivity Analysis for Different Activity Release Functions

Pu(IV)(C₂O₄)₂ data are used to perform a sensitivity analysis for different activity release rate scenarios. The exponentially decreasing release rate function is applied to the model as shown in Equation (4.14). From the data available (Appendix A), the release rate constant (k_{release}) is calculated from Equation (4.15) as 2.025×10^{-6} 1/h, and the resulting exponentially decreasing release rate function is given in Equation (5.2) as:

$$q_o = \frac{518.02 \left[e^{-2.025 \cdot 10^{-6} (t - \Delta t)} - e^{-2.025 \cdot 10^{-6} t} \right]}{\text{Area}_{\text{filter}} \Delta z \Delta t} \quad (5.2)$$

Figure 5.7 Comparison of two different activity release scenarios, exponentially decreasing and constant rate for the retardation factors of $R_r=10,000$ and $R_0=15$, oxidation and reduction rate constants of $k_0 = 3.0 \times 10^{-7}$ 1/h and $k_r = 7.0 \times 10^{-4}$ 1/h.

As seen in Figure 5.8, when the best fit simulation for this data set is reproduced with an exponentially decreasing release rate, the results showed very small difference in the distributions. The exponential release showed slightly more migration downward, probably due to more activity release into the domain earlier in the simulation and being exposed to transport mechanisms for a longer duration.

An additional release scenario where the total activity is released into the domain during first hour of the simulation period is also tested. The results indicated that the distribution characteristics are independent from the release function.

CHAPTER 6

DEVELOPMENT OF A VARIABLY SATURATED FLOW MODEL

As discussed in the earlier chapters, the lysimeter experiments used in this study are highly transient hydrodynamic systems. Although the steady-state flow assumption appears acceptable for testing the surface-mediated redox hypothesis with an averaged seepage velocity, it fails to include the potential effects of varying moisture content, and, most importantly, it does not include transpiration, and resulting upward flow, in the system caused by the plants growing in the lysimeters. Therefore, it is necessary to develop a variably saturated flow model with a root uptake module for a fully transient analysis of the data.

Variably Saturated Flow

Vadose zone hydrology has a highly dynamic and complicated nature due to the presence of both air and aqueous phases in the pore space. Different than saturated flow, in the vadose zone the pore water is under a negative pressure caused by surface tension and capillarity, and defined by pressure head, ψ , in units of energy per unit weight (length). The pressure head is a function of soil moisture; the lower the volumetric water content, the more negative the value of pressure head. The driving potential for the flow is the total head (h), which is the sum of the pressure head and the gravitational head (z , in units of length) in our system as shown in Equation (6.1) (Fetter, 1999).

$$h = \psi + z \quad (6.1)$$

The flow of water through a saturated homogeneous matrix is defined by Darcy's equation shown below:

$$\vec{q} = -K \cdot \vec{\nabla} h \quad (6.2)$$

where $\vec{q}$ is the volumetric flux or Darcy flux (in volume/area/time), K is the saturated hydraulic conductivity (in length/time), and $\vec{\nabla} h$ is the total head gradient vector.

Richards extended Darcy's law as shown in Equation (6.3) to describe the flow in unsaturated soils, where the soil moisture flux depends on an unsaturated hydraulic conductivity, $K(\psi)$, and the head gradient, which can be written in term of equation (6.1) in one dimension as shown in the equation:

$$q = -K(\psi) \cdot \left(\frac{\partial \psi}{\partial z} + 1 \right) \quad (6.3)$$

The continuity equation for water flow through variably saturated porous media is derived from a mass balance over an infinitesimally small control volume as represented in Equation (6.4) in vector notation.

$$\frac{\partial(\rho\theta)}{\partial t} = -\vec{\nabla} \cdot (\rho q) \pm \text{Sources and Sinks} \quad (6.4)$$

where ρ is the density of the water (mass/ volume) and θ is the volumetric water content (volume of water/ volume of void space). The divergence of the fluid flux ($\vec{\nabla} \cdot \rho q$) represents the net fluid flow out of the control volume, and the continuity equation states that the change in the mass of the fluid within the control volume with time is equal to net rate of mass flow out.

The conventional pressure-based form of Richard's equation for one-dimensional, unsaturated, vertical flow is given in Equation (6.5), when the chain rule is applied to the storage term and Darcy's Law is applied to the flux term.

$$C(\psi) \frac{\partial \psi}{\partial t} = - \frac{\partial \left[K(\psi) \frac{\partial \psi}{\partial z} \right]}{\partial z} + \frac{\partial K(\psi)}{\partial z} \quad (6.5)$$

where $C(\psi)$ is the specific water capacity of the soil and is defined as:

$$C(\psi) = \frac{\partial \theta}{\partial \psi} \quad (6.6)$$

Since conventional pressure-based numerical models for the variably saturated flow equations are known to suffer from computational difficulties when dealing with changes from unsaturated to saturated conditions, Clement (1993) presented an improved, physically-based, numerical scheme for solving a mixed form of the variably saturated

flow equation. He used the form of a storage term which is shown in Equation (6.7) in terms of water saturation (S_w) to develop the mixed form of the flow equation.

$$\frac{\partial(\rho\theta)}{\partial t} = \frac{\partial(S_w\eta\rho)}{\partial t} = -\nabla \cdot (\rho q) \pm \text{Sources and Sinks} \quad (6.7)$$

where η is the porosity of the domain and S_w is defined by:

$$S_w = \frac{\theta}{\eta} \quad (6.8)$$

Physically, the mass of water in storage changes with head due to compression or expansion of both the water and the aquifer. Assuming a slightly compressible fluid, and letting $\rho = \rho_o$ and $\eta = \eta_o$ at $\psi = 0$, one can develop experimentally simple linear variations for ρ and η given by:

$$\rho = \rho_o \left(1 + \frac{S_\rho \psi}{\eta_o} \right) \Rightarrow \frac{\partial \rho}{\partial t} = \rho_o \frac{S_\rho}{\eta_o} \frac{\partial \psi}{\partial t} \quad (6.9)$$

$$\eta = \eta_o \left(1 + \frac{S_\eta \psi}{\eta_o} \right) \Rightarrow \frac{\partial \eta}{\partial t} = \eta_o \frac{S_\eta}{\eta_o} \frac{\partial \psi}{\partial t} \quad (6.10)$$

where S_ρ and S_η are empirical constants. (The motivation for choosing the form of Equations (6.9) and (6.10) will become clear shortly.)

$$\begin{aligned}
\frac{\partial(S_w \eta \rho)}{\partial t} &= \eta \rho \frac{\partial S_w}{\partial t} + S_w \left(\eta \frac{\partial \rho}{\partial t} + \rho \frac{\partial \eta}{\partial t} \right) \\
&= \eta \rho \frac{\partial S_w}{\partial t} + S_w \eta \rho_o \frac{S_\rho}{\eta_o} \frac{\partial \psi}{\partial t} + S_w \eta_o \rho \frac{S_\eta}{\eta_o} \frac{\partial \psi}{\partial t} \\
&= \rho \frac{\partial q}{\partial z} + q \frac{\partial \rho}{\partial z}
\end{aligned} \tag{6.11}$$

To obtain a first order equation, we assume $\rho = \rho_o, \eta = \eta_o$, $q \frac{\partial \rho}{\partial z} \ll \rho \frac{\partial q}{\partial z}$, and

$\frac{\partial S_w}{\partial t} = \frac{1}{\eta} \frac{\partial \theta}{\partial t}$. This yields the equation:

$$\frac{\partial \theta}{\partial t} + \frac{\partial \psi}{\partial t} \left(S_\rho \frac{\theta}{\eta_o} + S_\eta \frac{\theta}{\eta_o} \right) = \frac{\partial q}{\partial z} \tag{6.12}$$

or

$$\frac{\theta S_s}{\eta} \frac{\partial \psi}{\partial t} + \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(\psi) \frac{\partial \psi}{\partial z} \right] + \frac{\partial K(\psi)}{\partial z} \pm \text{sources and sinks} \tag{6.13}$$

where $S_s = S_\rho + S_\eta$ is the specific storage coefficient, which is the volume of water that a unit volume of aquifer releases from storage under a unit decline in hydraulic head.

Under saturated conditions, it may be written in the well known form as

$$S_s = \rho_o g (\alpha + \eta_o \beta).$$

Equation (6.13) is a robust equation representing variably saturated flow in a one-dimensional system. When the system reaches a saturated condition, water content becomes equal to porosity (η_o) and $\frac{\partial \theta}{\partial t} = 0$, thus, the left side of the above equation takes form of the saturated flow equation $S_s \frac{\partial \psi}{\partial t}$. For the unsaturated case the influence of S_s is relatively insignificant compared to changes in the water content with time (Clement et al., 1994).

Root Water Uptake

As stated earlier, the lysimeters were placed into the ground with their tops open to the natural environmental conditions, and opportunistic plants, primarily grasses were permitted to grow on those top portions. In such systems, transpiration plays very important role in terms of the dynamics of the water balance. Transpiration refers to the water which evaporates to the atmosphere via the plant systems. In humid regions, transpiration can return 70% of the annual precipitation back to the atmosphere (Hanson, 1991).

In the vadose zone, water fluxes are the main mechanism that controls the transport of contaminants. They depend on the water balance in the zone, which consists mainly of precipitation/irrigation, evapotranspiration, and runoff. Most water leaves the soil by moving up through plant roots and out of plant canopies, rather than by direct evaporation at the soil surface (Feddes et al., 2001). Although the net flux of water is downward in the lysimeter system, root water uptake may cause some amount of upward movement of water causing upward migration of radionuclides (Burne et al., 1994; Wadey et al., 1994, 2001; Shaw et al., 2004).

There are two approaches used for dealing with water uptake by roots; one of them - the microscopic approach - depends on the properties of a single root and the other - the macroscopic approach - relies on the integrated properties of the entire root system (Molz, 1981; Feddes et al., 1974; 1978). Several microscopic root uptake models have been developed, but according to Mathur and Rao (1999), their effectiveness is limited by:

- Assumption of steady-state conditions for time dependency of the root system. In reality, a root system is a dynamic system and its geometry is time dependent.
- Position and time dependency of permeability.
- Differential absorption capacity depending on the age and the location of the roots.
- The experimental evaluation of root properties; detailed root measurements are often impractical.
- Experimental testing and defining boundary conditions.

Since the macroscopic approach does not take the individual roots into account, it eliminates the time dependency of the individual root geometry. Furthermore, boundary conditions are more easily determined with this approach. The macroscopic models also allow natural interaction with the transpiration processes (Mathur and Rao, 1999). Thus, this approach has proven to be more practical than the microscopic approach, and is used herein for modeling root water uptake in the lysimeter system.

Molz and Remson (1970) represented root water uptake as a volumetric sink term, included in the continuity equation, as shown in Equation (6.14). (Molz (1981) presents a review of the most widely used sink term functions). One way of calculating the sink term function is to assume that the transpiration rate is equal to the sum (integral) of the uptake rate over the root profile. Under this assumption, the sink term represents the volume of water taken up by the roots per unit bulk volume of the soil per unit time (Molz and Remson, 1970; Homae et al., 2002; Feddes et al., 1978; Chang and Corapcioglu, 1997). This approach allows direct integration of root water uptake with transient soil water flow (Vrugt et al., 2001).

$$\frac{\theta S_s}{\eta} \frac{\partial \psi}{\partial t} + \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(\psi) \frac{\partial \psi}{\partial z} \right] + \frac{\partial K(\psi)}{\partial z} - S(z, \psi) \quad (6.14)$$

There are several forms that can be selected for the root water uptake function, $S(z, \psi)$. For the computations that follow, the form utilized by Feddes et al. (1978) is selected. It is given by:

$$S(z, \psi) = \alpha(\psi) * RRD(z) * T_p \quad (6.15)$$

where $\alpha(\psi)$ represents the effect of plant water stress under dry conditions or oxygen stress under wet conditions on the transpiration rate, $RRD(z)$ is the relative root distribution (density), which spreads the water uptake over the root zone in proportion to

the root density, and T_p is the potential (maximum) transpiration rate under the prevailing climatic conditions. As a reasonable approximation, transpiration is assumed to occur at the potential rate unless it is limited by the availability of soil moisture or oxygen. $RRD(z)$ is defined so that

$$\int_0^{Z_R} RRD(z) dz = 1 \Rightarrow RRD(z) = \frac{RD(z)}{\int_0^{Z_R} RD(z) dz} \quad (6.16)$$

where $RD(z)$ is the measured root distribution in terms of root weight per unit volume of soil, and Z_R is the depth of the root zone. When moisture or oxygen is not limiting, $\alpha(\psi)=1$, the Equation (6.15) yields the relationship:

$$\int_0^{Z_R} S(z, \psi) dz = \int_0^{Z_R} RRD(z) T_p dz = T_p \quad (6.17)$$

When moisture or oxygen is limiting, $\alpha(\psi)<1$, the total water extraction rate is:

$$\int_0^{Z_R} S(z, \psi) dz = \int_0^{Z_R} RRD(z) T_p dz < T_p \quad (6.18)$$

Figure 6.1 shows the general shape of a stress-response function. It is an empirically derived function, where ψ_1 defines an ‘oxygen deficiency (anaerobiosis) point’, and ψ_4

represents a ‘wilting point’. Under conditions wetter than the ‘anaerobiosis point’, root growth is significantly limited due to lack of oxygen in the system. The saturated condition, where the pressure head value is zero, is usually selected as an ‘anaerobiosis point’. Under conditions drier than ‘wilting point’, the water uptake by roots is also assumed to be zero due to the unavailability of enough moisture for roots to survive (Feddes et al., 1978).

$$\alpha(\psi) = \begin{cases} 0 & \psi \geq \psi_1 \\ \frac{\psi_1 - \psi}{\psi_1 - \psi_2} & \psi_2 \leq \psi \leq \psi_1 \\ 1 & \psi_3 \leq \psi \leq \psi_2 \\ \frac{\psi - \psi_4}{\psi_3 - \psi_4} & \psi_4 \leq \psi \leq \psi_3 \\ 0 & \psi < \psi_4 \end{cases}$$

Figure 6.1 Schematic representation of stress-response function for different values of pressure head and general equations used to quantify the stress-response function for different ranges of pressure head values.

For reducing the uncertainty associated with the parameter values used in the modeling, the root densities for the Savannah River Site lysimeter soils measured for

three soil cores and the relative root distribution functions are calculated by the equation (6.16). Figure 6.2 shows the resulting distribution functions along the cores and Table 6.1 lists the calculated relative root distribution functions. The implications of the differences of these three density functions on Pu distribution characteristics will be discussed below.

Table 6.1 Calculated relative root distribution functions for three soil cores taken from the SRS lysimeter area.

Measured Core	Calculated Relative Root Density Functions
Core C	$RRD(z) = 0.114902 e^{-(0.114571 \cdot z)}$
Core D	$RRD(z) = 0.068777 e^{-(0.066457 \cdot z)}$
Core E	$RRD(z) = 0.034695 e^{-(0.025 \cdot z)}$

Figure 6.2 Three relative root density functions calculated from the measured root densities from the soil cores (Core C, Core D, and Core E) collected from the SRS lysimeter area.

Potential Transpiration

One of the main limitations of root uptake models is determining the actual transpiration rate due to complications associated with the soil conditions during the measurements. The concept of potential transpiration more readily lends itself to developing a predictive formula. Potential transpiration is assumed to be the maximum value of transpiration for any set of vegetation and field conditions and its amount is directly related to the climate. It occurs only during daylight hours due to photosynthesis, and it is more enhanced during the growing season. For this reason, any calculation of potential transpiration should include all these factors (Watson and Burnett, 1993).

The Thornthwaite equation, shown in Equation (6.19), is derived for calculating monthly potential transpiration, T_{pm} (in length), for especially humid climates like the eastern United States (Watson and Burnett, 1993). The equation includes a monthly adjustment factor related to hours of daylight for the location of interest in latitude (N_m), the mean monthly temperature in degrees C (T_m), the heat index for a year (I) calculated by the Equation (6.20), and constant (a) which is a function of the heat index as shown in Equation (6.21). $\beta_{transpiration}$ is the correction factor estimated from the data and simulation results by trial and error.

$$T_{pm} = \beta_{transpiration} 16N_m \left[\frac{10T_m}{I} \right]^a \quad (6.19)$$

$$I = \sum_{m=1}^{12} \left[\frac{T_m}{5} \right]^{1.5} \quad (6.20)$$

$$a = 6.7 \times 10^{-7} I^3 - 7.7 \times 10^{-5} I^2 + 1.8 \times 10^{-2} I + 0.49 \quad (6.21)$$

Table 6.2 below shows calculated potential monthly transpiration rates by the Thornthwaite equation for the lysimeter experiments. Two different time periods were chosen for different lysimeter experiments; the 1980-1983 period is calculated for the $\text{Pu(VI)O}_2(\text{NO}_3)_2$ experiment which lasted for the same period, and the 1980-1984 period is calculated for all the other experiments which were in the ground for about 11 years (since the leachate volumes were collected for this period). Mean monthly temperatures are downloaded from the national climatic data center station located in Aiken, SC. Mean daily duration of maximum possible sunshine hours were tabulated by Watson and Burnett (1993), and they are used to calculate the daylight hours for the Aiken station by interpolation between the latitude information of the location (the SRS is located at approximately 33°N). Detailed calculations of these potential transpiration values are tabulated in Appendix G.

Table 6.2 Calculated monthly potential transpiration rates for two different time periods.

Years	Averaged Monthly Potential Evapotranspiration Rates, T_{pm} (cm/d)											
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1980-1983	0.02	0.06	0.13	0.22	0.35	0.51	0.58	0.42	0.36	0.20	0.09	0.04
1980-1984	0.02	0.06	0.12	0.22	0.36	0.51	0.57	0.43	0.36	0.22	0.09	0.05

A correction factor ($\beta_{\text{transpiration}}$) for the monthly potential transpiration rates is estimated from the water balance for each lysimeter from the amount of total rainfall and the amount of total leachate volume for a given period. For the lysimeters which have longer durations than the leachate volume collection period, water balance is performed only for the period when the leachate volume was collected, and then the correction

factor is calculated from this water balance and the results of the simulations with different values for the factor by trial and error.

Hydraulic Parameters

Hydraulic parameters, unsaturated hydraulic conductivity, $K(\psi)$, and volumetric water content, $\theta(\psi)$, are estimated by using Rosetta with an input of measured average particle size distribution of the soil and the bulk density as described earlier. Resulting functions were compared to the measured unsaturated hydraulic conductivity values as shown in Figure 4.2. Van Genuchten parameter values resulted from Rosetta are listed in Table 6.3 and the Van Genuchten soil hydraulic functions are shown in equations (4.8) and (4.9).

Table 6.3 Van Genuchten soil hydraulic parameter values estimated by Rosetta.

Van Genuchten Parameters	Value
Retention Function	
Curve shape parameter, n	1.48013
Curve shape parameter, α (1/cm)	0.027816
Saturated water content, θ_{sat} (cm ³ /cm ³)	0.39188
Residual water content, θ_r (cm ³ /cm ³)	0.0589
Hydraulic Conductivity Function	
Saturated hydraulic conductivity, K_{sat} (cm/d)	15.984
Tortuosity/connectivity parameter, L	-1.0633

$$S_e = \left[1 + (0.027816|\psi|)^n \right]^{1/n-1}$$

$$K(\psi) = K_{sat} S_e^L \left\{ 1 - \left[1 - S_e^{n/(n-1)} \right]^{1-1/n} \right\}^2 \quad (4.8)$$

$$\theta(\psi) = \theta_r + \frac{\theta_{sat} - \theta_r}{\left[1 + (0.027816\psi)^n \right]^{1-1/n^4}} \quad (4.9)$$

Figures 6.3 and 6.4 show unsaturated hydraulic conductivity and volumetric water content functions respectively for varying pressure head values. As seen in Figure 6.3, the unsaturated hydraulic conductivity values drop an order of magnitude with a decrease in pressure head from the saturated condition to about -50 cm, which indicates that the system has very limited moisture conductivity in drying conditions. Figure 6.4 shows that the moisture content also drops quickly with decreasing pressure head reaching around 0.10 at a pressure head of -2000 cm.

