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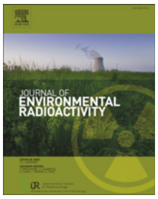

Uptake, distribution, and velocity of organically complexed plutonium in corn (*Zea mays*)

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ABSTRACT

Lysimeter experiments and associated simulations suggested that Pu moved into and through plants that invaded field lysimeters during an 11-year study at the Savannah River Site. However, probable plant uptake and transport mechanisms were not well defined, so more detailed study is needed. Therefore, experiments were performed to examine movement, distribution, and velocity of soluble, complexed Pu in corn. Corn was grown and exposed to Pu using a "long root" system in which the primary root extended through a soil pot and into a hydroponic container. To maintain solubility, Pu was complexed with the bacterial siderophore DFOB (Desferrioxamine B) or the chelating agent DTPA (diethylenetriaminepentaacetic acid). Corn plants were exposed to nutrient solutions containing Pu for periods of 10 min to 10 d. Analysis of root and shoot tissues permitted concentration measurement and calculation of uptake velocity and Pu retardation in corn. Results showed that depending on exposure time, 98.3–95.9% of Pu entering the plant was retained in the roots external to the xylem, and that 1.7–4.1% of Pu entered the shoots (shoot fraction increased with exposure time). Corn Pu uptake was 2–4 times greater as Pu(DFOB) than as $Pu_2(DTPA)_3$. Pu(DFOB) solution entered the root xylem and moved 1.74 m h $^{-1}$ or greater upward, which is more than a million times faster than Pu(III/IV) downward movement through soil during the lysimeter study. The Pu(DFOB) xylem retardation factor was estimated to be 3.7–11, allowing for rapid upward Pu transport and potential environmental release.

1. Introduction

Due to long-term human and environmental health concerns, plant uptake of Pu has previously been studied with objectives focused on bioaccumulation or phytoremediation (Adriano et al., 1986; Hossner et al., 1998; Lee et al., 2002; Whicker et al., 1999). These studies quantified Pu concentrations in edible plant parts or the entire aboveground biomass. Results indicated that small amounts of Pu were incorporated in aboveground plant tissue, within a growing season. In general, such concentrations were very small relative to soil concentrations, yet the distance transported in plants was relatively large. To understand how plants may impact root zone transport of Pu, discrete temporal and spatial analyses are required.

The main motivation for the present work is illustrated in Fig. 1, which is a plot of Pu soil concentration data versus depth from three lysimeters at the Savannah River Site (SRS), located in South Carolina, USA. The data result from reduced Pu (III, IV) sources on filter paper that were buried at 0.26 m depth and were in the field for about 11 years. Most of the Pu was observed near the sources, however for all sources significant transport was observed below and above the source burial depth. Native grasses (primarily, crabgrass (*Digitaria sanguinalis*), bahiagrass (*Paspalum notatum*), and broomsadge (*Andropogon virginicus*)) invaded the open lysimeters and were periodically cut and deposited on the soil (Demirkanli et al., 2008, 2009; Kaplan et al., 2006). Over long time periods in the field, plant transpiration accounts for a large water flux, so relatively small Pu uptake by plants may affect its distribution in the root zone (Kaplan et al., 2010).

The models used to simulate the Pu concentration data are based on soil water flow, transport of oxidized Pu (Pu(V) and Pu(VI), the mobile forms) and reduced Pu (Pu(III) and Pu(IV), the less mobile forms), redox transformation reactions on mineral surfaces, and equilibrium adsorption and desorption of both forms of Pu. (As detailed in Demirkanli et al. (2009), the interactions of these processes result in the overall shape of the Pu distribution curves

