

# Removal of Uranium from Water Using Terrestrial Plants

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Uranium (U) contamination of groundwater poses a serious environmental problem in uranium mining areas and in the vicinity of nuclear processing facilities. Preliminary laboratory experiments and treatability studies indicated that the roots of terrestrial plants could be efficiently used to remove U from aqueous streams (rhizofiltration). Certain sunflower plants were found to have a high affinity for U and were selected for treatment of contaminated water. Almost all of the U removed from the water in the laboratory was concentrated in the roots. Bioaccumulation coefficients based on the ratios of U concentrations in the roots vs U concentrations in the aqueous phase reached 30 000. Rhizofiltration technology has been tested in the field with U-contaminated water at concentrations of 21–874  $\mu\text{g/L}$  at a former U processing facility in Ashtabula, OH. The pilot-scale rhizofiltration system provided final treatment to the site source water and reduced U concentration to <20  $\mu\text{g/L}$  (EPA Water Quality Standard) before discharge to the environment. System performance was subsequently evaluated under different flow rates permitting the development of effectiveness estimates for the approach.

## Introduction

Radioactive contamination remains one of the most menacing legacies of the Cold War. Severe soil and water contamination occur in the areas of radioactive material mining and reprocessing. Radionuclide contaminants in water are usually removed by ion exchange, reverse osmosis, microfiltration, precipitation, or flocculation. These methods may be arduous to accomplish and can be prohibitively expensive for large water volumes, low metal concentrations, high total salt content, and low discharge limits. Recently, there has been some research into the use of living and non-living microbial biomass for the bioremediation and recovery of heavy metals from aqueous streams (1). Commercial applications of this research are still limited by the high cost of growing pure cultures of cells and microorganisms and by the need for their immobilization or separation from the aqueous stream.

Rhizofiltration (2, 3), an emerging new technology implementing the use of terrestrial plant roots in the remediation of aqueous streams, may provide a cost-effective method to treat pollutants at concentrations that are too low for efficient

removal by conventional methods while too high to allow discharge to the environment.

Plants have a unique ability to concentrate essential and non-essential elements from the environment in their tissues. Green plants use sunlight, the most abundant source of energy, to power this concentration process. In their continuous search for water and mineral resources, terrestrial plants develop an extensive root system and an advanced uptake mechanism. The total length of roots (including root hairs) of a single pot-grown rye plant is about 620 km (4), with a total surface area exceeding 3000  $\text{m}^2$ . The root system of the plant can be even bigger when field grown. Plants selectively accumulate in their tissues such heavy metals as Fe, Mn, Zn, Cu, Mg, Mo, and Ni. These metals play an important role in plants, serving as components of enzymes, structural proteins, pigments, and signal transduction and as a means of maintaining ionic balance and osmotic potential (5). Plants are not capable of distinguishing isotopes of the same element. Radioactive isotopes like  $^{14}\text{C}$ ,  $^{18}\text{O}$ ,  $^{32}\text{P}$ ,  $^{35}\text{S}$ ,  $^{64}\text{Cu}$ , and  $^{59}\text{Fe}$  are widely used as tracers in plant physiology and biochemistry. In some cases plants, react analogously to ions with similar physicochemical properties. It is known that Sr is an analog of Ca in living organisms (6), and the effect of K on  $^{137}\text{Cs}$  uptake in plants is well documented (7).

Rhizofiltration is defined as a process where plant roots are utilized to absorb, concentrate, and precipitate heavy metals from polluted effluents (8). Roots of many hydroponically grown terrestrial plants, e.g., Indian mustard (*Brassica juncea* (L.) Czern.), sunflower (*Helianthus annuus* L.), and various grasses can be used to remove toxic metals such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$  from aqueous solutions (9).

In the middle of the 20th century, the danger of releasing radioactive materials in the environment was recognized. The cooling system of a radioactive waste containment unit malfunctioned, and the tank with radioactive waste exploded in 1957 near the city of Kyshtym on the east side of the southern Urals (Russia). Studies of the consequence of the accident and systematic dumping of radioactive materials in the Techa River and Lake Karachay showed that plants played an important role in the radionuclides transfer in the contaminated ecosystems (10). One of the first prototypes of radioactive waste treatment based on plants (11) was proposed soon afterward.

This study was focused on removal of radionuclides from aqueous streams by rhizofiltration. This work demonstrates, through a field-scale evaluation, the feasibility of using rhizofiltration to remove uranium from water. Rhizofiltration, as a technology, could be beneficial for long-term treatment of large water volumes with low levels of radionuclide contamination.