Figure 6.3 Unsaturated hydraulic conductivity as a function of pressure head, where K_{sat} is the saturated hydraulic conductivity.

Figure 6.4 Volumetric water content as a function of pressure head, where θ_r is the residual water content and θ_{sat} is the saturated water content.

The specific water capacity function, $C(\psi)$, is calculated analytically by taking the derivative of the moisture content function with respect to the pressure head. Equation (6.22) shows the resulting capacity function.

$$C(\psi) = \frac{\partial \theta}{\partial \psi} = \frac{0.892728 |\psi|^{0.48143}}{\left(|\psi|^{1.48013} + 200.746 \right)^{1.32438}} \quad (6.22)$$

Numerical Modeling with Variably Saturated Flow

The governing equation for variably saturated flow with root water uptake is developed previously in this chapter based on the mixed form of Richard's equation and it is given here again (Equation (6.13)).

$$\frac{\theta S_s}{\eta} \frac{\partial \psi}{\partial t} + \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(\psi) \frac{\partial \psi}{\partial z} \right] + \frac{\partial K(\psi)}{\partial z} - S(z, \psi) \quad (6.13)$$

A fully implicit, finite difference approximation, as shown in Figure 6.5, of the governing equation is solved for the pressure head by using a tridiagonal algorithm. For the nonlinearity caused by the pressure head dependent hydraulic parameters, a Picard iteration scheme is used. Equations (6.23) and (6.24) are the finite difference approximations of the separate parts of the storage term in the governing equation as used by Clement et al. (1994): i denotes the current node for which the pressure head is being solved, j is the current time level, $j-1$ is the previous time level, and $m+1$ is the current iteration level while m is the previous.

Figure 6.5 Schematic representation of the one-dimensional nodal system which is used for solving the finite difference approximation of the governing equation for variably saturated flow.

$$\frac{\theta S_s}{\eta} \frac{\partial \psi}{\partial t} = \frac{S_s}{\eta} \theta^m(i, j) \left[\frac{\psi^{m+1}(i, j) - \psi(i, j-1)}{\Delta t} \right] \quad (6.23)$$

$$\frac{\partial \theta}{\partial t} = \left[\frac{\theta^{m+1}(i, j) - \theta(i, j-1)}{\Delta t} \right] \quad (6.24)$$

In Equation (6.24), the current time level value of the water content has to be expressed in terms of the pressure head, since the whole equation is solved for the current time level values of the pressure head at each node. Thus, Clement (1993) used a first-order, truncated Taylor series, in terms of the pressure head perturbation arising from Picard iteration, about the expansion point $(\theta^{m+1}(i, j), \psi^m(i, j))$, as:

$$\theta^{m+1}(i, j) \approx \theta^m(i, j) + \left. \frac{\partial \theta}{\partial \psi} \right|_{m(i, j)} [\psi^{m+1}(i, j) - \psi^m(i, j)] \quad (6.25)$$

As described in Equation (6.6), the pressure head derivative of the water content is represented by the specific water capacity function, $C(\psi)$, in units of 1/length. Therefore, by using equations (6.24), (6.25), and (6.6), the time derivative of water content is approximated as:

$$\frac{\partial \theta}{\partial t} = \left[\frac{\theta^m(i, j) - \theta(i, j-1)}{\Delta t} \right] + C(\psi^m(i, j)) \left[\frac{\psi^{m+1}(i, j) - \psi^m(i, j)}{\Delta t} \right] \quad (6.26)$$

Below are the finite-difference approximations for the right hand side of the governing equation, (Equation (6.13)). Although Clement (1993) used arithmetic averaging for the spatial derivative of the unsaturated hydraulic conductivity, harmonic averaging is used in this model, which increases the stability of the numerical calculations. The section around each node represents a layer of soil, which would carry the properties of the node. So, one can imagine the whole domain as layers of soil with slightly different properties. In a system, where the layers of soil with different conductivities are located in a series, the lower conductivity would dominate for the flow passing through the layers. As a result, harmonic averaging is proved to be more fitting physically since it yields the correct equivalent hydraulic conductivity.

$$\frac{\partial}{\partial z} \left[K(\psi) \frac{\partial \psi}{\partial z} \right] = \frac{1}{\Delta z} \left\{ \left[\frac{2K^m(i, j)K^m(i+1, j)}{K^m(i, j) + K^m(i+1, j)} \right] \left[\frac{\psi^{m+1}(i+1, j) - \psi^{m+1}(i, j)}{\Delta z} \right] - \left[\frac{2K^m(i, j)K^m(i-1, j)}{K^m(i, j) + K^m(i-1, j)} \right] \left[\frac{\psi^{m+1}(i, j) - \psi^{m+1}(i-1, j)}{\Delta z} \right] \right\} \quad (6.27)$$

$$\frac{\partial K}{\partial z} = \frac{1}{\Delta z} \left\{ \left[\frac{2K^m(i, j)K^m(i+1, j)}{K^m(i, j) + K^m(i+1, j)} \right] - \left[\frac{2K^m(i, j)K^m(i-1, j)}{K^m(i, j) + K^m(i-1, j)} \right] \right\} \quad (6.28)$$

$$S(z, \psi) = S(z(i), \psi^m(i, j)) \quad (6.29)$$

Combining equations (6.23), (6.26), (6.27), (6.28), and (6.29) gives the finite difference approximation of the governing equation as a whole as shown below.

$$\begin{aligned}
& \frac{S_s}{\eta} \theta^m(i, j) \left[\frac{\psi^{m+1}(i, j) - \psi(i, j-1)}{\Delta t} \right] + \left[\frac{\theta^m(i, j) - \theta(i, j-1)}{\Delta t} \right] + \\
& C(\psi^m(i, j)) \left[\frac{\psi^{m+1}(i, j) - \psi^m(i, j)}{\Delta t} \right] = \\
& \frac{1}{\Delta z} \left\{ \left[\frac{2K^m(i, j)K^m(i+1, j)}{K^m(i, j) + K^m(i+1, j)} \right] \left[\frac{\psi^{m+1}(i+1, j) - \psi^{m+1}(i, j)}{\Delta z} \right] \right. \\
& \left. - \left[\frac{2K^m(i, j)K^m(i-1, j)}{K^m(i, j) + K^m(i-1, j)} \right] \left[\frac{\psi^{m+1}(i, j) - \psi^{m+1}(i-1, j)}{\Delta z} \right] \right\} \\
& + \frac{1}{\Delta z} \left\{ \left[\frac{2K^m(i, j)K^m(i+1, j)}{K^m(i, j) + K^m(i+1, j)} \right] - \left[\frac{2K^m(i, j)K^m(i-1, j)}{K^m(i, j) + K^m(i-1, j)} \right] \right\} - S(z(i), \psi^m(i, j))
\end{aligned} \tag{6.30}$$

The governing equation is solved for pressure head values for each time step, these values are used in Darcy's law to calculate the flux values for each node. The seepage velocity is, therefore, calculated from dividing the flux values by the volumetric water content at each node at each time step. The calculated seepage velocities are then used to couple the variably saturated flow model to the reactive transport model. The transport model is also modified for the coupling since the velocity and volumetric water content are no longer constants in the system. The dispersion coefficient and the retardation factors are functions of varying seepage velocity and water content. The finite difference approximations of the transport governing equations, (C.6) and (C.10), for P_{uo} and P_{ur} respectively are:

$$\begin{aligned}
& \left(1 + \frac{\rho}{\theta(i)} K_{do}\right) \frac{[C_{Puo}^{m+1}(i, j) - C_{Puo}^m(i, j-1)]}{\Delta t} + C_{Puo}^{m+1}(i, j) \rho K_{do} \left[\frac{1}{\theta(i, j)} - \frac{1}{\theta(i, j-1)} \right] = \\
& -v(i, j) \frac{[C_{Puo}^m(i+1, j) - C_{Puo}^{m+1}(i-1, j)]}{2\Delta z} - C_{Puo}^{m+1}(i, j) \frac{[v(i+1, j) - v(i-1, j)]}{2\Delta z} + \\
& D(i, j) \frac{[C_{Puo}^m(i+1, j) - 2C_{Puo}^{m+1}(i, j) + C_{Puo}^{m+1}(i-1, j)]}{\Delta z^2} \\
& + \frac{[D(i+1, j) - D(i-1, j)]}{2\Delta z} \frac{[C_{Puo}^m(i+1, j) - C_{Puo}^{m+1}(i-1, j)]}{2\Delta z} \\
& + k_o \frac{\rho K_{dr}}{\theta(i, j)} C_{Pur}^m(i, j-1) - k_r \frac{\rho K_{do}}{\theta(i, j)} C_{Puo}^{m+1}(i, j) + \frac{q_{o,Puo}}{\theta} \delta(i - i_{source})
\end{aligned} \tag{6.31}$$

and

$$\begin{aligned}
& \left(1 + \frac{\rho}{\theta(i)} K_{dr}\right) \frac{[C_{Pur}^{m+1}(i, j) - C_{Pur}^m(i, j-1)]}{\Delta t} + C_{Pur}^{m+1}(i, j) \rho K_{dr} \left[\frac{1}{\theta(i, j)} - \frac{1}{\theta(i, j-1)} \right] = \\
& -v(i, j) \frac{[C_{Pur}^m(i+1, j) - C_{Pur}^{m+1}(i-1, j)]}{2\Delta z} - C_{Pur}^{m+1}(i, j) \frac{[v(i+1, j) - v(i-1, j)]}{2\Delta z} + \\
& D(i, j) \frac{[C_{Pur}^m(i+1, j) - 2C_{Pur}^{m+1}(i, j) + C_{Pur}^{m+1}(i-1, j)]}{\Delta z^2} \\
& + \frac{[D(i+1, j) - D(i-1, j)]}{2\Delta z} \frac{[C_{Pur}^m(i+1, j) - C_{Pur}^{m+1}(i-1, j)]}{2\Delta z} \\
& - k_o \frac{\rho K_{dr}}{\theta(i, j)} C_{Pur}^{m+1}(i, j-1) + k_r \frac{\rho K_{do}}{\theta(i, j)} C_{Puo}^{m+1}(i, j) + \frac{q_{o,Puo}}{\theta} \delta(i - i_{source})
\end{aligned} \tag{6.32}$$

Boundary Conditions

Boundary conditions are applied to the model at the top and bottom boundaries, and they are very important in terms of simulating real field conditions with the model. Neumann boundary conditions are used for defining both of these boundaries, which

specify a flux value through the boundary (Clement et al., 1994). Thus, the pressure head values at these boundaries would be determined by using a flux condition. Depending on the flux value chosen, this boundary condition could represent some special situations: for example, when the flux value is 0, it would represent a no flow boundary condition, and when the outside flux value changes equal to the flux value inside, right before the boundary, incoming flux would leave the domain without being altered.

The upper boundary condition is shown by Equation (6.33), where q_I represents the daily rainfall/infiltration rate. The daily rainfall rates are taken from the data collected in Area 200F at the SRS during the experiments and applied as flux values at the upper boundary. When the rainfall rate is zero, the boundary condition becomes a no flow boundary, which physically represents no water passing through the boundary.

$$q|_{i=N,j} = -K(\psi) \left(\frac{\partial \psi}{\partial z} + 1 \right) \Big|_{i=N,j} = q_I \quad (6.33)$$

Defining a lower boundary condition in a lysimeter mathematically is a more challenging issue, since the lower part of the lysimeter, in the actual field condition, opens to the atmospheric pressure and needs to be saturated at positive pressure before drainage occurs (Flury et al., 1999; Abdou and Flury, 2004). The closest numerical approximation of this situation is to apply a boundary condition where the incoming fluxes leave the domain in the same magnitude and direction. This boundary condition assumes a continuum between the lysimeter and the soil below. The lower boundary condition applied to the model is shown in Equation (6.34), where the flux value at the

boundary is calculated by using pressure head values of the previous time step. When the flux through the boundary overcomes the gravitational gradient flux and becomes upward, the boundary condition is set to no flow to avoid any water coming into the domain through the bottom boundary, shown by Equation (6.35). By this combination, the simulated drainage through the bottom of the domain is expected to be very close to actual conditions.

$$q|_{i=1,j} = -K(\psi) \left(\frac{\partial \psi}{\partial z} + 1 \right) \bigg|_{i=1,j-1} \quad \text{when} \quad \frac{\partial \psi}{\partial z} \bigg|_{i=1,j,m} > -1 \quad (6.34)$$

$$q|_{i=1,j} = 0 \quad \text{when} \quad \frac{\partial \psi}{\partial z} \bigg|_{i=1,j,m} \leq -1 \quad (6.35)$$

Adaptive Time Scaling

One of the most common sources of errors in numerical solutions of water flow and solute transport in a variably saturated flow system is insufficient spatial or temporal resolution in numerical modeling (Mansell et al., 2002). Special cases such as infiltration into initially dry soil profiles with very small values of hydraulic conductivity create very steep wetting fronts (large gradients of hydraulic head) due to the highly nonlinear relationship of hydraulic conductivity and pressure head. Behind the wetting front would be much smaller head gradients and much higher hydraulic conductivities with increased water content. Insufficient temporal resolution in such cases can result in numerical oscillation (Mansell et al., 2002).

Reliable numerical solutions are significant in terms of controlling such errors. Among the simple time stepping schemes are backward Euler and Crank-Nicolson schemes, the Douglas-Jones predictor-corrector method, and the implicit Runge-Kutta scheme (Kavetski et al., 2002). However, their major weakness is the approach for the stepsize selection. The most common stepsize selection strategies are: (1) uniform time increments; and (2) heuristic approaches (stepsize selection according to the convergence of the nonlinear solver) (Kavetski et al., 2002). In cases such as described above with a steep wetting front, to control the oscillations, very small time steps would be required, which would not be needed for the whole simulation period. Thus, this technique usually is very inefficient in terms of long-term simulations, such as lysimeter experiment simulations. Heuristic approaches, on the other hand, lack the quantitative link between discretization errors and solver performance, and their applicability to different nonlinear solvers are also limited (Kavetski et al., 2002). Thus, an implicit, first order time stepping scheme is used with a newly developed adaptive time scaling method to simulate lysimeter experiments.

During the lysimeter experiments, there is a periodical wetting and drying in the system. Steep wetting fronts usually occur with a high rainfall rate following a long, dry period and require very small time steps to maintain numerical stability. However, where the changes in the pressure head values between time steps and in the whole domain during one specific time step are very small, stepsize can be much bigger than what is necessary to maintain stability in a steep wetting front condition. Therefore, an adaptive method is developed to quantify an efficient stepsize for each time step as a function of a maximum and a minimum time step, and the maximum change in the pressure head as

shown in equation (6.36). Figure 6.6 also shows how the time step changes as a function of pressure head difference in the domain, where $\Delta t_{\max}$ is the maximum time step that can be used in a steady-state case (where there is no change in the pressure head values in the domain; the maximum time step can only be 1 day since the rainfall conditions change daily at the top boundary), $\Delta t_{\min}$ is the minimum time step that is used during highly transient conditions, and $\Delta \psi_c$ is the critical pressure head difference value, beyond which would require the minimum time steps taken for maintaining stability.

$$\Delta t(j) = (\Delta t_{\min})^{\max|\Delta \psi(j)| / \Delta \psi_c} (\Delta t_{\max}^*)^{(1 - \max|\Delta \psi(j)| / \Delta \psi_c)} \quad (6.36)$$

where $\Delta t_{\max}^* = \Delta t_{\max} \sqrt{\frac{K_{sat}}{K_{\max}}}$; $K_{\max}$ is the maximum unsaturated hydraulic conductivity in the domain at the time of the solution.

Figure 6.6 Schematic representation of the time step in logarithmic scale as a function of pressure head difference when $K_{\max}=K_{sat}$.

Figure 6.7 Daily rainfall rates between 7/24/90 and 8/27/90 including the maximum rainfall rate of entire experiment period on 8/21/90.

Figure 6.8 Calculated time steps during the simulations for the period between 7/24/90 and 8/27/90.

Figure 6.7 and 6.8 show the resulting time step values taken from the simulations for a period of time in which the maximum daily rainfall rate occurs. For the simulations, maximum time step is set as 1 d since the rainfall rates changes daily, and minimum time step is set as 1.0×10^{-5} d determined through a set of test simulations for maintaining numerical stability in steep wetting front conditions.

The maximum pressure head difference in Equation (6.36) is the largest head gradient that the domain is anticipated to have during the current time step. It can not be directly determined since the current time step values of the pressure head in the domain are solved after the time step is determined. Two important pressure head differences to be considered for the maximum pressure head difference for the current time level are: (1) the maximum pressure head difference in the whole domain and (2) the pressure head difference at the top boundary when the rainfall rate of the current time level is applied. While the maximum pressure head difference in the whole domain keeps track of any major pressure changes between the nodes, the estimated pressure head difference at the top boundary monitors the effect of the daily rainfall rate for the current time level in advance.

The maximum pressure head difference in the whole domain is determined by taking the differences between the previous time step ($j-1$) values at the nodes as shown in Equation (6.37).

$$\max |\Delta \psi|(i, j-1) = \max (|\psi(i+1, j-1) - \psi(i, j-1)| \quad i = 1, N) \quad (6.37)$$

The pressure head difference at the top boundary, $|\Delta\psi|(N, j)$, as shown in Equation (6.38), can not be directly calculated since the pressure head values for each node are not known for the time level j and hydraulic conductivity values can not be calculated before the pressure head values are solved.

$$|\Delta\psi|(N, j) = \left| -\Delta z \left(\frac{q_I(j)}{K(N, j)} - 1 \right) \right| \quad (6.38)$$

Therefore, a value is estimated for the pressure head at the node N for the current time level, $\psi_E(N, j)$, by using the previous time step values of pressure head and hydraulic conductivity, and the current value of the rainfall rate at the boundary as shown in equation (6.39).

$$\psi_E(N, j) = \left(-\frac{q_I(j)}{K(N, j-1)} - 1 \right) \Delta z + \psi(N-1, j-1) \quad (6.39)$$

By using the Van Genuchten Equations and estimated pressure head value, a hydraulic conductivity value is estimated at the node N for the current time level j , $K_E(N, j)$. Harmonic average of this estimated hydraulic conductivity value and the previous time step hydraulic conductivity value of the node $N-1$, $K_E(N - \frac{\Delta z}{2}, j)$, is used for calculating an estimated value for the pressure head difference for the boundary at the current time level as shown in Equation (6.40).

$$|\Delta\psi|_E(N, j) = \left| -\Delta z \left(\frac{q_I(j)}{K_E(N - \frac{\Delta z}{2}, j)} - 1 \right) \right| \quad (6.40)$$

Using the two the calculated pressure head differences, where one is for the whole domain and one is for the top boundary, the largest value is selected for calculating the time step in order to be on the safe side.

CHAPTER 7

RESULTS OF THE REACTIVE TRANSPORT MODEL WITH VARIABLY SATURATED FLOW AND DISCUSSIONS

The variably saturated flow model is coupled to the transport model to simulate the activity distributions resulting from the lysimeter experiments. In this chapter, results of this fully transient approach are presented and compared to the steady-state flow analysis. Also in the discussion section, the model is used as a research tool to further analyze the data.

For all the transport model simulations, the daily rainfall data collected at Area-200F for the period of field experiments is applied to the variably saturated flow model as the surface boundary condition and used in the water balance calculations for each lysimeter. This facility is located approximately 1 km from where the lysimeters use to be. The values for the transport model parameters are described in the transport model development section (Chapter 4). However, the parameters, which are functions of the velocity or the volumetric water content, are calculated in the model for each time step and each node for changing values of those parameters. In order to be consistent, the resulting partitioning coefficients from the best fit of the earlier transport analysis with steady-state flow are used also in the fully transient simulations, i.e.: $K_{do}=2.52 \text{ cm}^3/\text{g}$ and $K_{dr}=1800.0 \text{ cm}^3/\text{g}$ which correspond to $R_o=15$ and $R_r=10,000$, respectively, for a volumetric water content value of 0.25.