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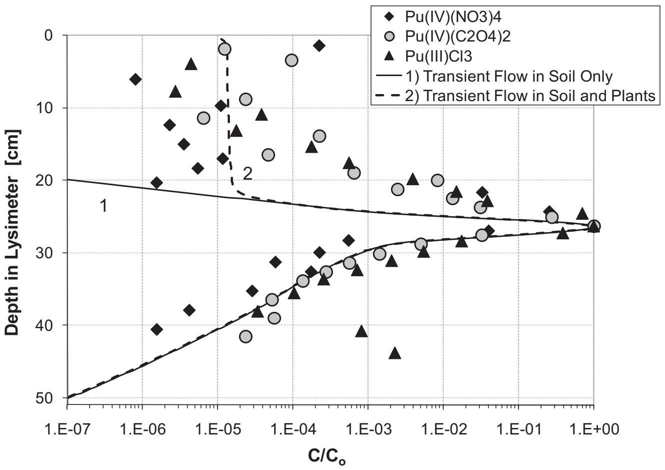

Fig. 1. Best-fit model simulations compared with the measured distributions for Savannah River Site lysimeters containing reduced Pu sources that were buried for 11 years. C/C_o is the soil Pu concentration relative to the source concentration. Curve 1 results from Pu transport in the soil only, while curve 2 allows for transport in both the soil and plants. Little transport above the source (26 cm depth) occurs without including plant transport. (Figure formed by partial combination of Figs. 2 and 7 from Demirkanli et al. (2009)).

shown in Fig. 1.). Simulations of Pu transport in soil only (curve 1) and in both soil and lysimeter plants (curve 2) indicate that significant upward transport can only be obtained with Pu uptake by roots, movement in the xylem and redistribution into the surrounding plant tissues during each growing season. Previous studies (Demirkanli et al., 2008, 2009) demonstrated that evaporation, diffusion, hydraulic hysteresis, and dynamic Pu redox changes induced by variable saturation were not responsible for the Pu upward movement. Simulations including only these processes did not even fit the data above the source qualitatively. Comparing curves 1 and 2, the concentration data above 20 cm depth imply that Pu was transported to the ground surface and possibly deposited there. Motivated by this observation, isotopic ratio analyses of surface soils from these lysimeters confirmed that a Pu residue detected on the ground surface originated from the sources below (Kaplan et al., 2010). Transport of reduced Pu in soil is highly retarded (Choppin et al., 2001; Demirkanli et al., 2008; Kaplan et al., 2006), with a soil distribution coefficient of 1800 $cm^3\ g^{-1}$ (1.8 $m^3\ kg^{-1}$) for curves 1 and 2 of Fig. 1 ($Retardation_{soil} \approx 12{,}000$; velocity ratio of water to plutonium), whereas oxidized Pu is relatively quite mobile with a soil distribution coefficient of 3 $cm^3\ g^{-1}$ (0.003 $m^3\ kg^{-1}$; $Retardation_{soil} \approx 15$). The effect of a 15 $cm^3\ g^{-1}$ (0.015 $m^3\ kg^{-1}$) Pu xylem distribution coefficient is shown in curve 2 of Fig. 1 ($Retardation_{plants} \approx 10$, where xylem density is 0.32 g cm^{-3} (0.00032 kg m^{-3}) and porosity is 0.74). This plant xylem distribution coefficient implies that Pu is moving upward in the xylem as a mobile complex, and obtaining experimental support for such an implication is a main objective of this study.

Since plants have no known need for Pu, the uptake of Pu may occur in response to a nutrient requirement for iron (Neu et al., 2002). Fe(III) and Pu(IV) are similar in that they have: (1) identical charge/ionic radius ratios of 47 nm^{-1}; (2) similar first hydrolysis constants (Fe^{3+} Log K = 11.1, Pu^{4+} Log K = 12.2); and (3) nearly identical complexation constants with Desferrioxamine B (DFOB) (Fe^{3+} Log K = 30.6, Pu^{4+} Log K = 30.8) (Neu et al., 2002). It has been suggested that bacterial and plant siderophores that incorporate Fe can complex Pu and enhance mobility of Pu in plants (John et al., 2001; Neu et al., 2002; Ruggiero et al., 2002). John et al. (2001) demonstrated that siderophores enhanced Pu accumulation in a bacterium (*Microbacterium flavescens*), and that plutonium uptake interfered with iron uptake. However, similar demonstrations have not been made for plants.