Pu(VI)O₂(NO₃)₂ Simulation Results

A total amount of 29.6 μCi activity is released into the domain at a constant rate of $1.4115 \times 10^{-3} \mu\text{Ci}/\text{cm}^3/\text{h}$ over the 890 d field period. A water balance on the rainfall and leachate volume data is used to adjust the monthly potential transpiration rates calculated by the Thornthwaite equation and given in Table 6.2. The total rainfall depth for the experimental period for this particular lysimeter is 314.55 cm from the data collected at Area-200F and it is also known that the total volume of the leachate from the lysimeter for the same time period is 73.2 L, which corresponds to 85.58 cm. As a result of the water balance, approximately 228.97 cm is expected to be transpired by the root-plant leaves during the experiment, (neglecting soil evaporation and possible surface runoff). Simulations done with the calculated monthly transpiration rates, with a correction factor of $\beta_{\text{transpiration}}=1$ and the relative root density as calculated for Core D in Figure 6.2 and given in Table 6.1, yield about 118.24 cm transpiration for the same period of time. When $\beta_{\text{transpiration}}$ is equal to 3.7, the total amount of transpiration becomes 228.19 cm, which is assumed to be close enough to estimated value from the water balance. Thus, for further simulations with varying oxidation and reduction rate constants, a correction factor of 3.7 is used for this lysimeter with the relative root density function as calculated for Core-D.

Figure 7.1 shows the results of the transport model simulations with variably saturated flow for varying rate constants. Simulation 1 is the best fit from the steady-state flow analysis shown in Figure 5.1c, which has an oxidation rate constant of $1.0 \times 10^{-8} \text{ 1/h}$ and a reduction rate constant of $3.3 \times 10^{-4} \text{ 1/h}$. As seen in the figure, with the same oxidation and reduction rate constants the model with variably saturated flow yields a

slight increase in mobility, but otherwise there is little change. The reason for this observation may be that when the high rainfall rates create higher flux values than the steady state value, the oxidized Pu moves farther down in the domain for a given time step, and due to the reduction, it stays there until another higher flux value carries it farther down.

Figure 7.1 Results of the fully transient analysis for the $\text{Pu(VI)O}_2(\text{NO}_3)_4$ lysimeter with $K_{\text{do}}=2.52 \text{ cm}^3/\text{g}$ and $K_{\text{dr}}=1800 \text{ cm}^3/\text{g}$.

The best fit to the measured data is obtained with the transport model with variably saturated flow when the oxidation rate constant is about $1.0 \times 10^{-8} \text{ 1/h}$ and the reduction rate constant is about $5.0 \times 10^{-4} \text{ 1/h}$, which is slightly higher than the best fit value of the steady-state flow case. The fully transient model also shows little sensitivity to different oxidation rate constants for this data set as observed previously in the steady-

state flow analysis (simulations 4 and 5). The reason for this was earlier attributed to the short experiment duration for this particular lysimeter and very slow oxidation. Hence, the same discussion is also valid for fully transient model results.

A sensitivity analysis is also conducted for different measured root distribution functions shown in Figure 6.2. The results presented in Figure 7.2 show that the other two measured root distributions from Core-C and Core-E have very little effect on the distribution characteristics of Pu for this lysimeter.

Figure 7.2 Results of the fully transient analysis for the $\text{Pu(VI)O}_2(\text{NO}_3)_4$ lysimeter with $K_{\text{do}}=2.52 \text{ cm}^3/\text{g}$ and $K_{\text{dr}}=1800 \text{ cm}^3/\text{g}$ for the three different measured root distribution functions: Core-D, Core-C, and Core-E.

As seen in Figure 7.1, although the variably saturated flow model creates a dynamic flow system, the small predicted upward fluxes due to transpiration are not enough to create significant upward migration. Therefore, the system behaves almost the

same both upward and downward as in the steady-state flow analysis where only a constant downward velocity is applied to the system.

Pu(IV)(NO₃)₄, Pu(IV)(C₂O₄)₂, and Pu(III)Cl₃ Simulation Results

For the simulations of the lysimeters with a reduced Pu source, the amount of activities and the constant release rates are used as given in Table 5.2. The total amount of rainfall for the period of 1437 days (the period for which leachate volume data is available) from the beginning of the field experiment is 506.17cm, for the same period of time, the total leachate is 248.7 cm (212.7 L) for the Pu(IV)(NO₃)₄ lysimeter, 232.67 cm (199.0 L) for the Pu(IV)(C₂O₄)₂ lysimeter, and 172.45 cm (147.50 L) for the Pu(III)Cl₃ lysimeter. Therefore, the total transpiration amounts for each lysimeter for the given period can be estimated approximately as 257.5 cm, 273.5 cm, and 333.7 cm respectively. For the simulations in which $\beta_{\text{transpiration}}$ is equal to 1 and the relative root density function taken as calculated for Core-D, as shown in Figure 6.2 and given in Table 6.1, the model yields a total transpiration amount of 285.88 cm for the same period. A correction factor value of 0.82 yields a total transpiration amount of 256.4 cm, 0.93 yields 275.2, and 1.35 yields 330 cm for the given period. Therefore, these values are used for the Pu(IV)(NO₃)₄, Pu(IV)(C₂O₄)₂, and Pu(III)Cl₃ lysimeters simulations, respectively, along with the relative root density function of Core-D. Figure 7.3, 7.4, and 7.5 show results of the simulations of the transport model with variably saturated flow for different oxidation and reduction rate constants for Pu(IV)(NO₃)₄, Pu(IV)(C₂O₄)₂, and Pu(III)Cl₃ lysimeters, respectively.

In all three of the figures, simulation 1 shows the best fit from the transport with the steady-state flow analyses for the particular lysimeters, and simulation 2 shows the

transport model with variably saturated flow results with the same, best fit oxidation and reduction rate constants. The fully transient analysis yields a slightly increased migration behavior for all the lysimeters resulting from the dynamic nature of the flow. The best fit for each of the lysimeters, simulation 3 for the $\text{Pu(IV)(NO}_3)_4$, simulation 6 for the $\text{Pu(IV)(C}_2\text{O}_4)_2$, and simulation 4 for the Pu(III)Cl_3 lysimeters, from the fully transient analyses has slightly increased reduction rate constants to overcome the enhanced migration. However, overall, the behavior of the plutonium transport is the same in both steady-state flow and variably saturated flow cases. The differences in the rate constants of the best fits are not significant. More importantly, a fully transient analysis does not produce the observed upward migration in any case either.

Oxidation and reduction rate constants have the same effect on the migration behavior of plutonium as the steady-state flow case. Simulations 4 and 3 from Figure 7.3, 6 and 7 from Figure 7.4, and 6 and 5 from Figure 7.5 show the effect of oxidation. As observed in the steady-state flow case, the value of this rate constant (k_o) determines the fraction of plutonium which moves farthest into the domain: thus, oxidation creates the very small, high-mobility fraction of Pu. Again, as seen in steady-state flow case, the reduction rate determines the retardation that the high-mobility fraction undergoes. Both oxidation and reduction reactions are needed to produce the observed transport characteristics.

Figure 7.3 Results of the fully transient analysis for the $\text{Pu(IV)(NO}_3)_4$ lysimeter with $K_{\text{do}}=2.52 \text{ cm}^3/\text{g}$ and $K_{\text{dr}}=1800 \text{ cm}^3/\text{g}$.

Figure 7.4 Results of the fully transient analysis for the $\text{Pu(IV)(C}_2\text{O}_4)_2$ lysimeter with $K_{\text{do}}=2.52 \text{ cm}^3/\text{g}$ and $K_{\text{dr}}=1800 \text{ cm}^3/\text{g}$.

Figure 7.5 Results of the fully transient analysis for the Pu(III)Cl₃ lysimeter with $K_{do}=2.52 \text{ cm}^3/\text{g}$ and $K_{dr}=1800 \text{ cm}^3/\text{g}$.

For the fully transient analysis, the measured root distribution from Core-D is used so far for the simulations. To be able to see the effect of different root distributions, the Pu(III)Cl₃ data set is used to simulate the transport with two other measured functions: Core-C and Core-E. The transpiration correction factor is used as estimated for the Core-D distribution function for this specific lysimeter (yielding 330 cm total transpiration), $\beta_{\text{transpiration}}=1.35$, corresponding total transpiration amounts are 332.2 cm for Core-E and 323.88 cm for Core-C distribution functions (total transpiration was estimated as 333.7 from the water balance). Results are shown in Figure 7.6 and indicate that the root distribution has a very little affect on the overall migration characteristic of Pu.

Figure 7.6 Results of the fully transient analysis for the Pu(III)Cl_3 lysimeter with $K_{d0}=2.52 \text{ cm}^3/\text{g}$ and $K_{dr}=1800 \text{ cm}^3/\text{g}$ with three different measured relative root distribution functions: Core-C, Core-D, and Core-E.

Discussion

One of the main outcomes of this fully transient analysis is that even when the dynamic nature of the flow system is applied to the transport, instead of a steady downward flow, it does not result in the upward migration observed in the experimental data. Overall, the fully transient analysis shows the same behavior for upward and downward migration of plutonium as the transport with steady-state flow, being essentially fully consistent with that result. One main reason for this is that the simulated root system extracts water mainly from the immediate vicinity of the roots. There is little upward flux in the soil due to rapidly decreasing hydraulic conductivity under drying conditions. Furthermore, very slow oxidation and fast reduction causes most of the

released plutonium to stay in the reduced and less mobile form, unaffected from the very low upward fluxes created by the transpiration.

Several hypotheses are developed to further investigate the possible reasons for the lack of upward migration. These are: modified root distribution with higher density at the top, hysteresis, and modified oxidation rate constant as a function of water content. These hypotheses will be discussed in the remainder of this section.

Modified Root Distribution

As discussed above, a root system with a fairly uniform distribution would only extract water from the vicinity of the roots, thus it would only create very small upward fluxes of water in the soil system itself. However, there is a possibility of having a root system which is mainly active near the soil surface. In this case, as the root system pulls water from the soil, it would create a drier area towards the soil surface and, consequently, a higher pressure head gradient upward in the soil system.

To investigate this possibility, the data set with the oxidized Pu ($\text{Pu(VI)O}_2(\text{NO}_3)_4$) and one of the sets with a reduced Pu ($\text{Pu(IV)(C}_2\text{O}_4)_2$) source are used to simulate this situation with a modified root distribution function. For this purpose, the measured distribution function of Core-D is chosen, and it is modified by assuming that 99 % of the total root density is within 5 cm of the surface. Below the surface, the distribution decreases exponentially, and the total amount of root density along the core is equal to the amount measured for Core-D. If $R(z)$ is the root distribution function, it can be written for the modified case as:

$$\begin{aligned}
 z = 0 \quad R(z = 0) &= R_o \\
 z = 5\text{cm} \quad R(z = 5) &= (0.01)R_o \\
 R(z) &= R_o e^{-kz} = \int_0^{51} R(z)_{\text{Core-D}}
 \end{aligned}
 \tag{7.1}$$

From the above relationship k , the distribution constant, can be calculated as 0.921034, and the resulting root distribution function can be written as:

$$R(z) = 0.182157 e^{-0.921034 z} \tag{7.2}$$

From Equation (6.16), the relative root distribution can be calculated as:

$$RRD(z) = 0.921034 e^{-0.921034 z} \tag{7.3}$$

Figure 7.7 Modified relative root distribution function versus measured function for Core-D.

Figure 7.7 shows the resulting relative root distribution as a function of depth in the lysimeter and compares the modified function to the measured function of Core-D. Figure 7.8 and Figure 7.9 show the results of the transport model simulations with the modified root distribution function of Core-D in comparison to the best fit results of the transport model simulations with the measured root distribution function of the same core for the data sets with the oxidized, $\text{Pu(VI)O}_2(\text{NO}_3)_2$, and the reduced, $\text{Pu(IV)(C}_2\text{O}_4)_2$ Pu sources respectively. The best fit for the $\text{Pu(VI)O}_2(\text{NO}_3)_2$ lysimeter is simulation 4, taken from Figure 7.1, with the oxidation rate constant of 1.0×10^{-8} 1/h and the reduction rate constant of 5.0×10^{-4} 1/h; for the $\text{Pu(IV)(C}_2\text{O}_4)_2$ lysimeter, it is simulation 6, taken from Figure 7.4, with the oxidation rate constant of 3.0×10^{-7} 1/h and the reduction rate constant of 1.2×10^{-3} 1/h. $\beta_{\text{transpiration}}$, chosen for the both lysimeters, is adjusted so that the simulations with the resulting modified root water uptake functions would yield the same amount of total transpiration estimated from the water balance for each lysimeter. These values were found as 228.97 cm for the $\text{Pu(VI)O}_2(\text{NO}_3)_2$ lysimeter and 273.5 cm for the $\text{Pu(IV)(C}_2\text{O}_4)_2$ lysimeter.

As seen in the figures below, a root distribution with 99% of the total density located within the top 5 cm creates a slightly upward movement for the lysimeter with a Pu_{ox} source. However, for the lysimeter with the Pu_{red} source, the change in the root distribution has almost no effect on the transport behavior. Therefore, the observed upward migration in the data sets can not be explained by different root distributions.

Figure 7.8 Comparison of the transport model result with modified, measured root distribution function of Core-D to the best fit of transport model results with the measured root distribution function of the same core for $\text{Pu(VI)O}_2(\text{NO}_3)_2$ lysimeter data set.

Figure 7.9 Comparison of the transport model result with modified, measured root distribution function of Core-D to the best fit of transport model results with the measured root distribution function of the same core for $\text{Pu(IV)(C}_2\text{O}_4)_2$ lysimeter data set.

Hysteresis

Hysteresis refers to the non-unique relationship between the pressure head and the water content in the soil (Simunek et al., 1999); it exhibits a significant variation in the values for water content for a given pressure head depending upon the wetting history of the soil (Figure 7.10). When the soil is drained from complete saturation, the water retention curve is called the initial drainage curve. However, when the soil wets from an initially dry condition, it behaves according to another moisture retention curve called main wetting curve (Stephens, 1996), as illustrated in Figure 7.10. The figure also shows the moisture retention curve for partially wetted and drained soil (scanning curves). The difference between the main draining and wetting curves depends upon the capillary characteristics of the soil matrix. During drainage, large pores overlaying smaller pores would not drain until pressure head drops sufficient enough to overcome the capillary force created by very small diameters. Therefore, if a soil reaches to a certain pressure head value by draining, it would retain more water in the large pores than if it reaches the same pressure head value by wetting (Stephens, 1996). Thus, for a given pressure head value, a drying process would have higher hydraulic conductivities than a wetting process. This might enhance the upward mobility of Pu released into the system.

For evaluating its effect on the Pu migration, hysteresis is implemented approximately into the variably saturated flow model. It usually is neglected in flow studies due to lack of necessary data and the relatively time consuming and costly methods for measuring the hysteretic soil hydraulic properties (Simunek et al., 1999). However, Simunek and Van Genuchten (2005), adopted a procedure to include hysteresis in the model that they developed (HYDRUS 1D) for simulating water, heat, and multiple solutes in variably-saturated porous media, and this procedure is also used in our

transport modeling. By the adopted procedure, two curves are described as main wetting and drying curves. The only independent parameters in the retention function are assumed to be water content and α (Van Genuchten curve shape parameter). When actual data are lacking, they assumed α_{wetting} is equal to $2\alpha_{\text{drying}}$, and the resulting water retention curves used in the variably saturated flow model are shown in Figure 7.11.

Figure 7.10 Schematic hysteric soil water retention function showing main, primary, and secondary wetting and drying curves (Stephens, 1996).

Figure 7.11 Schematic hysteric soil water retention function used in the model (Simunek and Van Genuchten, 2005).

Figure 7.12 and 7.13 present the resulting hysteric water content and unsaturated hydraulic conductivity functions respectively for $\alpha_{\text{wetting}} = \alpha = 0.027816 \text{ 1/cm}$ (original estimated value from Rosetta) for the main wetting curve and $\alpha_{\text{drying}} = \alpha/2 = 0.013908 \text{ 1/cm}$ for the main drying curve.

Numerical implementation of hysteresis into the variably saturated flow model requires estimating the wetting or drying history of the given node. Consequently, a control loop is added to the variably saturated flow model to keep track of wetting history of the given node and, depending on this, choosing the proper α value. When $\psi(i, j-1) - \psi^{m-1}(i, j) \leq 0$, the model assumes that the soil section corresponding to the node is wetting and when $\psi(i, j-1) - \psi^{m-1}(i, j) > 0$, it assumes the soil section is drying.

The results of the transport model simulations with variably saturated flow including hysteresis are shown in Figures 7.14 and 7.15 for the lysimeters with the oxidized ($\text{Pu(VI)O}_2(\text{NO}_3)_2$) and the reduced ($\text{Pu(IV)(C}_2\text{O}_4)_2$) sources respectively. As expected, for the both lysimeters, hysteresis enhanced the mobility as seen in the below filter portions of the lysimeters. However, even though hysteresis increases the upward mobility very slightly in the oxidized Pu source case, it has no effect on the upward migration for the lysimeter with the reduced Pu source. Thus, it is unlikely that neglected hysteresis can be the reason for the observed upward migration of Pu in the data sets.

Figure 7.12 Van Genuchten water content function including hysteresis.

Figure 7.13 Van Genuchten unsaturated hydraulic conductivity function including hysteresis.

Figure 7.14 Comparison of the transport model simulation with hysteresis with the best fit fully transient $\text{Pu(VI)O}_2(\text{NO}_3)_2$ lysimeter simulation with no hysteresis.

Figure 7.15 Comparison of the transport model simulation with hysteresis with the best fit fully transient $\text{Pu(IV)(C}_2\text{O}_4)_2$ lysimeter simulation with no hysteresis.

Modified Oxidation Rate Constant

Oxidation is the process by which the released Pu converts into a more mobile form. So, any increase in oxidation rate would create more production of the more mobile Pu form in the lysimeter system. Originally, in the transport model, the oxidation is defined as a first order reaction with a constant rate of k_o . It is possible that the mineral phase may be a semiconductor, capable of providing a pathway for electron mobility (Powell et al., 2006). Thus, an increase in electron acceptors (e.g. O_2) in a system might create more oxidation and enhance the mobility of Pu.

To test this possibility, a hypothetical reaction equation is developed for the oxidation as a function of water content, which allows more oxidation when the water content goes down (more O_2 available) and vice versa. The new oxidation function is shown in Equation (7.4), where τ is a factor which is used to increase the overall rate constant.

$$k_o = k_o \left[1 + \tau \frac{(\theta(z, t) - \theta_{sat})}{(\theta_r - \theta_{sat})} \right] \quad (7.4)$$

When the water content, $\theta(z, t)$ for a given depth and time becomes equal to the saturated value, the term $\tau \frac{(\theta(z, t) - \theta_{sat})}{(\theta_r - \theta_{sat})}$ goes to zero, and the oxidation rate constant retains its original value. When the water content is equal to the residual value, the oxidation rate constant increases by a factor of $(1+\tau)$.

Figure 7.16 and 7.17 present the results of the transport model simulations with the oxidation rate constant as a function of water content in the system. Simulation 1 in each figure shows the best fit from Figure 7.1 for the $\text{Pu(VI)O}_2(\text{NO}_3)_2$ source and Figure 7.4 for the $\text{Pu(IV)(C}_2\text{O}_4)_2$ source. Simulation 2 shows the same simulation as simulation 1 with the modified oxidation rate constant when $\tau=9$ and simulation 3 is when $\tau=99$, for the given water content value equal to the residual, these constants would yield $10\times k_o$ and $100\times k_o$ respectively. Results, shown below, indicate that the changing oxidation rate constant as a function of available oxygen makes no difference in the transport behavior of Pu regardless of the oxidation state of the source term. Thus, a fully transient flow and transport model, with three possible modifications, does not seem capable of simulating the upward Pu transport observed in the experiments.

Figure 7.16 Comparison of the transport model simulation with the modified oxidation rate constant with the best fit fully transient $\text{Pu(VI)O}_2(\text{NO}_3)_2$ lysimeter simulation.

Figure 7.17 Comparison of the transport model simulation with the modified oxidation rate constant with the best fit fully transient $\text{Pu(IV)(C}_2\text{O}_4)_2$ lysimeter simulation.

CHAPTER 8

DEVELOPMENT OF A PLUTONIUM ROOT UPTAKE/TRANSPORT MODEL

As presented in the previous chapter, the transport model including equilibrium, reversible partitioning between aqueous and solid phases, surface mediated kinetic oxidation and reduction, one dimensional advection, and hydrodynamic dispersion in a variably saturated flow system with root water uptake can not explain the observed upward migration characteristics of Pu in the data from the lysimeter experiments. In this chapter, the development of a Pu root uptake and transport model is presented to further investigate this observed upward migration. This model describing vertical, 1-D Pu transport in plant roots is coupled to the existing model describing Pu transport in the soil.

Pu plant uptake has been studied in the literature by a number of researchers (Sokolik et al., 2004; Lee et al., 2002b; Pinder et al., 1990; Adriano et al., 1986) and it is usually quantified by a concentration ratio, “CR,” determined by the ratio of activity concentration in the plant to activity concentration in the soil. This ratio shows a wide range of values between 10^{-10} and 10^{-2} in the literature (Sokolik et al., 2004; Lee et al., 2002b; Pinder et al., 1990; Adriano et al., 1986).

Based on these findings, the Pu root uptake model is developed conceptually assuming that a very small fraction “E” of the calculated aqueous activity concentrations in the soil from the transport model can be carried into the root system by water extracted due to transpiration (Figure 8.1). The amount of activity being transferred into

the root system is then a function of the amount of water being transferred into the system, which is determined by the root water uptake term, S , as the volume of water extracted by the roots per unit volume of soil per time. Thus, the root Pu uptake term is incorporated into the general reactive Pu transport model using the sink term as shown in Equations (8.1) and (8.2) for P_{ur} and P_{uo} , respectively.

$$E_{P_{ur}} \times C_{P_{ur}}(z, t) \times S(z, \psi) \quad (8.1)$$

$$E_{P_{uo}} \times C_{P_{uo}}(z, t) \times S(z, \psi) \quad (8.2)$$

E is the uptake efficiency for the Pu, and depending on the oxidation state of the Pu source in the lysimeter, it can either represent the uptake efficiency for P_{ur} ($E_{P_{ur}}$) or for P_{uo} ($E_{P_{uo}}$). Its value ranges between 0 and 1, where zero indicates no Pu uptake by the root system and one indicates 100% activity uptake by the root system. It is used as a fitting parameter in the model. Terms $C_{P_{ur}}(z, t)$ and $C_{P_{uo}}(z, t)$ represent the activity concentrations in the aqueous phase within the lysimeter soil calculated by the reactive Pu transport model for the soil system.

Figure 8.1 shows a schematic representation of the conceptual Pu root uptake model. Even though the roots are distributed in different directions randomly and irregularly in the soil, in a one dimensional system they can be thought of schematically as a collection of root xylems. Consequently, one can imagine the sum of the cross-sectional area of all the roots in a given depth as one total area of the root xylems for the same depth in the lysimeter, shown as $A_r(z)$ in the figure. Thus, $A_r(z)$ represents the

relative root area over the total soil area (cm^2/cm^2) for a given depth, and it can be assumed as proportional to the $RRD(z)$, which represents the spatial distribution of the normalized root density. As a result, $A_r(z)$ represents the spatial distribution of the root area per unit total soil area for a given location, as given in Equation (8.3).

$$A_r(z) = \beta \times RRD(z) \quad (8.3)$$

Figure 8.1 Schematic representation of the conceptual model for the Pu root uptake/transport.

For developing the Pu root uptake and transport model, a control volume approach is used, as shown in Figure 8.1. A mass balance is applied to the control volume as:

$$\left[\begin{array}{c} \text{Activity Inflow} \\ \text{Rate} \end{array} \right] - \left[\begin{array}{c} \text{Activity Outflow} \\ \text{Rate} \end{array} \right] + \left[\begin{array}{c} \text{Activity Intake} \\ \text{Rate} \end{array} \right] = \left[\begin{array}{c} \text{Activity Storage} \\ \text{Change Rate} \end{array} \right]$$

$$\begin{aligned} & A_r \left[v_r C_r - D_r \frac{\partial C_r}{\partial z} \right] \eta_r \Big|_z - A_r \left[v_r C_r - D_r \frac{\partial C_r}{\partial z} \right] \eta_r \Big|_{z+\Delta z} + q_c(z) RSA(z) (1. \Delta z) \\ &= \frac{\partial [A_r(z) \Delta z (\eta_r \overline{C_r} + \rho_r \overline{S_r})]}{\partial t} \end{aligned} \quad (8.4)$$

where C_r ($\mu\text{Ci}/\text{cm}^3$) is the aqueous and S_r ($\mu\text{Ci}/\text{g}$) is the adsorbed activity concentrations in the root system, which can either be for P_{uo} or P_{ur} . The surface area of the root system, $RSA(z)$, represents the root surface area per unit volume of soil at a given location in the lysimeter through which the roots take up water and activity from the soil. η_r and ρ_r are the root porosity and the density, respectively; q_c is the activity flux into the roots in units of $\mu\text{Ci}/\text{cm}^2/\text{h}$ $\left(q_c = \frac{E \times C(z, t) \times S(z, \psi)}{RSA(z)} \right)$; and v_r and D_r are the water flux (velocity) and the diffusion coefficient in the root system in units of cm/h and cm^2/h , respectively. The velocity at each elevation is calculated as the cumulative root water uptake divided by the xylem cross-sectional area, i.e:

$$\begin{aligned} Q_r(z) &= \int_0^z S(z, \psi) dz \\ v_r &= \frac{Q_r(z)}{A_r(z)} \end{aligned} \quad (8.5)$$

The resulting governing equations for the Pu root uptake and transport are given as Equations (8.6) and (8.7) for Pur and Puo, respectively:

$$R_{r_Pur} \frac{\partial C_{r_Pur}}{\partial t} = D_r \frac{\partial^2 C_{r_Pur}}{\partial z^2} - \frac{\partial}{\partial z} (v_r C_{r_Pur}) - \frac{\partial(\ln A_r)}{\partial z} \left(v_r C_{r_Pur} - D_r \frac{\partial C_{r_Pur}}{\partial z} \right) + \frac{E_{Pur} C_{Pur} S}{\eta_r A_r} \quad (8.6)$$

and

$$R_{r_Puo} \frac{\partial C_{r_Puo}}{\partial t} = D_r \frac{\partial^2 C_{r_Puo}}{\partial z^2} - \frac{\partial}{\partial z} (v_r C_{r_Puo}) - \frac{\partial(\ln A_r)}{\partial z} \left(v_r C_{r_Puo} - D_r \frac{\partial C_{r_Puo}}{\partial z} \right) + \frac{E_{Puo} C_{Puo} S}{\eta_r A_r} \quad (8.7)$$

where R_{r_Pur} and R_{r_Puo} are the retardation factors in the root system for Pur and Puo, respectively.

Numerical Pu Root Uptake Modeling

The governing equations (Equation (8.6) and (8.7) above) are used to develop the numerical Pu root uptake and translocation model. Fully implicit, finite-difference approximations of these governing equations, shown as Equations (8.8) and (8.9), are solved for the activity concentration values by using a tridiagonal algorithm for the one-dimensional, finite-difference grid system shown in Figure 8.2. In these equations, i represents the spatial node and j denotes the j^{th} discrete time level for which the concentration values are solved. The one-dimensional root Pu uptake model domain is 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.

$$\begin{aligned}
 R_{r_Pur} \frac{[C_{r_Pur}(i, j) - C_{r_Pur}(i, j-1)]}{\Delta t} = & \\
 D_r \frac{[C_{r_Pur}(i+1, j) - 2C_{r_Pur}(i, j) + C_{r_Pur}(i-1, j)]}{(\Delta z)^2} & \\
 - \left\{ \left(\frac{v_r(i+1, j) - v_r(i-1, j)}{2\Delta z} \right) C_{r_Pur}(i, j) + v_r(i, j) \left(\frac{C_{r_Pur}(i+1, j) - C_{r_Pur}(i-1, j)}{2\Delta z} \right) \right\} & \quad (8.8) \\
 - \frac{1}{A_r(i)} \left(\frac{A_r(i+1) - A_r(i-1)}{2\Delta z} \right) \left(v_r(i, j) C_{r_Pur}(i, j) - D_r \frac{[C_{r_Pur}(i+1, j) - C_{r_Pur}(i-1, j)]}{2\Delta z} \right) & \\
 + \frac{E_{Pur} C_{Pur}(i, j) S(i, j)}{\eta_r A_r(i)} &
 \end{aligned}$$

$$\begin{aligned}
 R_{r_Puo} \frac{[C_{r_Puo}(i, j) - C_{r_Puo}(i, j-1)]}{\Delta t} = & \\
 D_r \frac{[C_{r_Puo}(i+1, j) - 2C_{r_Puo}(i, j) + C_{r_Puo}(i-1, j)]}{(\Delta z)^2} & \\
 - \left\{ \left(\frac{v_r(i+1, j) - v_r(i-1, j)}{2\Delta z} \right) C_{r_Puo}(i, j) + v_r(i, j) \left(\frac{C_{r_Puo}(i+1, j) - C_{r_Puo}(i-1, j)}{2\Delta z} \right) \right\} & \quad (8.9) \\
 - \frac{1}{A_r(i)} \left(\frac{A_r(i+1) - A_r(i-1)}{2\Delta z} \right) \left(v_r(i, j) C_{r_Puo}(i, j) - D_r \frac{[C_{r_Puo}(i+1, j) - C_{r_Puo}(i-1, j)]}{2\Delta z} \right) & \\
 + \frac{E_{Pur} C_{Puo}(i, j) S(i, j)}{\eta_r A_r(i)} &
 \end{aligned}$$

Figure 8.2 Schematic representation of the one-dimensional, finite-difference grid system for the numerical Pu root uptake model.

The boundary conditions for the top and bottom boundaries are set as Neumann conditions with zero flux (no flow) as shown in Equation (8.10) and (8.11). Thus, all the Pu taken up by the root system is retained in the plant and the roots during the simulations.

$$\left. \frac{\partial C_{r_Pu}}{\partial z} \right|_{i=N_p} = 0 \quad (8.10)$$

$$\left. \frac{\partial C_{r_Pu}}{\partial z} \right|_{i=1} = 0 \quad (8.11)$$

CHAPTER 9

RESULTS OF THE REACTIVE TRANSPORT MODEL WITH VARIABLY SATURATED FLOW AND PLUTONIUM ROOT UPTAKE

The Pu root uptake/transport model is coupled to the Pu reactive transport model with variably saturated flow through the calculated aqueous activity concentrations in the lysimeter domain. In this chapter, the results of the best fit simulations of the transport model with variably saturated flow for each lysimeter are compared to the results of the simulations when the root Pu uptake is included. All the simulations presented herein use the relative root density distribution of Core-D and the best fit oxidation and reduction rate constant values resulting from the reactive transport model simulations with variably saturated flow. Partitioning coefficients for the soil are the same as the best fit coefficients as well: $K_{do}=2.52 \text{ cm}^3/\text{g}$ and $K_{dr}=1800.0 \text{ cm}^3/\text{g}$ (corresponding to $R_o=15$ and $R_r=10,000$, respectively, for a volumetric water content value of 0.25). (For the root Pu uptake/transport model parameter values see Appendix H).

Pu(VI)O₂(NO₃)₂ Simulation Results

The previous best fit result of the reactive transport modeling of the Pu(VI)O₂(NO₃)₂ lysimeter was presented in Figure 7.1 as simulation 4 for the variably saturated flow case with an oxidation rate constant of $1 \times 10^{-8} \text{ 1/h}$ and a reduction rate constant of $5 \times 10^{-4} \text{ 1/h}$, and it is shown as simulation 1 here in Figure 9.1. When the same simulation is repeated with a Pu root uptake efficiency of 100% for both Pu_o and Pu_r

($E_{Pu0}=1$ and $E_{Pur}=1$), the resulting Pu distribution is shown as simulation 2 in Figure 9.1 below. As seen in the figure, the root Pu uptake mechanism is able to transfer Pu upward in the lysimeter from the source. As the uptake efficiency decreases, the amount of Pu moving upward also decreases as seen in simulations 3 and 4. As stated earlier, the amount of Pu extracted by a root/plant system is quantified by the concentration ratio (CR) values and, in the literature, the range given for those are between 10^{-2} and 10^{-10} . To determine an approximate CR value from the lysimeter simulations with root Pu uptake, the concentration values at the location of source are taken from the simulation 4 (Figure 9.1). The ratio of the sorbed concentration at the source location of total Pu in the lysimeter to that in the root system yields a CR value of 0.022. This value is at the higher end of the reported range for CR in the literature, but it should also be noted that this is for the lysimeter with an oxidized, relatively less adsorbed form of Pu at the source.

Figure 9.1 Comparison of the best fit simulation result of the reactive transport model with variably saturated flow to the same simulation with Pu root uptake included for the $Pu(VI)O_2(NO_3)_2$ lysimeter.

Pu(IV)(NO₃)₄, Pu(IV)(C₂O₄)₂, and Pu(III)Cl₃ Simulation Results

The best fit simulation results of the reactive transport model with variably saturated flow for each lysimeter were shown as simulation 3 in Figure 7.3, simulation 6 in Figure 7.4, and simulation 4 in Figure 7.5 for the Pu(IV)(NO₃)₄, Pu(IV)(C₂O₄)₂, and Pu(III)Cl₃ lysimeters, respectively. In this section, the previous simulations are compared to the simulations with Pu root uptake in Figure 9.2 for the Pu(IV)(NO₃)₄ lysimeter, Figure 9.3 for the Pu(IV)(C₂O₄)₂ lysimeter, and Figure 9.4 for the Pu(III)Cl₃ lysimeter.

Figure 9.2 Comparison of the best fit simulation result of the reactive transport model with variably saturated flow to the same simulation with Pu root uptake included for the Pu(IV)(NO₃)₄ lysimeter.

Figure 9.3 Comparison of the best fit simulation result of the reactive transport model with variably saturated flow to the same simulation with Pu root uptake included for the $\text{Pu(IV)(C}_2\text{O}_4)_2$ lysimeter.

Figure 9.4 Comparison of the best fit simulation result of the reactive transport model with variably saturated flow to the same simulation with Pu root uptake included for the Pu(III)Cl_3 lysimeter

Simulation 1 in each figure shows the results from the earlier, fully transient analysis with the best fit oxidation and reduction rate constant values, and simulation 2 shows the results of the same exact simulation when the Pu root uptake is included in the model with 100% uptake efficiency ($E_{PuO}=1$ and $E_{PuR}=1$). As the uptake efficiency decreases, the amount of Pu transferred into the root system also decreases for each lysimeter. As conducted for the Pu(VI) data set simulations, an approximate CR value for each lysimeter at the source location are calculated from the sorbed concentrations of the lysimeter soil and the root system at this location. Resulted CR values are 1.2×10^{-4} for the Pu(IV)(NO₃)₄ lysimeter, 1.4×10^{-3} for the Pu(IV)(C₂O₄)₂, and 1.3×10^{-4} for the Pu(III)Cl₃ lysimeter.

Although the upward distributions from the simulations with Pu root uptake and transport do not fit the measured data in detail, overall, the results indicate that the observed upward migration implied by the data might be due to a root Pu uptake mechanism, instead of transport within the lysimeter soil system.

CHAPTER 10

DISCUSSION AND CONCLUSIONS

The theory of surface-mediated redox reactions of Pu in the subsurface and Pu migration characteristics in the vadose zone are herein tested and evaluated by developing a reactive transport model based on the results of lysimeter experiments done in the SRS vadose zone. The model includes equilibrium, reversible partitioning between aqueous and solid phases; kinetic oxidation/reduction reactions in the sorbed phase; and one-dimensional advection and hydrodynamic dispersion. Two different hydraulic systems applied to the model were steady-state and variably saturated flow fields with root water uptake. Further investigation of the Pu migration pattern both upward and downward was done by using the model as a research tool with the addition of other possible phenomena such as: water content dependent oxidation, different root distribution functions, hysteresis, and the development of a Pu root uptake model.

Based on the results of reactive transport model simulations with both the transient and steady-state flow fields applied, we conclude that the surface-mediated, oxidation-reduction hypothesis is *consistent* with the observed upward and downward Pu activity profiles in the lysimeter experiments, provided that Pu uptake and transport in the plant roots is included. The implication of these possible redox reactions is that Pu(V/VI) sources release activity that moves downward (net flow direction) more slowly than expected based on adsorptive retardation alone, and Pu(III/IV) sources result in a small fraction of activity that moves downward more rapidly than expected. These two phenomena in combination with varying adsorptive effects produced simulated activity

profiles that agreed rather well with the anomalous activity profiles observed in the experiments. In principle, other mechanisms that can be represented with first-order rate equations could produce equally good fits, so this study does not prove the surface-mediated, oxidation-reduction hypothesis conclusively. However, direct laboratory experiments conducted with these lysimeter sediments strangely support the oxidation/reduction hypothesis (Kaplan et al., 2004). It would appear that alternative processes would have to take place on the matrix surfaces, simply because the Pu ions are so strongly sorbed. At any given time, only a small percentage of activity is found in the aqueous phase. One alternative explanation for unexpected Pu migration is colloidal transport. However, this mechanism would only enhance the migration, not retard it as observed below the Pu(V/VI) source. Also, it would not cause the observed upward migration of Pu.

The calibrated parameter values were robust and relatively well-defined throughout all sets of simulations for all the lysimeters regardless of the flow field and additional mechanisms tested. The Pu(V/VI) retardation factors were about 15, and the Pu(III/IV) retardation factors were about 10,000, as defined by the data. For these values of retardation factors, the approximate best fit oxidation and reduction rate constants for each of the lysimeters are given in Table 10.1. For both flow systems, the oxidation rate constant values for the best fits remained the same throughout all simulations. However, the reduction rate constant values increased slightly (average of 79%) for the simulations with variably saturated flow. Addition of hysteresis, modified root distribution functions, air content dependent oxidation rate constants, and the Pu root uptake/translocation

model resulted in no significant difference in the downward migration characteristics of Pu, and the best fit oxidation and reduction rate constant were unchanged.

Table 10.1. Best fit oxidation and reduction rate constants from the reactive transport model simulations with both steady-state and variably saturated flow when $R_o=15$ and $R_r=10,000$.

Plutonium Source	Steady-State Flow		Variably Saturated Flow	
	Rate Constants (1/h)		Rate Constants (1/h)	
	Oxidation	Reduction	Oxidation	Reduction
	k_o	k_r	k_o	k_r
Pu(VI)O ₂ (NO ₃) ₂	1.0×10^{-8}	3.3×10^{-4}	1.0×10^{-8}	5.0×10^{-4}
Pu(IV)(NO ₃) ₄	5.0×10^{-8}	1.0×10^{-3}	5.0×10^{-8}	2.0×10^{-3}
Pu(IV)(C ₂ O ₄) ₂	3.0×10^{-7}	7.0×10^{-4}	3.0×10^{-7}	1.2×10^{-3}
Pu(III)Cl ₃	6.0×10^{-7}	8.0×10^{-4}	6.0×10^{-7}	2.0×10^{-3}

As expected, due to the enhanced conditions in a laboratory setting, the rate constant values in Table 10.1 are about two orders of magnitude lower than the laboratory measured values by Kaplan et al. (2004). However, our model's prediction of 4 to 5 orders of magnitude faster reduction rates compared to the oxidation rates is consistent with the Kaplan et al. (2004) data. The faster rates measured in the laboratory are likely attributed to the fact that in the laboratory batch tests, there is appreciably greater mixing between the aqueous and solid phases, purposely trying to remove any diffusional limitations. The laboratory study also probes a larger effective surface area by breaking up aggregates in the batch test. By far, the most important variable affecting transport, as one would expect, is the oxidation state [Pu(III/IV) or Pu(V/VI)] of the source material.