Plants regulate their internal nutrient concentrations by homeostasis (Marschner, 1995) and have specific transport pathways for water, K^+, Fe^{2+}, Fe^{3+}, and other materials. Transport in plants occurs within the context of the soil–plant–atmosphere continuum. Water and some soluble nutrients move across root cell layers into the xylem in the transpiration stream, driven by vapor loss at leaf surfaces (Sperry et al., 2003). Once inside the xylem, transport of soluble constituents is mainly an advective process (Bollard, 1960; Mori et al., 2000) subject to applicable retardation. The use of complexants to increase the plant uptake of Pu is believed to enhance transport through the root tissues (Garland et al., 1987). Rapid siderophore-facilitated root transport pathways have been demonstrated with Fe (Romheld and Marschner, 1986; Schaaf et al., 2004; Yehuda et al., 1996) and with Zn (Suzuki et al., 2006). However, the mechanisms of root uptake of Pu are poorly understood.

Garland et al. (1981) and Cataldo et al. (1988) characterized the Pu fluids inside soybeans by analyzing xylem exudates collected by cutting the stem below the first leaf node. They demonstrated that after passing through the roots, Pu_2DTPA_3 changed to an unidentified plant-complexed Pu species not subject to rapid hydrolysis (DTPA is diethylenetriaminepentaacetic acid, a commercial chelating agent). Cataldo et al. (1988) compared the behavior of organo-complexed Pu^{4+}, Fe^{3+}, Ni^{2+}, and Cd^{2+} by gel electrophoresis and found that Pu^{4+} and Fe^{3+} exhibited similar behavior.

A considerable body of research has quantified the partitioning of Pu between shoot and root tissues after fairly long exposure time intervals (weeks to years) (Adriano et al., 2000; Garland et al., 1981; Nisbet and Shaw, 1994), yet a fundamental understanding of the movement of Pu into living plants is lacking. The objectives of the present study are to record and measure the short-term uptake and distribution of organically complexed Pu in corn (*Zea mays*) using exposure times of minutes to days. Potential plant barriers to Pu transport will be identified and a more refined estimate will be made of Pu transport velocity and retardation factor in living corn xylem (Thompson, 2010). We chose to use complexed Pu because that is the form found in plants (Garland et al., 1981); uncomplexed Pu does not tend to enter the plant root, and if it does, it immediately becomes complexed, like Fe, with organic molecules (Garland et al., 1981; Namba and Murata, 2010). Importantly, by using complexed Pu, this study is limited to statements about where and how rapidly the complexed Pu moves in corn, and is not addressing the rate with which Pu moves from soil to plant root. We selected corn because we were interested in studying complexed Pu uptake in annual grasses (*Poaceae*). Corn has many structural and physiological similarities to grasses, along with the advantages of growing larger and faster than grasses.

2. Materials and methods

Plants grew in soil pots resting on nutrient solution containers (Fig. 2). As shown in Fig. 2 (left), plants grew on a bench under plant lights. The photograph at right reveals the primary root with the soil and nutrient containers removed and the roots spread apart. Experiments were conducted using plants with their distal roots in solution and proximal roots in soil. This experimental arrangement was devised to permit the roots to develop a more natural physiology in the soil while permitting introduction of the organically complexed Pu into the hydroponic solution without soil sorption or soil microbial degradation of the siderophore.

The nutrient solution was based on one formulated by Garland et al. (1981), that contained (in mg L^{-1}): 946 $Ca(NO_3)_2 \cdot 4H_2O$, 150 KCl, 120 $MgSO_4$, 68 KH_2PO_4, 0.69 H_3BO_3, 0.06 $ZnSO_4 \cdot 7H_2O$, 0.024