Returning again to the question of why a steady-state, net downward flow model might be expected to reproduce the activity profiles in experiments exposed to highly transient boundary conditions (natural climate), we note that most of the material transported is dominated by the strong adsorption of Pu(III/IV), which has a retardation factor on the order of 10^4 . This means that a given ion spends roughly 99.99% of its time in the adsorbed state. For a Pu(V/VI) ion with a retardation factor of 15, about 93% of its time is spent on surfaces. However, with a first order reduction rate constant of $7.1 \times 10^{-4} \text{ hr}^{-1}$, Pu(V/VI) changes essentially irreversibly to Pu(III/IV) with a reaction half life of 60 days. So collectively, one can visualize the ions as spending most of their time on the surfaces, hopping off briefly to sample the velocity of the liquid phase and undergo advection and dispersion, and returning to the surfaces. This process would happen repeatedly, but with very brief stays in the liquid phase. Under such conditions, one would expect the advective transport to reflect the long-term average movement of the pore fluid, which is in the net downward direction. As mentioned previously, however, this conceptualization does not explain significant Pu migration above the source as observed in the experiments.

One can speculate that a reason for the upward migration is that the surface mediated oxidation reactions are a function of available oxygen in the pores and enhanced towards the drier surface, which would cause formation of more mobile Pu forms above the source. Thus, to further test this hypothesis, the fully transient simulations (reactive transport model simulations with variably saturated flow and root water uptake) were repeated with an oxidation rate equation as a function of volumetric water content in the domain. The results showed no change in Pu distributions therefore,

the reason for upward migration can not possibly be explained by a variable oxidation rate constant only.

Another possible process which can enhance the upward migration is hysteresis in the water retention curve and hydraulic conductivity function. Depending on the wetting history of the soil, this phenomenon would cause an increase in hydraulic conductivities in a drying process compared to a wetting process. The results of the addition of hysteresis into the variably saturated flow model showed a slight increase in the upward movement of Pu over the entire domain for an oxidized Pu source, and essentially no increase for the reduced sources.

A modified root distribution with 90% of the total density located within 5 cm from the surface was also tested to evaluate its effect on the upward migration. For the oxidized Pu source, it caused a slight increase in the upward migration above the source along with a slightly enhanced downward movement of Pu below the source compared to the results of simulations with a more uniform root distribution. The same modified root distribution function showed no effect on the Pu distribution when the source was reduced Pu. Apparently in this soil-plant system, the roots are primarily removing water from their immediate vicinity. As the soil dries and a potential distribution is set up that would induce upward flow, the hydraulic conductivity drops so rapidly in the drying soil that very little upward flux occurs.

Very small amounts of Pu uptake by plant roots is reported in the literature. Therefore, this phenomenon was formulated and included in the reactive transport model to test its effect on the upward migration of Pu in a fully transient system. Results presented herein indicate that this formulation creates a realistic mechanism for upward

Pu migration. The simulated distributions above the source were reproduced with a plant root Pu uptake, advection diffusion model with retardation only. Simulated distribution profiles were quite reasonable compared to the data, so, these results suggest that the upward migration of Pu is probably due to Pu uptake and transport in the plant roots rather than transport in the soil itself.

The importance of understanding Pu geochemistry and transport characteristics in the vadose zone is critical in terms of future planning and handling of Pu bearing waste. Reliable reactive transport models developed with a better understanding of Pu geochemistry and migration behavior may be valuable tools in a decision making process. The results obtained from this research are useful in terms of determining possible geochemical, hydrological, and transport mechanisms that are important in predicting Pu behavior in the vadose zone, such as surface-mediated redox reactions. However, the observations presented above with the modified root distribution, the modified oxidation rate constant, hysteresis, and most significantly Pu root uptake should be verified further with experimental data. Nevertheless, the present results should be considered when determining the direction of future research on Pu behavior in the vadose zone.

APPENDICES

Appendix A

Data from Lysimeter ExperimentsTable A.1 PuO₂(NO₃)₂ Lysimeter data

Lysimeter	M8
Waste Loaded	PuO ₂ (NO ₃) ₂
Date Installed	11/25/1980
Date Covered	5/4/1983
Storage Duration	0 years
Initial Activity on the Filter	477 µCi
Activity Recovered on the Filter	234 µCi
Activity Recovered in the Core	29.6 µCi

Table A.2 PuO₂(NO₃)₂ Lysimeter measured data

		Sample					Activity Measurements	
		Top	Bottom	Middle	Length	Weight	Pu-239/240	Pu-239/240
		(cm)	(cm)	(cm)	(cm)	(g)	(µCi/g)	(µCi)
TOP		40.60	38.60	39.60	2.00	227.16	7.640E-05	1.736E-02
		38.60	35.40	37.00	3.20	363.46	3.050E-04	1.109E-01
		35.40	33.60	34.50	1.80	204.45	4.180E-04	8.546E-02
		33.60	30.40	32.00	3.20	363.46	2.250E-03	8.178E-01
Filter Location		30.40	28.40	29.40	2.00	227.16	5.840E-02	1.327E+01
		28.40	25.40	26.90	3.00	340.74	2.610E-02	8.893E+00
		25.40	23.20	24.30	2.20	249.88	1.750E-02	4.373E+00
		23.20	20.40	21.80	2.80	318.03	2.380E-03	7.569E-01
		20.40	18.00	19.20	2.40	272.59	2.340E-03	6.379E-01
		18.00	15.40	16.70	2.60	295.31	8.540E-04	2.522E-01
		15.40	13.00	14.20	2.40	272.59	5.390E-04	1.469E-01
		13.00	10.20	11.60	2.80	318.03	3.140E-04	9.986E-02
		10.20	8.00	9.10	2.20	249.88	3.010E-04	7.521E-02
		8.00	5.00	6.50	3.00	340.74	7.640E-05	2.603E-02
		5.00	3.00	4.00	2.00	227.16	2.700E-05	6.133E-03
		3.00	0.00	1.50	3.00	340.74	1.350E-05	4.600E-03
BOTTOM								

Table A.3 Pu(NO₃)₄ Lysimeter data

Lysimeter	M9
Waste Loaded	Pu(NO ₃) ₄
Date Installed	11/25/1980
Date Covered	8/15/1991
Storage Duration	10 years
Initial Activity on the Filter	527 µCi
Activity Recovered on the Filter	24.2 µCi
Activity Recovered in the Core	153 µCi

Table A.4 Pu(NO₃)₄ Lysimeter measured data

	Sample					Activity Measurements	
	Top	Bottom	Middle	Length	Weight	Pu-239/240	Pu-239/240
	(cm)	(cm)	(cm)	(cm)	(g)	(μCi/g)	(μCi)
TOP	41.74	37.10	39.42	4.64	317.40	3.779E-04	1.200E-01
	37.10	33.46	35.28	3.64	249.27	1.356E-06	3.380E-04
	33.46	30.81	32.13	2.65	181.27	1.860E-05	3.372E-03
	30.81	28.16	29.48	2.65	181.27	3.874E-06	7.022E-04
	28.16	26.17	27.16	1.99	135.92	5.991E-06	8.143E-04
	26.17	24.84	25.51	1.33	90.64	1.968E-05	1.784E-03
	24.84	22.86	23.85	1.99	135.99	9.189E-06	1.250E-03
	22.86	21.53	22.19	1.33	90.64	2.604E-06	2.360E-04
	21.53	18.88	20.21	2.65	181.27	5.586E-02	1.013E+01
	18.88	16.89	17.89	1.99	135.92	4.365E-01	5.933E+01
Filter Location	16.89	16.23	16.56	0.66	45.35	1.698E+00	7.702E+01
	16.23	14.91	15.57	1.33	90.64	6.802E-02	6.165E+00
	14.91	13.25	14.08	1.66	113.28	9.324E-04	1.056E-01
	13.25	11.93	12.59	1.33	90.64	3.824E-04	3.466E-02
	11.93	10.60	11.26	1.33	90.64	9.910E-05	8.982E-03
	10.60	7.95	9.28	2.65	181.27	2.950E-04	5.348E-02
	7.95	5.30	6.63	2.65	181.27	4.865E-05	8.819E-03
	5.30	2.65	3.98	2.65	181.27	7.072E-06	1.282E-03
	2.65	0.00	1.33	2.65	181.27	2.613E-06	4.736E-04
BOTTOM							

Table A.5 Pu(C₂O₄)₂ Lysimeter data

Lysimeter	M7
Waste Loaded	Pu(C ₂ O ₄) ₂
Date Installed	11/25/1980
Date Covered	8/15/1991
Storage Duration	10 years
Initial Activity on the Filter	527 µCi
Activity Recovered on the Filter	24.2 µCi
Activity Recovered in the Core	153 µCi

Table A.6 Pu(C₂O₄)₂ Lysimeter measured data

	Sample					Activity Measurements	
	Top	Bottom	Middle	Length	Weight	Pu-239/240	Pu-239/240
	(cm)	(cm)	(cm)	(cm)	(g)	(µCi/g)	(µCi)
TOP	44.13	42.23	43.18	1.91	130.31	7.883E-06	1.027E-03
	42.23	40.64	41.43	1.59	108.59	9.189E-06	9.979E-04
	40.64	35.24	37.94	5.40	369.22	7.207E-05	2.661E-02
	35.24	32.70	33.97	2.54	173.75	1.757E-05	3.052E-03
	32.70	30.16	31.43	2.54	173.75	4.865E-06	8.453E-04
	30.16	27.62	28.89	2.54	173.75	1.671E-04	2.904E-02
	27.62	25.08	26.35	2.54	173.75	3.541E-05	6.152E-03
	25.08	24.13	24.61	0.95	65.16	4.820E-04	3.140E-02
	24.13	22.86	23.50	1.27	86.87	6.306E-03	5.479E-01
	22.86	21.59	22.23	1.27	86.87	1.829E-03	1.589E-01
	21.59	20.32	20.96	1.27	86.87	1.000E-02	8.687E-01
	20.32	19.05	19.69	1.27	86.87	2.320E-02	2.015E+00
	19.05	17.78	18.42	1.27	86.87	2.081E-01	1.808E+01
	17.78	16.51	17.15	1.27	86.87	7.523E-01	6.535E+01
Filter Location	16.51	15.24	15.88	1.27	86.87	2.450E-02	2.129E+00
	15.24	13.97	14.61	1.27	86.87	3.734E-03	3.244E-01
	13.97	12.70	13.34	1.27	86.87	1.068E-03	9.274E-02
	12.70	11.43	12.07	1.27	86.87	4.257E-04	3.698E-02
	11.43	10.16	10.80	1.27	86.87	2.059E-04	1.788E-02
	10.16	7.62	8.89	2.54	173.75	1.014E-04	1.761E-02
	7.62	5.08	6.35	2.54	173.75	3.928E-05	6.825E-03
BOTTOM	5.08	2.54	3.81	2.54	173.75	4.221E-05	7.334E-03
	2.54	0	1.27	2.54	173.75	1.752E-05	3.045E-03

Table A.7 PuCl₃ Lysimeter data

Lysimeter	M12
Waste Loaded	PuCl ₃
Date Installed	11/25/1980
Date Covered	8/15/1991
Storage Duration	12.4 years
Initial Activity on the Filter	585.6 µCi
Activity Recovered on the Filter	81.1 µCi
Activity Recovered in the Core	165.3 µCi

Table A.8 PuCl₃ Lysimeter measured data

		Sample					Activity Measurements	
		Top	Bottom	Middle	Length	Weight	Pu-239/240	Pu-239/240
		(cm)	(cm)	(cm)	(cm)	(g)	(µCi/g)	(µCi)
TOP		43.18	39.69	41.43	3.49	210.05	3.779E-06	7.938E-04
		39.69	35.56	37.62	4.13	248.24	2.342E-06	5.815E-04
		35.56	33.34	34.45	2.22	133.67	3.275E-05	4.377E-03
		33.34	31.12	32.23	2.22	133.67	1.514E-05	2.023E-03
		31.12	28.89	30.00	2.22	133.67	1.514E-04	2.023E-02
		28.89	26.67	27.78	2.22	133.67	4.775E-04	6.382E-02
		26.67	24.45	25.56	2.22	133.67	3.356E-03	4.486E-01
		24.45	23.18	23.81	1.27	76.38	1.279E-02	9.771E-01
		23.18	21.91	22.54	1.27	76.38	3.297E-02	2.519E+00
		21.91	19.69	20.80	2.22	133.67	6.036E-01	8.068E+01
Filter Location		19.69	18.42	19.05	1.27	76.38	8.559E-01	6.537E+01
		18.42	17.78	18.10	0.63	38.19	3.324E-01	1.270E+01
		17.78	16.19	16.99	1.59	95.48	1.500E-02	1.432E+00
		16.19	14.92	15.56	1.27	76.38	4.685E-03	3.578E-01
		14.92	13.65	14.29	1.27	76.38	1.757E-03	1.342E-01
		13.65	12.38	13.02	1.27	76.38	6.126E-04	4.679E-02
		12.38	11.11	11.75	1.27	76.38	2.194E-04	1.676E-02
		11.11	8.57	9.84	2.54	152.76	8.874E-05	1.356E-02
		8.57	6.03	7.30	2.54	152.76	2.901E-05	4.432E-03
		6.03	3.18	4.60	2.86	171.86	6.982E-04	1.200E-01
BOTTOM		3.18	0.00	1.59	3.18	190.95	1.941E-03	3.707E-01

Appendix B

Leachate Volume (Liter) and Rainfall Data

Table B.1 Monthly precipitation values collected at the Area-200F.

Year	Monthly Precipitation (inch) at Area-200F											
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1980	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.47	1.96
1981	0.93	3.91	3.87	2.71	4.51	5.05	4.39	5.92	0.85	2.88	0.91	8.45
1982	4.73	3.86	1.95	4.90	2.37	4.07	10.5	6.45	5.02	3.61	2.06	4.58
1983	4.00	8.06	5.49	4.71	3.00	2.77	3.71	6.21	3.52	2.21	4.98	3.66
1984	3.53	5.34	6.05	7.11	10.7	1.82	6.46	3.52	1.06	0.40	0.97	1.16
1985	2.98	3.36	1.06	0.83	3.49	4.88	9.82	2.90	0.90	3.77	7.51	2.74
1986	1.18	3.05	2.75	0.96	3.47	2.60	2.61	8.59	0.80	3.05	5.76	4.94
1987	6.79	7.50	4.35	0.75	1.86	5.02	5.68	4.20	2.91	0.32	2.28	1.37
1988	3.74	1.03	2.48	4.88	0.97	6.67	2.24	2.98	4.79	3.50	1.92	1.66
1989	1.24	2.91	4.83	5.89	3.36	5.82	9.51	0.39	4.84	5.51	3.65	3.35
1990	2.91	1.84	1.88	0.94	2.16	3.87	7.65	10.6	0.50	17.8	1.25	2.55
1991	6.73	1.80	7.86	5.43	3.93	3.35	14.4	8.69	NA	NA	NA	NA

Table B.2 Rainfall and leachate volume (liter) data collected between 11/25/1980 and 11/1/1984 for each lysimeter.

DATES	Experiment Area		AREA 200F		Experiment Area-LITER DATA											
	Rainfall (inch)	Total Rainfall	Rainfall (inch)	Total Rainfall	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12
1/20/1981	2.69	2.69	3.00	3.00												
2/17/1981	3.88	6.57	3.50	6.50												
3/17/1981	0.59	7.16	2.14	8.64	5.10		12.50			10.00	9.00	12.00		12.00		
4/14/1981	3.30	10.46	3.57	12.21												
6/3/1981	3.88	14.34	9.10	21.31												
6/29/1981	5.02	19.36	1.96	23.27	2.00	5.00	4.50	6.00	6.80	5.20	8.00	10.00	4.30	5.30	4.50	4.00
8/3/1981	7.17	26.53	7.78	31.05	5.50	7.60	8.00	7.30	7.30	0.50	9.50		7.30	0.50	5.50	5.00
9/2/1981	2.48	29.01	2.67	33.72												
10/2/1981	1.03	30.04	0.85	34.57												
11/1/1981	2.46	32.50	2.88	37.45												
12/1/1981	0.55	33.05	1.79	39.24												
1/6/1982	9.43	42.48	8.73	47.97												
2/3/1982	2.48	44.96	4.63	52.60												
3/3/1982	3.66	48.62	2.80	55.40												
4/1/1982	3.35	51.97	1.95	57.35												
5/4/1982	4.88	56.85	4.90	62.25												
6/3/1982	2.65	59.50	3.32	65.57												
6/30/1982	3.14	62.64	3.12	68.69		4.00	3.60	4.20	5.00	6.00	4.40	2.00		3.00	0.20	
8/3/1982	7.96	70.60	10.53	79.22												
9/1/1982	5.31	75.91	6.45	85.67	8.50	7.50	8.70	12.10		6.00	9.50	3.50	36.00	6.00	7.00	20.70
10/5/1982	5.13	81.04	5.02	90.69	4.10	6.10	7.50	5.70	6.40	3.80	8.60	1.20	7.40	2.20	4.50	4.00
10/28/1982	2.89	83.93	3.61	94.30	3.60	3.40		4.00	4.00	3.50	4.60	3.50	4.10	4.10	1.00	2.50
11/29/1982	2.12	86.05	2.06	96.36	11.00	0.70	2.30	1.50	1.50	1.60	1.80	0.70	3.50	3.50	0.40	0.70
1/7/1983	5.42	91.47	5.57	101.93	8.40	7.00	8.80	7.70	8.00	8.50	8.60	8.00	9.00	8.20	3.50	6.50
2/3/1983	3.73	95.20	4.06	105.99	6.00		6.50	6.00	5.50	6.20	7.40	6.50	6.50	6.50	3.50	6.00
3/3/1983	6.83	102.03	7.01	113.00	8.50	7.80	9.20	9.00	8.10	8.60	10.50	9.50	10.40	9.40	5.00	8.90
4/7/1983	5.64	107.67	6.15	119.15	8.00	7.00	9.00	8.80	8.40	8.00	9.60	9.00	9.00	9.00	6.50	9.50
5/4/1983	4.59	112.26	4.69	123.84	5.50	5.00	7.50	6.50	5.00	7.50	7.00	7.30	7.50	7.30	6.90	5.10
6/8/1983	4.39	116.65	3.89	127.73	2.40	1.50	4.50	3.00	2.50	3.00	3.50		3.50	2.50	3.50	1.00
6/29/1983	1.41	118.06	1.14	128.87	1.00	1.00	2.50	1.00	1.00	1.00	1.50		1.00	0.60	1.50	0.60
10/5/1983	12.15	130.21	13.54	142.41	5.50	0.50	8.00	0.50	7.70	7.10	9.50		10.50	6.50	11.40	4.50
1/17/1984	11.43	141.64	12.10	154.51	12.50	3.00	16.2	3.50	14.30	11.90	25.00		20.00	23.00	20.00	21.00
4/2/1984	14.22	155.86	13.67	168.18	12.00	19.00	24.5	0.50	21.00	17.00	14.50		24.00	12.50	9.00	11.00
8/1/1984	26.08	181.94	26.16	194.34	37.00	31.50	42	56.00	37.50	32.00	42.00		44.50	32.00	32.50	34.50
11/1/1984	7.88	189.82	4.94	199.28	4.40	0.50	8.6	0.50	4.40	3.60	4.50		4.20	4.00	0.50	2.00
	Volume (L)	412.38	Volume (L)	432.93	151.0	118.1	194.4	143.8	154.4	151.0	199.0	73.2	212.7	158.1	126.9	147.5
OUTFLOW VOLUME (L)

Table B.3 Water balance on rainfall and leachate volume (liter) data collected between 11/25/1980 and 5/4/1983 for the $\text{PuO}_2(\text{NO}_3)_2$ lysimeter.

Table B.4 Water balance on rainfall and leachate volume (liter) data collected between 11/25/1980 and 11/1/1984 for the $\text{Pu}(\text{NO}_3)_4$ lysimeter.

Table B.5 Water balance on rainfall and leachate volume (liter) data collected between 11/25/1980 and 11/1/1984 for the $\text{Pu}(\text{C}_2\text{O}_4)_2$ lysimeter.

Table B.6 Water balance on rainfall and leachate volume (liter) data collected between 11/25/1980 and 11/1/1984 for the PuCl_3 lysimeter.

Appendix C

Derivation of the Transport Equations for Pu_o and Pu_r

Mass Balance equations for the control volume with a volume of $A\Delta z$ shown in Figure 4.1 for each Pu class are written for the time period Δt as:

$$[\text{Activity In}] - [\text{Activity Out}] + [\text{Sources}] - [\text{Sinks}] = [\text{Change in Activity Stored}]$$

Transport mechanisms are advection and dispersion, thus fluxes in the system for each Pu class, $J_{\text{Pu}o}$ and $J_{\text{Pu}r}$, are:

$$J_{\text{Pu}o} = -D \frac{\partial C_{\text{Pu}o}}{\partial z} + v C_{\text{Pu}o} \quad (\text{C.1})$$

$$J_{\text{Pu}r} = -D \frac{\partial C_{\text{Pu}r}}{\partial z} + v C_{\text{Pu}r} \quad (\text{C.2})$$

While these transport mechanisms cause Pu to enter or leave the control volume, oxidation and reduction reactions on the solid surfaces are either sources or sinks for each Pu class. For Pu_o, oxidation of reduced Pu is a source and reduction of oxidized Pu is a sink; for Pu_r, oxidation of reduced Pu is a sink and reduction of oxidized Pu is a source. The mass balance equations for each class of Pu are given below, where k_o and k_r are the oxidation and reduction rates in units of [1/time]; $S_{\text{Pu}o}$ and $S_{\text{Pu}r}$ are the sorbed concentrations for Pu_o and Pu_r in [$\mu\text{Ci/g}$] respectively; other parameters in the equations are defined in chapter 4.

For Puo:

[Activity In] - [Activity Out] + [Oxidation of Sorbed Pur] – [Reduction of Sorbed Puo] = [Change in Activity Stored]

$$A\theta J_{Puo}|_z \Delta t - A\theta J_{Puo}|_{z+\Delta z} \Delta t + (k_o S_{Pur}) \rho A \Delta z \Delta t - (k_r S_{Puo}) \rho A \Delta z \Delta t \approx A \Delta z \left\{ \left[\theta C_{Puo} + \rho S_{Puo} \right]_{t+\Delta t} - \left[\theta C_{Puo} + \rho S_{Puo} \right]_t \right\} \quad (C.3)$$

It is also assumed that there is a linear, reversible partitioning between sorbed and aqueous phases, which is defined as:

$$S_{Puo} = K_{do} C_{Puo} \quad (C.4)$$

When we divide equation C.3 by $\Delta z A \theta \Delta t$, insert C.4, and rearrange:

$$-\frac{[J_{Puo}|_{z+\Delta z} - J_{Puo}|_z]}{\Delta z} + k_o C_{Pur} \frac{\rho}{\theta} - k_r C_{Puo} \frac{\rho}{\theta} \approx \frac{\left\{ \left[C_{Puo} + \frac{\rho}{\theta} K_{do} C_{Puo} \right]_{t+\Delta t} - \left[C_{Puo} + \frac{\rho}{\theta} K_{do} C_{Puo} \right]_t \right\}}{\Delta t} \quad (C.5)$$

When we take the limit as Δt and $\Delta z \rightarrow 0$, then equation C.5 yields the governing equation for Puo:

$$-\frac{\partial \left[v C_{Puo} - D \frac{\partial C_{Puo}}{\partial z} \right]}{\partial z} + k_o C_{Pur} \frac{\rho}{\theta} - k_r C_{Puo} \frac{\rho}{\theta} = \frac{\partial \left\{ C_{Puo} \left[1 + \frac{\rho}{\theta} K_{do} \right] \right\}}{\partial t} \quad (C.6)$$

For Pur:

[Activity In] - [Activity Out] - [Oxidation of Sorbed Pur] + [Reduction of Sorbed Puo] = [Change in Activity Stored]

$$A\theta J_{Pur}|_z \Delta t - A\theta J_{Pur}|_{z+\Delta z} \Delta t - (k_o S_{Pur}) \rho A \Delta z \Delta t + (k_r S_{Puo}) \rho A \Delta z \Delta t \approx A \Delta z \left\{ \left[\theta C_{Pur} + \rho S_{Pur} \right]_{t+\Delta t} - \left[\theta C_{Pur} + \rho S_{Pur} \right]_t \right\} \quad (C.7)$$

It is also assumed that there is a linear, reversible partitioning between sorbed and aqueous phases, which is defined as:

$$S_{Pur} = K_{dr} C_{Pur} \quad (C.8)$$

When we divide equation C.7 by $\Delta z A \theta \Delta t$, insert C.8, and rearrange:

$$-\frac{[J_{Pur}|_{z+\Delta z} - J_{Pur}|_z]}{\Delta z} - k_o C_{Pur} \frac{\rho}{\theta} + k_r C_{Puo} \frac{\rho}{\theta} \approx \frac{\left\{ \left[C_{Pur} + \frac{\rho}{\theta} K_{dr} C_{Pur} \right]_{t+\Delta t} - \left[C_{Pur} + \frac{\rho}{\theta} K_{dr} C_{Pur} \right]_t \right\}}{\Delta t} \quad (C.9)$$

When we take the limit as Δt and $\Delta z \rightarrow 0$, then equation C.9 yields the governing equation for Pur:

$$-\frac{\partial \left[v C_{Pur} - D \frac{\partial C_{Pur}}{\partial z} \right]}{\partial z} - k_o C_{Pur} \frac{\rho}{\theta} + k_r C_{Puo} \frac{\rho}{\theta} = \frac{\partial \left\{ C_{Pur} \left[1 + \frac{\rho}{\theta} K_{dr} \right] \right\}}{\partial t} \quad (C.10)$$

Appendix D

Particle Size Distribution Analysis

Table D.1 Particle size distribution for SRS lysimeter sediment.

Sieve Size (μm)	Passed < Sieve Size %	Retained >Sieve Size %
2	19.2	80.8
63	28.8	71.2
106	30.5	69.5
252	44.2	55.8
420	70.4	29.6
1000	95.5	4.5

Figure D.1 Particle size distribution curve for SRS lysimeter sediment.

Appendix E

Seepage Velocity CalculationsTable E.1 Seepage velocity calculation for the $\text{PuO}_2(\text{NO}_3)_2$ lysimeter.

	M8- $\text{PuO}_2(\text{NO}_3)_2$
Experiment Duration (days)	890
Leachate Volume Collection Period (days)	890
Leachate Volume Collected (L)	73.20
Darcy Velocity (cm/h)*	4.01×10^{-3}
Seepage Velocity (cm/h)**	0.016

* Diameter of lysimeter (cm) = 33

** Average $\theta = 0.25$ Table E.2 Seepage velocity calculations for the $\text{Pu}(\text{NO}_3)_4$, $\text{Pu}(\text{C}_2\text{O}_4)_2$, and PuCl_3 lysimeters.

	M9- $\text{Pu}(\text{NO}_3)_4$	M7- $\text{Pu}(\text{C}_2\text{O}_4)_2$	M12- PuCl_3
Experiment Duration (days)	3915	3915	3915
Leachate Volume Collection Period (days)	1437	1437	1437
Total Rainfall at the Area 200F during the Leachate Collection (L)	432.93	432.93	432.93
Total Leachate Volume (L)	212.70	199.00	147.50
% Percolation	49.13	45.97	34.07
Total Rainfall at the Area 200F for the whole Experiment Duration (L)	1142.35	1142.35	1142.35
Estimated Leachate Volume (L)	561.24	525.09	389.20
Estimated Darcy Velocity (cm/h)*	6.98×10^{-3}	6.53×10^{-3}	4.84×10^{-3}
Estimated Seepage Velocity (cm/h)**	0.0279	0.0261	0.0194

* Diameter of lysimeter (cm) = 33

** Average $\theta = 0.25$

Appendix F

Results of Transport Model Simulations with a Steady-State Flow

Pu(VI)O₂(NO₃)₂ Results

Figure F.1 Comparison of activity distribution measurements with modeling results for the Pu(VI)O₂(NO₃)₂ data set for different oxidation (k_o) and reduction (k_r) rate constants, and for the retardation factors, (a) $R_o=20$, $R_r=10,000$; (b) $R_o=10$, $R_r=10,000$.

Pu(IV)(NO₃)₄ Results

(a)

(b)

(c)

Figure F.2 Comparison of activity distribution measurements with modeling results for the $\text{Pu(IV)(NO}_3)_4$ data set for different oxidation (k_o) and reduction (k_r) rate constants, and for the retardation factors, (a) $R_o=10$, $R_r=5000$; (b) $R_o=10$, $R_r=10,000$; (c) $R_o=10$, $R_r=15,000$.

(a)

(b)

(c)

Figure F.3 Comparison of activity distribution measurements with modeling results for the Pu(IV)(NO₃)₄ data set for different oxidation (k_o) and reduction (k_r) rate constants, and for the retardation factors, (a) $R_o=15$, $R_r=5000$; (b) $R_o=15$, $R_r=10,000$; (c) $R_o=15$, $R_r=15,000$.

(a)

(b)

(c)

Figure F.4 Comparison of activity distribution measurements with modeling results for the $\text{Pu(IV)(NO}_3)_4$ data set for different oxidation (k_o) and reduction (k_r) rate constants, and for the retardation factors, (a) $R_o=20$, $R_r=5000$; (b) $R_o=20$, $R_r=10,000$; (c) $R_o=20$, $R_r=15,000$.

Pu(IV)(C₂O₄)₂ Results

(a)

(b)

(c)

Figure F.5 Comparison of activity distribution measurements with modeling results for the $\text{Pu(IV)(C}_2\text{O}_4)_2$ data set for different oxidation (k_o) and reduction (k_r) rate constants, and for the retardation factors, (a) $R_o=10$, $R_r=5000$; (b) $R_o=10$, $R_r=10,000$; (c) $R_o=10$, $R_r=15,000$.

(a)

(b)

(c)

Figure F.6 Comparison of activity distribution measurements with modeling results for the Pu(IV)(C₂O₄)₂ data set for different oxidation (k_o) and reduction (k_r) rate constants, and for the retardation factors, (a) $R_o=15$, $R_r=5000$; (b) $R_o=15$, $R_r=10,000$; (c) $R_o=15$, $R_r=15,000$.

(a)

(b)

(c)

Figure F.7 Comparison of activity distribution measurements with modeling results for the $\text{Pu(IV)(C}_2\text{O}_4)_2$ data set for different oxidation (k_o) and reduction (k_r) rate constants, and for the retardation factors, (a) $R_o=20$, $R_r=5000$; (b) $R_o=20$, $R_r=10,000$; (c) $R_o=20$, $R_r=15,000$.

Pu(III)Cl₃ Results

(a)

(b)

(c)

Figure F.8 Comparison of activity distribution measurements with modeling results for the Pu(III)Cl_3 data set for different oxidation (k_o) and reduction (k_r) rate constants, and for the retardation factors, (a) $R_o=10$, $R_r=5000$; (b) $R_o=10$, $R_r=10,000$; (c) $R_o=10$, $R_r=15,000$.

(a)

(b)

(c)

Figure F.9 Comparison of activity distribution measurements with modeling results for the Pu(III)Cl_3 data set for different oxidation (k_o) and reduction (k_r) rate constants, and for the retardation factors, (a) $R_o=15$, $R_r=5000$; (b) $R_o=15$, $R_r=10,000$; (c) $R_o=15$, $R_r=15,000$.

(a)

(b)

(c)

Figure F.10 Comparison of activity distribution measurements with modeling results for the Pu(III)Cl_3 data set for different oxidation (k_o) and reduction (k_r) rate constants, and for the retardation factors, (a) $R_o=20$, $R_r=5000$; (b) $R_o=20$, $R_r=10,000$; (c) $R_o=20$, $R_r=15,000$.

Appendix G

Calculations of Monthly Potential Transpiration Values

Table G.1 Monthly temperature values collected for Aiken, SC.

	Year	Monthly Temperatures, T _m (°F)											
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	
	1980	45.1	41.9	-	-	70.2	78.6	83.2	62.6	78.3	-	53.6	-
	1981	39.8	47.6	50.9	67.1	67.5	81.4	81.7	77.0	70.7	62.3	52.9	42.1
	1982	42.7	52.7	60.2	63.0	72.7	77.5	80.6	79.0	72.2	62.9	-	50.9
	1983	41.2	47.1	55.4	58.0	71.6	75.1	82.7	81.9	71.5	64.1	53.0	43.9
	1984	42.1	48.4	53.0	61.2	71.2	71.2	79.1	79.7	73.0	70.6	51.6	54.8
°F	80-83	42.2	47.3	55.5	62.7	70.5	78.2	82.1	75.1	73.2	63.1	53.2	45.6
	80-84	42.2	47.5	54.9	62.3	70.6	78.3	81.5	76.0	73.1	65.0	52.8	47.9
°C	80-83	5.7	8.5	13.1	17.1	21.4	25.6	27.8	24.0	22.9	17.3	11.8	7.6
	80-84	5.7	8.6	12.7	16.9	21.5	25.7	27.5	24.5	22.9	18.3	11.6	8.9

Table G.2 Mean daily duration of maximum possible sunshine hours given by Watson and Burnett (1993) and interpolated values for the latitude of 33°N.

North Latitude	Mean Daily Duration of Maximum Possible Sunshine Hours (N)											
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
30	10.4	11.1	12.0	12.9	13.6	14.0	13.9	13.2	12.4	11.5	10.6	10.2
35	10.1	11.0	11.9	13.1	14.0	14.5	14.3	13.5	12.4	11.3	10.3	9.8
33	10.2	11.0	11.9	13.0	13.8	14.3	14.1	13.4	12.4	11.4	10.4	10.0

Table G.3 Monthly potential transpiration rate calculations for 1980-1983.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	
T _m (°C)	5.67	8.51	13.06	17.06	21.39	25.64	27.81	23.96	22.98	17.28	11.76	7.57	I=79.69 (annual) Unadjusted
I _{monthly}	1.21	2.22	4.22	6.30	8.85	11.61	13.11	10.49	9.79	6.42	3.61	1.86	
T _{pm} (mm) (a=1.77)	8.74	17.99	38.42	61.73	92.26	127.3	147.0	112.8	103.9	63.17	31.91	14.62	
N (for lat. 33°N)	10.22	11.04	11.94	13.02	13.84	14.30	14.14	13.38	12.40	11.38	10.42	9.96	Adjusted
T _{pm} (mm)	7.44	16.55	38.23	66.98	106.4	151.6	173.2	125.8	107.4	59.90	27.71	12.13	
T _{pm} (cm/d)	0.02	0.06	0.13	0.22	0.35	0.51	0.58	0.42	0.36	0.20	0.09	0.04	

Table G.4 Monthly potential transpiration rate calculations for 1980-1984.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	
T _m (°C)	5.66	8.63	12.71	16.85	21.47	25.72	27.48	24.47	22.86	18.32	11.54	8.85	I=80.63 (annual) Unadjusted
I _{monthly}	1.20	2.27	4.05	6.18	8.90	11.67	12.88	10.82	9.77	7.01	3.51	2.35	
T _{pm} (mm) (a=1.79)	8.48	18.09	36.16	59.93	92.51	127.9	144.0	117.0	103.5	69.63	30.43	18.90	
N (for lat. 33°N)	10.22	11.04	11.94	13.02	13.84	14.30	14.14	13.38	12.40	11.38	10.42	9.96	Adjusted
T _{pm} (mm)	7.22	16.64	35.98	65.02	106.7	152.4	169.7	130.4	107.0	66.03	26.42	15.68	
T _{pm} (cm/d)	0.02	0.06	0.12	0.22	0.36	0.51	0.57	0.43	0.36	0.22	0.09	0.05	

Appendix H

Plutonium Root Uptake/Transport Model Parameters

Table H.1 Initial rough estimates for the Pu root uptake/transport model parameters.

Model Parameters	Values
Partitioaning coefficient for Pu_o in the root, K_{do_root} (cm^3/g)	5.6
Partitioaning coefficient for Pu_r in the root, K_{dr_root} (cm^3/g)	4000
Root porosity, η_r	0.6
Root density, ρ_r (g/cm^3)	1.5
Root Diffusion Coefficient, D_r (cm^2/h)	5.4×10^{-2}

Appendix I

Code of Reactive Trasnport Model with Steady-State Flow

```

program constant_PuIV_Source_FB
implicit none

double precision
n,D,RV,RIV,ko,kr,v,dz,maxerrV,maxerrIV,BB,CC,DDV,DDIV,AAV,AAIV
double precision errV,errIV,z,q,dt,tend,t,tot_act,KdV,KdIV,rho,koo,krr
double precision aq_act,ads_act,vol,act_out_IV,act_out_V, Dd,w, alfaL
real time_ini,time_end
integer Ni,i,iter,j
double precision, dimension(0:1000)::CV,CIV,oldCV,oldCIV,pCV,pCIV,SV,SIV
double precision, dimension(1:50):: zobs, yobs, ypred
double precision sumyobs, manyobs, SStotal, SSres, rsq

open(1,file="results.dat")
open(2,file="data.txt")

call cpu_time(time_ini)

n=0.25d0
w=0.4d0 !tortuosity
alfaL=0.25d0 ! diffusivity cm
Dd=1.8d-2 !cm2/h
!D=0.002d0
!tend=190530
!tend=102930
tend=181560 !h
!tend=93960
!v=0.013374/n
v=0.00698/n !cm/h
dz=0.2d0
dt=1.d0
rho=1.5d0
D=w*Dd+v*alfaL

print*, "RV="
read*,RV
KdV=(RV-1.d0)*n/rho
print*, "RIV="
read*,RIV
KdIV=(RIV-1.d0)*n/rho
print*, "ko="
read*,koo

```

```

print*, "kr="
read*, krr
write(2, ('n=", F5.2, 5x, "D=", 2x, G10.5, 5x, "v=", 2x, G10.4, 2x, "Bulk
density=", 2x, G10.4)) n, D, v, rho
write(2, ('A3, F12.3, 5x, "KdV=", 1x, F10.3, 5x, A4, F12.3, 5x, "KdIV=", 1x, F10.3)) "RV
=", RV, KdV, "RIV=", RIV, KdIV
write(2, ('A3, G12.3, 5x, A4, G12.3)) "ko=", koo, "kr=", krr

Ni=256

do i=1, Ni
    CV(i)=0.0d0
    CIV(i)=0.0d0
enddo

Act_out_IV=0.d0
act_out_V=0.d0

do t=dt, tend, dt
    if (t.gt.93960) then
        v=0.d0
        Dd=1.14d-2
        D=w*Dd+alfaL*v
    endif

    do i=1, Ni
        oldCV(i)=CV(i)
        oldCIV(i)=CIV(i)
    enddo

    AAV=RV/dt+kr*(RV-1.d0)+2.d0*D/(dz**2)
    BB=-v/(2.d0*dz)+D/(dz**2)
    CC=v/(2.d0*dz)+D/(dz**2)
    AAIV=RIV/dt+ko*(RIV-1.d0)+2.d0*D/(dz**2)

    iter=0

    do
        maxerrV=0.d0
        maxerrIV=0.d0
        iter=iter+1
        do i=1, Ni
            pCV(i)=CV(i)
            pCIV(i)=CIV(i)
        enddo
        CV(1)=0.d0

```

```

CIV(1)=0.d0
CV(Ni+1)=2*CV(Ni)-CV(Ni-1)
CIV(Ni+1)=2*CIV(Ni)-CIV(Ni-1)

do i=2,Ni,1
    q=0.d0
    ko=koo
    kr=krr
    if (i.eq.125) then
        q=0.001658
        ko=0.d0
        kr=0.d0
    endif
!   if (i.eq.249) q=9.951d-3 !502.7mCI-released
!   if (i.eq.249) q=0.0035d0
    if (t.gt.93960) q=0.d0

    DDV=ko*(RIV-1.d0)*CIV(i)+RV*oldCV(i)/dt
    DDIV=kr*(RV-1.d0)*CV(i)+RIV*oldCIV(i)/dt+q/n

    CV(i)=(CV(i+1)*BB+CV(i-1)*CC+DDV)/AAV
    CIV(i)=(CIV(i+1)*BB+CIV(i-1)*CC+DDIV)/AAIV

enddo

do i=2,Ni
    errV=abs(CV(i)-pCV(i))
    errIV=abs(CIV(i)-pCIV(i))
    if (errV.gt.maxerrV) maxerrV=errV
    if (errIV.gt.maxerrIV) maxerrIV=errIV
enddo

if (mod(t,168.d0).eq.0) print*,t/168,"weeks"

if ((maxerrV.lt.1E-5).and.(maxerrIV.lt.1E-5)) exit
enddo
Act_out_IV=act_out_IV+(-D*(CIV(Ni+1)-CIV(Ni-
1)))/(2.d0*dz)+v*CIV(Ni))*n*4.90874d0*dt
Act_out_V=act_out_V+(-D*(CV(Ni+1)-CV(Ni-
1)))/(2.d0*dz)+v*CV(Ni))*n*4.90874d0*dt

enddo

do i=1,Ni
    z=(i-1)*dz

```

```

        if (CV(i).lt.1.d-90) CV(i)=0.d0
        if (CIV(i).lt.1.d-90) CIV(i)=0.d0
        SV(i)=KdV*CV(i)
        SIV(i)=KdIV*CIV(i)
        write(1,'(F12.3,3x,4E14.4)') z, CV(i), CIV(i), SV(i), SIV(i)
    enddo

    vol=4.90874d0*dz
    tot_act=0
    do i=2, Ni-1
        aq_act=vol*(CV(i)+CIV(i))
        ads_act=vol*rho*(SV(i)+SIV(i))
        tot_act=tot_act+aq_act+ads_act
    enddo
    aq_act=(vol/2.d0)*(CV(Ni)+CIV(Ni))
    ads_act=(vol/2.d0)*rho*(SV(Ni)+SIV(Ni))
    tot_act=tot_act+aq_act+ads_act

! R2 calculations:
    zobs(1)=24.8d0
    yobs(1)=1.d0
    zobs(2)=25.6d0
    yobs(2)=4.0d-2
    zobs(3)=26.8d0
    yobs(3)=5.49d-4
    zobs(4)=28.4d0
    yobs(4)=2.25d-4
    zobs(5)=29.8d0
    yobs(5)=5.84d-5
    zobs(6)=31.2d0
    yobs(6)=1.74d-4
    zobs(7)=33.8d0
    yobs(7)=2.86d-5
    zobs(8)=36.4d0
    yobs(8)=4.16d-6
    zobs(9)=39.d0
    yobs(9)=1.54d-6

    sumyobs=0
    do i=1,9
        j=zobs(i)/dz+1
        ypred(i)=(SV(j)+SIV(j))/(SV(125)+SIV(125))
        sumyobs=sumyobs+yobs(i)
    enddo
    manyobs=sumyobs/9

```

```

SStotal=0
SSres=0
do i=1,9
    SStotal=SStotal+(yobs(i)-meanyobs)**2
    SSres=SSres+(yobs(i)-ypred(i))**2
enddo
rsq=(SStotal-SSres)/SStotal
print*, "R square=", rsq

write(2,('Total activity=",2x,G12.4)') tot_act
print*, "Total Activity=", tot_act
write(2,('Activity Out PuIV=",2x,G12.4,2x,"Activity Out PuV =",2x,G12.4)')
act_out_IV, act_out_V
write(2,('R sq =",2x,G12.4)') rsq
print*, "Activity Out PuIV=", act_out_IV
print*, "Activity Out PuV =", act_out_V
call cpu_time(time_end)
print*, "Time of execution=", (time_end-time_ini)/60, "minutes."
end

```

Appendix J

Code of Reactive Trasnport Model with Variably Saturated Flow and Pu Root
Uptake/Translocation

Module Variables

```

    implicit none
    save

    integer i,iter,endnode,limit,m,x,r,BC,input_info,p,qImonth,pN
    double precision
dt,dttrans,t,HM1,HM2,HM3,tflux_end,Se,g,flux,DS,sumDS,E,sumE,total_DS,bot_gradie
nt,ini_t,dh,maxdhdomain,total_E
    double precision maxerr,err_t,err,
maxerr_t,alfa_root,time_ini,time_end,errorpercent,top,bottom,total_bottom,total_top,K_c
onst,qbottom,amountreleased,totamountrel
    double precision
dhdomain,qI,train,day,nextqI,hNE,KNE,KE,dhborder,maxdh,dtmax,dtmin,dhc,Kmax,qto
p_total,qI_total
    double precision, dimension
(0:5000)::aa,bb,cc,dd,h,oldh,z,ph,teta,oldteta,C,S,initeta,RRD
    double precision, dimension (0:5000):: K,oldK,oldS,q,q_img,oldq
    double precision, dimension (1:1000)::opt
    double precision, dimension (1:12)::Tp
    double precision,
dimension(0:5000)::CV,CIV,oldCV,oldCIV,pCV,pCIV,SV,SIV
    double precision
act_out_IV,act_out_V,aq_act,ads_act,tot_act,kr,ko,koo,top_daily,oldqI,correction_f
    double precision
maxerrV,maxerrIV,BBVIV,CCVIV,DDV,DDIV,AAV,AAIV,sourceox,sourcered
    double precision
errV,errIV,actrootV,actrootIV,tot_act_root,tot_act_transV,tot_act_transIV
    double precision, dimension (0:5000)
::v,D,CrV,CrIV,volp,Ap,vol,act_transV,act_transIV,SrV,SrIV,lnA,RV,RIV,oldRV,oldRI
V

```

! Soil Hydraulic Parameters and Van Genuchten Constants Declaration:

```

    real,parameter :: n_genuchten=1.48013d0, L_genuchten=-1.0633d0,
alfa=0.027816d0, Ksat=15.984d0
    real,parameter :: teta_s=0.39188d0, teta_r=0.0589d0, gamma=1.d0-
(1.d0/n_genuchten),rho=1.39d0
    real,parameter :: perm=teta_s, Ss=3.1d-5

```

! Dispersion/Diffusion Parameters:

```

    real,parameter :: alfaL=0.25d0 !cm

```

```

real,parameter :: w=0.4
real,parameter :: Dif=1.8d-2 !cm2/h

! Time Parameters:
double precision, parameter :: tfield=3915.d0 !d
double precision, parameter :: tstorage=3650.d0 !d
double precision, parameter :: tend=tfield+tstorage !d

! Domain/Model Constant Declarations:
real,parameter :: L=51.d0 !cm
integer,parameter :: N=256
real,parameter :: dz=L/(N-1)
real,parameter :: Alys=855.3d0 !cm2
real,parameter :: Areleasedox=0.d0 !microCi
real,parameter :: Areleasedred=152.98d0 !microCi
real,parameter :: sourcelocation=26.2d0 !cm
integer, parameter :: sourcenode=sourcelocation/dz+1
double precision, parameter ::
sourcevalueox=Areleasedox/(4.9087385*dz*tfield*24) !mCi/cm3/h
double precision, parameter ::
sourcevaluered=Areleasedred/(4.9087385*dz*tfield*24) !mCi/cm3/h

! Retardation Factors:
!real, Parameter :: RIV=10000,RV=15
real,parameter :: KdV=2.52d0, KdIV=1800.0d0 !cm3/g

! Root Pu Transport Parameters:
real,parameter :: uptake_effV=0.000d0
real,parameter :: uptake_effIV=0.000d0
real,parameter :: por_p=0.6d0
real,parameter :: dens=1.5d0
real,parameter :: Dr=3.d0*1.8d-2 !cm2/h
real,parameter :: Aroot_coef=1.45412d0 !1/cm
RRD(51)*Aroot_coef=0.1=Ap(51)
real,Parameter :: KdrV=5.6d0
real,parameter :: KdrIV=4000.d0
real,parameter :: Rro=1.d0+dens**KdrV/por_p
real,parameter :: Rrr=1.d0+dens**KdrV/por_p
real,parameter :: Lp=61 !cm 61-51=10 cm plant
integer, parameter :: Np=Lp/dz+1

```



```

contains
! Initial Head Values:
subroutine ini_input
implicit none
t=0.d0
do i=0,N+1
    z(i)=(i-1)*dz
    h(i)=-100.d0
enddo

end subroutine ini_input

```

```

! Tridiagonal Solution:
subroutine tridiagonalsolution(Nj,AA,BB,CC,DD,hh)
implicit none
integer j,Nj
double precision, dimension (0:5000):: AA,BB,CC,DD,hh
do j=2,Nj
    BB(j)=BB(j)-AA(j)*CC(j-1)/BB(j-1)
    DD(j)=DD(j)-AA(j)*DD(j-1)/BB(j-1)
enddo
hh(Nj)=DD(Nj)/BB(Nj)
Do j=Nj-1,1,-1
    hh(j)=(DD(j)-CC(j)*hh(j+1))/BB(j)
enddo
end subroutine tridiagonalsolution

```

```

! Lysimeter Volumes corresponding to the nodes:
subroutine volume
implicit none
do i=2,N-1
    vol(i)=4.9087385*dz
enddo
vol(1)=4.9087385*dz/2.d0
vol(N)=4.9087385*dz/2.d0
end subroutine volume

```

```

!Water Capacity Function:
subroutine watercap
implicit none
do i=0,endnode+1

```

```

    C(i)=(0.892728d0*((abs(h(i)))**0.48013d0)/((((abs(h(i)))**n_genuchten)+200.7
46)**1.32438d0)

```

```

        if (h(i).ge.0) C(i)=0
    enddo
end subroutine watercap

```

!Water Content Function:

```

subroutine watercontent
implicit none
do i=0,endnode+1
    g=(1.d0+((alfa*abs(h(i)))**n_genuchten)**gamma
    teta(i)= teta_r+ (teta_s-teta_r)/g
    if (h(i).ge.0) teta(i)=teta_s
enddo
end subroutine watercontent

```

!Hydraulic Conductivity Function:

```

subroutine hydcond
implicit none
do i=0,endnode+1
    Se=(1.d0+((alfa*abs(h(i)))**n_genuchten)**(-gamma)
    K(i)=Ksat*(Se**L_genuchten)*((1-(1-
Se**(1.d0/gamma)**gamma)**2.d0)
    if (h(i).ge.0.d0) K(i)=Ksat
enddo
end subroutine hydcond

```

!Root Density Function:

```

subroutine rootdensityarea
implicit none
do i=1,Np
    RRD(i)=0.068777d0*exp(-0.066457d0*(L-z(i))) ! CORE-
D
    !RRD(i)=0.034695d0*exp(-0.025d0*(L-z(i))) ! CORE-E
    !RRD(i)=0.114902d0*exp(-0.114571d0*(L-z(i))) ! CORE-
C
    if (i.gt.endnode) RRD(i)=RRD(endnode)
    Ap(i)=Aroot_coef*RRD(i)
enddo
do i=1,Np
    if (i.eq.1) Ap(0)=Ap(2)
    if (i.eq.Np) Ap(Np+1)=Ap(Np-1)
    lnA(i)=1.d0/Ap(i)*(Ap(i+1)-Ap(i-1))/(2.d0*dz)

    volp(i)=Ap(i)*vol(i)
    if (i.gt.endnode) volp(i)=volp(endnode)
enddo

```

```

        do i=endnode+1,Np
            S(i)=0.d0
        enddo
    end subroutine rootdensityarea

!Root Water Uptake Function:
    subroutine rootfunction
    implicit none
        do i=1,endnode
            if (h(i).ge.0.d0) then
                alfa_root=0.d0
            elseif ((h(i).ge.-20.d0).and.(h(i).lt.0.d0)) then
                alfa_root=h(i)/-20.d0
            elseif ((h(i).ge.-200.d0).and.(h(i).lt.-20.d0)) then
                alfa_root=1.d0
            elseif ((h(i).ge.-2000).and.(h(i).lt.-200.d0)) then
                alfa_root=(h(i)+2000.d0)/(-200.d0+2000.d0)
            else
                alfa_root=0.d0
            endif
            !alfa_root=1.0d0
            S(i)=alfa_root*Tp(qImonth)* RRD(i)! CORE-D
            !S(i)=alfa_root*Tp(qImonth)*0.114902d0*exp(-
0.114571d0*(L-z(i))) !CORE-C
            !S(i)=alfa_root*0.2415d0*exp(-0.0479*(L-z(i))) !
            !if (qI.ne.0.d0) S(i)=0.d0 ! NO root uptake during a rain
event
            !S(i)=0.d0
        enddo
    end subroutine rootfunction

! Pu Transport in the Roots:
    subroutine roottransport
    implicit none
        double precision, dimension (0:5000) ::
aar,bbrIV,bbrV,ccr,ddrV,ddrIV,vp,Qp,oldCrV,oldCrIV

        do i=1,Np
            oldCrV(i)=CrV(i)
            oldCrIV(i)=CrIV(i)
        enddo

        Qp(1)=0.d0
        do i=2,Np

```

```

                                Qp(i)=Qp(i-1)+(S(i)+S(i-1))*dz/2.d0
                                enddo
                                do i=1,Np
                                    vp(i)=Qp(i)/Ap(i)
                                    if (i.eq.1) vp(0)=vp(2)
                                    if (i.eq.Np) vp(Np+1)=vp(Np-1)
                                enddo

                                do i=1,Np
                                    !Tridiagonal arrays:

                                    aar(i)=Dr/(dz**2)+vp(i)/(2.d0*dz)-
lnA(i)*Dr/(2.d0*dz)
                                    bbrV(i)=-Rro/dttrans-2.d0*Dr/(dz**2)-(vp(i+1)-
vp(i-1))/(2.d0*dz)-lnA(i)*vp(i)
                                    ccr(i)=Dr/(dz**2)-
vp(i)/(2.d0*dz)+lnA(i)*Dr/(2.d0*dz)
                                    ddrV(i)=-
uptake_effV*CV(i)*S(i)/(por_p*24.d0*Ap(i))-Rro*oldCrV(i)/dttrans
                                    bbrIV(i)=-Rrr/dttrans-2.d0*Dr/(dz**2)-(vp(i+1)-
vp(i-1))/(2.d0*dz)-lnA(i)*vp(i)
                                    ddrIV(i)=-
uptake_effIV*CIV(i)*S(i)/(por_p*24.d0*Ap(i))-Rrr*oldCrIV(i)/dttrans
                                enddo

                                !bottom boundary:
                                ccr(1)=ccr(1)+aar(1) ! No FLow

                                !Upper Boundary:
                                aar(Np)=aar(Np)+ccr(Np) ! No FLow

                                call tridiagonalsolution(Np,aar,bbrV,ccr,ddrV,CrV)
                                call tridiagonalsolution(Np,aar,bbrIV,ccr,ddrIV,CrIV)
                                !do i=1,Np
                                !      print*,"CrV=",CrV(sourcenode),"
CrIV=",CrIV(sourcenode)
                                !enddo

                                end subroutine roottransport

                                !Mass Balance:
                                subroutine massbalance
                                implicit none

```

```

oldq(1)=-oldK(1)*((-3.d0*oldh(1)+4.d0*oldh(2)-
oldh(3))/(2.d0*dz)+1)
oldq(N)=-oldK(N)*((oldh(N-2)-4.d0*oldh(N-
1)+3.d0*oldh(N))/(2.d0*dz)+1)

bottom=(q(1)+oldq(1))*dt/2.d0
top=(q(N)+oldq(N))*dt/2.d0
top_daily=top_daily+top

sumDS=0.d0
sumE=0.d0
do i=1,N-1
    E=(dt*dz/4.d0)*(S(i)+S(i+1)+oldS(i)+oldS(i+1))
    sumE=E+sumE
    DS=((teta(i)+teta(i+1))-(oldteta(i)+oldteta(i+1)))*dz/2.d0
    sumDS=sumDS+DS
enddo
total_bottom=total_bottom+bottom
total_top=total_top+top
total_E=total_E+sumE
total_DS=total_DS+sumDS
end subroutine massbalance

```

! VARIABLELY SATURATED FLOW MODEL

```

subroutine flowmodel
implicit none

Kmax=0.d0
Do i=1,N
    if (K(i).gt.Kmax) Kmax=K(i)
enddo
!Self Adaptive Time Scaling:
!dt=6.25d-5! d
if((day-t).le.dtmax) flux=nextqI ! to catch the next flux value near
the end of the day
if (mod(t,1.d0).eq.0) then ! checking if the simulation has
completed a day exactly
    top_daily=0.d0
    oldqI=qI
    qI=nextqI
    flux=nextqI

```

```

        if (day.lt.(int(tfield)-1)) read(5,*) qImonth,nextqI
        day=day+1.d0
        qI_total=qI_total+qI
    endif
    dhborder=abs((-flux/KE-1.d0)*dz)
    maxdh=max(maxdhdomain,dhborder)

    dt=(dtmin**((maxdh/dhc))*((dtmax*((Ksat/Kmax)**0.5d0))**(1.d0-maxdh/dhc))
    if(dt.lt.1.d-5) dt=01.d-5

    if ((day-t).lt.dt) then
        dt=day-t
    endif
    !output time adjustment:
    if (((opt(p)-t).lt.dt).and.(t.lt.opt(p))) then
        dt=opt(p)-t
    endif

    t=t+dt

    maxerr_t=0.0d0
    m=m+1
    do i=0,N+1
        oldh(i)=h(i)
        oldteta(i)=teta(i)
        oldK(i)=K(i)
        oldS(i)=S(i)
    enddo

    iter=0

    !ITERATION LOOP
    do

        maxerr=0.d0
        iter=iter+1
        do i=0,endnode+1
            ph(i)=h(i) ! previous iteration values
        enddo

        call watercap
        call hydcond
        call watercontent
        call rootfunction

```

```

!Flux and gradient at the bottom boundary:
bot_gradient=(h(2)-h(0))/(2.d0*dz)
qbottom=-K(1)*((oldh(2)-oldh(0))/(2.d0*dz)+1.d0)

do i=1,endnode
    HM1=(2.d0/(dz**2))*(K(i+1)*K(i)/(K(i+1)+K(i)))
    HM2=(2.d0/(dz**2))*(K(i-1)*K(i)/(K(i-1)+K(i)))
    HM3=(2.d0/dz)*((K(i+1)*K(i)/(K(i+1)+K(i)))-(K(i-
1)*K(i)/(K(i-1)+K(i))))

    !Tridiagonal arrays:
    aa(i)=-HM2
    bb(i)=Ss*teta(i)/(perm*dt) + C(i)/dt+HM1+HM2
    cc(i)=-HM1
    dd(i)=Ss*teta(i)*oldh(i)/(perm*dt) - (teta(i)-
oldteta(i))/dt + C(i)*ph(i)/dt+HM3-S(i)
enddo

!bottom boundary:
if (bot_gradient.le.-1.d0) then
    qbottom=0.d0 ! No flow
    BC=0
else
    BC=1
endif
cc(1)=cc(1)+aa(1)
dd(1)=dd(1)-aa(1)*(qbottom/K(1)+1.d0)*2.d0*dz !Flux

!Upper Boundary:
aa(N)=aa(N)+cc(N) !flux
dd(N)=dd(N)+2.d0*dz*cc(N)*(qI/K(N)+1.d0) ! flux

call tridiagonalsolution(endnode,aa,bb,cc,dd,h)

!if (h(N).gt.0.d0) h(N)=0.d0

h(0)=h(2)+(qbottom/K(1)+1.d0)*2.d0*dz
h(N+1)=h(N-1)-2.d0*dz*(qI/K(N)+1.d0)

do i=1,N
    err=abs(h(i)-ph(i))
    if (err.gt.maxerr) maxerr=err
enddo

if (maxerr.lt.1E-7) exit ! Exit from the iteration loop
if (iter.gt.limit) then

```

```

                                exit
                            endif

                    enddo !End of Iteration Loop

                    call watercontent
                    call hydcond

                    hNE=(-flux/K(N)-1.d0)*dz+h(N-1)
                    Se=(1.d0+((alfa*abs(hNE))**n_genuchten))**(-gamma)
                    KNE=Ksat*(Se**L_genuchten)*((1-(1-
h(i))/(dz+1.d0)Se**(1.d0/gamma))**gamma)**2.d0)
                    if (hNE.ge.0.d0) KNE=Ksat
                    KE=2.d0*KNE*K(N-1)/(KNE+K(N-1))

                    !FLux Calculations:
                    maxdhdomain=0.d0
                    do i=1,N-1
                        dhdomain=abs(h(i+1)-h(i))
                        if(dhdomain.gt.maxdhdomain) maxdhdomain=dhdomain
                        q_img(i)=-2.d0*K(i)*K(i+1)/(K(i)+K(i+1))*((h(i+1)-
                    enddo
                    do i=2,N-1
                        q(i)=(q_img(i-1)+q_img(i))/2.d0
                    enddo
                    q(1)=-K(1)*((-3.d0*h(1)+4.d0*h(2)-h(3))/(2.d0*dz)+1)
                    q(N)=-K(N)*((h(N-2)-4.d0*h(N-1)+3.d0*h(N))/(2.d0*dz)+1)

                    call massbalance
                    dttrans=dt*24 !h

                    !OUTPUT FILE:
                    if ((mod(opt(p),t).eq.0).and.(p.le.pN)) then
                        do i=1,N
                            write(1,'(F12.7,4x,
I8,5x,F10.5,4E12.3,5F30.10,5x,I10)')
t,i,z(i),h(i),CV(i),CIV(i),SV(i),SIV(i),S(i),teta(i),q(i),K(i),BC
                        enddo
                        p=p+1
                    endif

                    write(8,'("t= ",G15.8,"dt= ", G12.5)') t,dt

```



```

        print ('t=",G15.7," dt=", G10.5 ," qI=",F8.3," flux=",F8.3," max
dh=",G12.5)' ,t,dt,qI,flux,maxdh
        if (t.eq.1437)then
            write(9,('Total Change in Storage=",E20.10)')total_DS
            write(9,('Total Bottom Flow=",E20.10)')total_bottom
            write(9,('Total Top Flow=",E20.10)')total_top
            write(9,('Total Extraction=",E20.10)')total_E
            write(9,('Total qI=",E20.10)') qI_total
        endif

    end subroutine flowmodel
end module variables

```

```

*****
!Pu REACTIVE TRANSPORT MODEL COUPLED
!with VARIABLELY SATURATED FLOW MODEL and ROOT Pu UPTAKE
!
!Deniz Inci Demirkanli
*****

```

```

    program transportmodeling
    use variables
    implicit none

    endnode=N
    limit=20

    print*, "ko [1/h]="
    read*,koo ![1/h]
    print*, "kr [1/h]="
    read*,kr ![1/h]

    correction_f=0.82d0 ! correction factor for the transpiration rates from the water
balance
    ! Monthly Transpiration Rates: [cm/d]
    Tp(1)=correction_f*0.02d0 !January
    Tp(2)=correction_f*0.06d0 !February
    Tp(3)=correction_f*0.13d0 !March
    Tp(4)=correction_f*0.22d0 !April
    Tp(5)=correction_f*0.35d0 !May
    Tp(6)=correction_f*0.51d0 !June
    Tp(7)=correction_f*0.58d0 !July
    Tp(8)=correction_f*0.42d0 !August
    Tp(9)=correction_f*0.36d0 !September
    Tp(10)=correction_f*0.2d0 !October

```

```

Tp(11)=correction_f*0.09d00 !November
Tp(12)=correction_f*0.04d0 !December

call cpu_time(time_ini)

open (1,file="RESULTS.dat")
open(11,file="ACTIVITYRESULTS.dat")
open(12,file="ACTIVITYRESULTSROOTS.dat")
open (2,file="FINALRESULTS.dat")
open (4,file="headinput.dat")
open (5,file="raininput.dat")
open (7,file="outputtimes.dat")
open (8,file="dtFILE.dat")
open (9,file="WATERBALANCE.dat")
open (13,file="data.dat")

!OUTPUT ARRAY:
print*, "Enter the number of output times ="
read*, pN
print*, "Output Times:"
do p=1,pN
    read(7,*) opt(p)
    print*, opt(p)
enddo
read*

write(1,('L [cm]= ',F7.3,3x,"N=",I5,x,"dz [cm]=",F8.5)) L,N,dz
write(1,('Ao. Released=",4x, G10.3,1x,"[microCi]")') Areleasedox
write(1,('Ar. Released=",4x, G10.3,1x,"[microCi]")') Areleasedred
write(1,('t Field [d]=', G10.2,1x,"t Storage [d]=",1x,G10.2,3x,"t TOTAL
[d]=",4x,G17.5)) tfield, tstorage,tend
write(1,('ko [1/h]=',1x,E12.5,2x,"kr [1/h]='2x,E12.5)) ko,kr
write(1,*)
write(1,('RESULTS'))
write(1,('6x,"t [d]",8x,"dt [d]",6x,"Node#, i",6x,"z [cm]",4x,"CV
[mCi/cm3]",5x,"CIV [mCi/cm3]",5x,"SV [mCi/g]",7x,"SIV [mCi/g]",8x,"h
[cm]",8x,"FLUX [cm3/cm2/d]", "Theta [cm3/cm3]",3x,"K [cm/d]",5x,"S
[cm3/cm3/d]",1x)')

! INITIAL PRESSURE HEAD VALUES and ACTIVITY
CONCENTRATION VALUES
print*, "1.Continuing Simulation"
print*, "2.New Simulation"
read*, input_info
if(input_info.eq.1) then
    read(4,('F12.7,10x,F30.10')) t,h(i)

```

```

else
    call ini_input
endif

do i=1,N
    CV(i)=0.0d0 ! Initial Concentration in the domain
    CIV(i)=0.0d0
    CrV(i)=0.d0 ! Initial Concentration in the roots
    CrIV(i)=0.d0
enddo

maxdhdomain=0.d0
do i=1,N-1
    dhdomain=abs(h(i+1)-h(i))
    if (dhdomain.gt.maxdhdomain) maxdhdomain=dhdomain
Enddo

read(5,*) qImonth,nextqI

call volume
call watercap
call watercontent
call hydcond
call rootdensityarea
call rootfunction

do i=1,N+1

    write(1,'(E15.5,2x,E10.6,2x,I8,6x,F10.5,3x,E15.5,2x,E15.5,2x,E15.5,2x,E15.5,2x,
F15.5,1x,F20.8,3F15.5)') t,dt,i,z(i),CV(i),CIV(i),SV(i),SIV(i),h(i),q(i),teta(i),K(i),S(i)
enddo

DO i=1,N+1
    initeta(i)=teta(i)
enddo

m=0
total_DS=0.d0
total_bottom=0.d0
total_top=0.d0
total_E=0.d0
day=0.d0
t=0.d0

qtop_total=0.0d0
qI_total=0.d0

```

```

act_out_IV=0.d0
act_out_V=0.d0

hNE=(-nextqI/K(N)-1.d0)*dz+h(N-1)
Se=(1.d0+((alfa*abs(hNE))**n_genuchten))**(-gamma)
KNE=Ksat*(Se**L_genuchten)*((1-(1-
Se**(1.d0/gamma))**gamma)**2.d0)
if (hNE.ge.0.d0) KNE=Ksat
KE=2.d0*KNE*K(N-1)/(KNE+K(N-1))

p=1
dhc=400
dtmin=6.25d-5
dtmax=0.0023d0

tot_act_transV=0.d0
tot_act_transIV=0.d0
totamountrel=0.d0

! TIME LOOP -- FIELD PERIOD
do while (t.le.tfield)
  call flowmodel

  do i=1,N
    v(i)=(q(i)/24.d0)/teta(i) ! cm/h
    D(i)=w*Dif+alfaL*abs(v(i)) !cm2/h
  enddo
  v(0)=v(1)
  D(0)=D(1)

  do i=1,N
    oldCV(i)=CV(i)
    oldCIV(i)=CIV(i)
  enddo

  iter=0

  do
    maxerrV=0.d0
    maxerrIV=0.d0
    iter=iter+1
    do i=1,N
      pCV(i)=CV(i)
      pCIV(i)=CIV(i)
    enddo

```

```

CV(N)=0.d0
CIV(N)=0.d0
CV(0)=2.d0*CV(1)-CV(2)
CIV(0)=2.d0*CIV(1)-CIV(2)

amountreleased=0.d0
do i=1,N-1,1
    sourceox=0.d0
    sourcered=0.d0
    if (i.eq.sourcenode) then
        sourceox=sourcevalueox !microCi/cm3/h
        sourcered=sourcevaluered
    endif
    !ko=koo*(1.d0+9.d0*(teta(i)-0.39188d0)/(0.107d0-
0.39188d0))

    ko=koo

    RV(i)=1.d0+rho*KdV/teta(i)
    RIV(i)=1.d0+rho*KdIV/teta(i)
    !AAV=RV(i)/dttrans+kr*(RV(i)-
1.d0)+2.d0*D(i)/(dz**2)+uptake_effV*S(i)/24.d0+(v(i+1)-v(i-
1))/(2.d0*dz)+(rho*KdV/dttrans)*(1.d0/teta(i)-1.d0/oldteta(i))
    !AAIV=RIV(i)/dttrans+ko*(RIV(i)-
1.d0)+2.d0*D(i)/(dz**2)+uptake_effIV*S(i)/24.d0+(v(i+1)-v(i-
1))/(2.d0*dz)+(rho*KdIV/dttrans)*(1.d0/teta(i)-1.d0/oldteta(i))

    AAV=RV(i)/dttrans+kr*(RV(i)-
1.d0)+2.d0*D(i)/(dz**2)+uptake_effV*S(i)/24.d0+(v(i+1)-v(i-1))/(2.d0*dz)
    AAIV=RIV(i)/dttrans+ko*(RIV(i)-
1.d0)+2.d0*D(i)/(dz**2)+uptake_effIV*S(i)/24.d0+(v(i+1)-v(i-1))/(2.d0*dz)

    BBVIV=-v(i)/(2.d0*dz)+D(i)/(dz**2)+(D(i+1)-D(i-
1))/(4.d0*(dz**2))

    CCVIV=v(i)/(2.d0*dz)+D(i)/(dz**2)-(D(i+1)-D(i-
1))/(4.d0*(dz**2))

    DDV=ko*(RIV(i)-
1.d0)*CIV(i)+RV(i)*oldCV(i)/dttrans+sourceox/teta(i)
    DDIV=kr*(RV(i)-
1.d0)*CV(i)+RIV(i)*oldCIV(i)/dttrans+sourcered/teta(i)

    amountreleased=amountreleased+sourcered*4.9087385*dz*dttrans

    CV(i)=(CV(i+1)*BBVIV+CV(i-
1)*CCVIV+DDV)/AAV

```

```

CIV(i)=(CIV(i+1)*BBVIV+CIV(i-
1)*CCVIV+DDIV)/AAIV
SV(i)=KdV*CV(i)
SIV(i)=KdIV*CIV(i)

enddo

do i=2,N
    errV=abs(CV(i)-pCV(i))
    errIV=abs(CIV(i)-pCIV(i))
    if (errV.gt.maxerrV) maxerrV=errV
    if (errIV.gt.maxerrIV) maxerrIV=errIV
enddo

if ((maxerrV.lt.1E-5).and.(maxerrIV.lt.1E-5)) exit
enddo ! END OF ITERATION LOOP
do i=1,N
    if (CV(i).lt.1.0d-50) CV(i)=0.d0
    if (CIV(i).lt.1.0d-50) CIV(i)=0.d0

    SV(i)=KdV*CV(i)
    SIV(i)=KdIV*CIV(i)
enddo
totamountrel=totamountrel+amountreleased
tot_act=0 ! TOTAL ACTIVITY in the LYSIMETER
do i=1, N
    aq_act=vol(i)*(CV(i)+CIV(i))
    ads_act=vol(i)*rho*(SV(i)+SIV(i))
    tot_act=tot_act+aq_act+ads_act
enddo
print*, "Areleased=", totamountrel, " total A=", tot_act

act_out_IV=act_out_IV+(-D(1)*(CIV(2)-
CIV(0))/(2.d0*dz)+v(1)*CIV(1))*teta(1)*4.90874d0*dttrans
act_out_V=act_out_V+(-D(1)*(CV(2)-
CV(0))/(2.d0*dz)+v(1)*CV(1))*teta(1)*4.90874d0*dttrans
do i=1,Np
    act_transV(i)=uptake_effV*CV(i)*S(i)*vol(i)*dt
    act_transIV(i)=uptake_effIV*CIV(i)*S(i)*vol(i)*dt
    tot_act_transV=tot_act_transV+act_transV(i)
    tot_act_transIV=tot_act_transIV+act_transIV(i)
enddo
!print*, "Activity trans V=", tot_act_transV, " a trans IV=",
tot_act_transIV

```

```

!do i=1,N
!print*,"i=",i," CV=",CV(i)," CIV=",CIV(i)
!enddo
!read*

call roottransport
tot_act_root=0.d0
do i=1,Np
    SrV(i)=KdrV*CrV(i)
    SrIV(i)=KdrIV*CrIV(i)
    actrootV=volp(i)*(por_p*CrV(i)+dens*SrV(i))
    actrootIV=volp(i)*(por_p*CrIV(i)+dens*SrIV(i))
    tot_act_root=tot_act_root+actrootV+actrootIV
enddo

enddo ! End of FIELD Time Loop

do i=1,N
    if (CV(i).lt.1.0d-50) CV(i)=0.d0
    if (CIV(i).lt.1.0d-50) CIV(i)=0.d0

    SV(i)=KdV*CV(i)
    SIV(i)=KdIV*CIV(i)
enddo

tot_act=0 ! TOTAL ACTIVITY in the LYSIMETER
do i=1, N
    aq_act=vol(i)*(CV(i)+CIV(i))
    ads_act=vol(i)*rho*(SV(i)+SIV(i))
    tot_act=tot_act+aq_act+ads_act
enddo

print*,"Total Activity=",tot_act
print*,"Activity Out PuIV=",act_out_IV
print*,"Activity Out PuV =",act_out_V
print*,"Total Puo ACTivity Transferred to the Root
System=",tot_act_transV
print*,"Total Pur ACTivity Transferred to the Root
System=",tot_act_transIV
print*,"total activity in the roots=", tot_act_root
read*

!DIFFUSION PERIOD
do i=1,N

```

```

v(i)=0.d0 ! cm/h
D(i)=w*Dif+alfaL*abs(v(i)) !cm2/h
teta(i)=0.2d0
RV(i)=1.d0+rho*KdV/teta(i)
RIV(i)=1.d0+rho*KdIV/teta(i)
enddo
dttrans=1.d0 !h

do while ((t.le.tend).and.(t.gt.tfield))
  do i=1,N
    oldCV(i)=CV(i)
    oldCIV(i)=CIV(i)
  enddo

  iter=0

  do
    maxerrV=0.d0
    maxerrIV=0.d0
    iter=iter+1
    do i=1,N
      pCV(i)=CV(i)
      pCIV(i)=CIV(i)
    enddo
    CV(N+1)=CV(N-1)
    CIV(N+1)=CIV(N-1)
    CV(0)=CV(2) !No Flow
    CIV(0)=CIV(2) !No Flow

    do i=1,N,1
      AAV=2.d0*D(i)/(dz**2)+kr*(RV(i)-
1.d0)+RV(i)/dttrans
      BBVIV=D(i)/(dz**2)
      CCVIV=D(i)/(dz**2)
      AAIV=2.d0*D(i)/(dz**2)+ko*(RIV(i)-
1.d0)+RIV(i)/dttrans
      DDV=ko*(RIV(i)-
1.d0)*CIV(i)+RV(i)*oldCV(i)/dttrans
      DDIV=kr*(RV(i)-
1.d0)*CV(i)+RIV(i)*oldCIV(i)/dttrans

      CV(i)=(CV(i+1)*BBVIV+CV(i-
1)*CCVIV+DDV)/AAV
      CIV(i)=(CIV(i+1)*BBVIV+CIV(i-
1)*CCVIV+DDIV)/AAIV
      SV(i)=KdV*CV(i)

```



```

SIV(i)=KdIV*CIV(i)

enddo

do i=2,N
    errV=abs(CV(i)-pCV(i))
    errIV=abs(CIV(i)-pCIV(i))
    if (errV.gt.maxerrV) maxerrV=errV
    if (errIV.gt.maxerrIV) maxerrIV=errIV
enddo
t=t+dttrans/24.d0 !d
print*, "t=",t

    if ((maxerrV.lt.1E-5).and.(maxerrIV.lt.1E-5)) exit
enddo ! END OF ITERATION LOOP

enddo !END OF DIFFUSION PERIOD

do i=1,N

    write(1,'(E15.5,2x,E10.6,2x,I8,6x,F10.5,3x,E15.5,2x,E15.5,2x,E15.5,2x,E15.5,2x,
F15.5,1x,F20.8,3F15.5)') t,dt,i,z(i),CV(i),CIV(i),SV(i),SIV(i),h(i),q(i),teta(i),K(i),S(i)

    write(2,'(E15.5,2x,E10.6,2x,I8,6x,F10.5,3x,E15.5,2x,E15.5,2x,E15.5,2x,E15.5,2x,
F15.5,1x,F20.8,3F15.5)') t,dt,i,z(i),CV(i),CIV(i),SV(i),SIV(i),h(i),q(i),teta(i),K(i),S(i)
    write(4,'(F12.7,10x,F30.10)') t,h(i)
enddo

do i=1,N

enddo

do i=1,N
    if (CV(i).lt.1.0d-50) CV(i)=0.d0
    if (CIV(i).lt.1.0d-50) CIV(i)=0.d0
    SV(i)=KdV*CV(i)
    SIV(i)=KdIV*CIV(i)
    write(11,'(F12.3,3x,4E12.3)') L-
z(i),CV(i),CIV(i),SV(i),SIV(i)
enddo

do i=1,Np
    SrV(i)=KdrV*CrV(i)
    SrIV(i)=KdrIV*CrIV(i)
    write (12,'(F12.3,3x,5E12.3)') L-
z(i),CrV(i),CrIV(i),SrV(i),SrIV(i),volp(i)

```

```

enddo

tot_act=0
do i=1, N
    aq_act=vol(i)*(CV(i)+CIV(i))
    ads_act=vol(i)*rho*(SV(i)+SIV(i))
    tot_act=tot_act+aq_act+ads_act
enddo

print*, "Total Activity=", tot_act
print*, "Activity Out PuIV=", act_out_IV
print*, "Activity Out PuV =", act_out_V
write (13, '("Total Activity=", 2x, F15.5, 2x, "ko=", 2x, F14.10, 2x, "kr=", 2x,
F14.7)) tot_act, ko, kr
write (13, '("Activity out IV=", 1x, F15.5, 2x, "Aout V=", 2x,
F10.5)) act_out_IV, act_out_V

! TTotal ACTivity In Roots
tot_act_root=0.d0
do i=1, Np
    actrootV=volp(i)*(por_p*CrV(i)+dens*SrV(i))
    actrootIV=volp(i)*(por_p*CrIV(i)+dens*SrIV(i))
    tot_act_root=tot_act_root+actrootV+actrootIV
enddo
print*, "Total activity in the root system =", tot_act_root
write (13, '("Total A root =", 2x, F15.5, 2x, "ArootIV=", 2x,
F10.5, 2x, "ArootV=", 2x, F10.5)) tot_act_root, actrootIV, actrootV

print*, "Total Change in Storage=", total_DS
print*, "Total Bottom Flow=", total_bottom
print*, "Total Top Flow=", total_top
print*, "Total Extraction=", total_E
print*, "Total qI=", qI_total
errorpercent=(1.d0-(total_bottom-total_top-total_E)/total_DS)*100
write (13, '("DS=", 13x, F15.5, 2x, "TBF", 2x, F15.5, 2x, "TTF", 2x,
F15.5, 2x, "TE", 2x, F15.5, 2x, "TqI", 2x, F15.5)) total_DS, total_bottom,
total_top, total_E, qI_total
call cpu_time(time_end)
print*, "Time of Execution= ", (time_end-time_ini)/60, " minutes"
end

```

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