## Experimental Section

**Materials and Methods.** *Plant Material.* Indian mustard seeds cv. 426308 were obtained from the USDA/ARS Plant Introduction Station of Iowa State University. Sunflower hybrid 187 (SF-187) was provided through the courtesy of Cargill Hybrid Seeds. The seeds of other plants were purchased from local seed markets. Seedlings were cultivated hydroponically in an aerated nutrient solution [1 g/L Hydrosol supplemented with 0.6 g/L  $\text{Ca}(\text{NO}_3)_2$ ]. Each hydroponic unit consisted of a PVC plastic cylinder (12 cm tall, 10.5 cm in diameter), which contained two plants supported by an aluminum grid (positioned 7 cm from the bottom), and a 2 cm deep feeder layer of Pro-Mix potting soil placed on top of the grid. Eight hydroponic units were placed in a common tray containing 4 L of the nutrient solution. After 2–4 weeks,

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plants were selected for uniformity. Prior to metal uptake experiments, roots were rinsed in deionized water to remove traces of the nutrient solution.

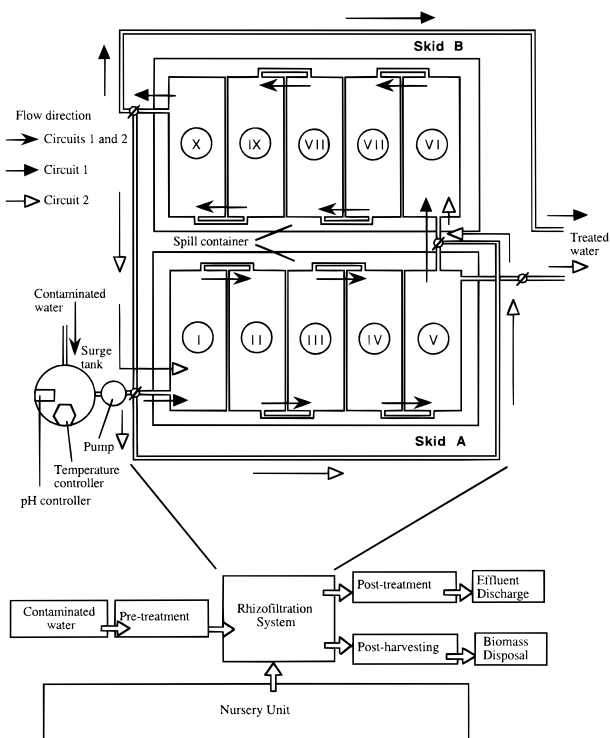
**Experimental Systems. Growth Chamber Experiments.** The screening of cultivars and the measurement of metal removal from water by sunflower roots were conducted in a growth chamber. The cylinders containing plants were put on top of a 13 cm deep plastic jar that contained 750 mL of continuously aerated media. The total volume of the solution was kept constant by adding deionized water to compensate for water lost through plant transpiration, sampling, and evaporation. Experiments were done in a growth chamber at 25 °C, 75% relative humidity, and 16 h photoperiod (600  $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) provided by a combination of incandescent and cool-white fluorescent lights. Control treatments did not contain plant material. The Ashtabula site water or salts of  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{CsNO}_3$  were used as the source of metals in the growth chamber experiment. As necessary, the pH of the solutions was adjusted daily using reagent-grade  $\text{HNO}_3$  or  $\text{KOH}$ .

**Greenhouse Experiments.** Miniature batch rhizofiltration systems were used to determine the impact of U concentration and pH in the solution on U concentrations in plant tissues. Plastic tubs with an internal volume of 80 L were filled with 60 L of U solution of known concentration. Uranyl acetate salt added to tap water was used as the source of U in the greenhouse experiments. As necessary, the pH of the solutions was adjusted to 5.0 or 7.0 daily using reagent-grade  $\text{HNO}_3$  or  $\text{KOH}$ .

Sunflower plants were grown hydroponically as described above for 3 weeks. Roots were rinsed with deionized water, and plants were placed on floating Styrofoam platforms so that the roots were exposed to the U solution. The solution was continuously aerated, and the uptake experiments were conducted in a greenhouse at 24 °C and 16 h photoperiod. After 1 week of treatment, the roots and shoots were harvested separately, rinsed in deionized water, dried, and analyzed for U content.

Rhizofiltration technology was tested with a field-scale system with uranium-contaminated water at concentrations of 21–874  $\mu\text{g/L}$  at a former uranium processing facility in Ashtabula, OH. Following site identification, water samples were sent to Phytotech for chemical analysis and treatability studies. The Ashtabula site source water used for the treatability study was stored at 5 °C and brought to room temperature before treatment.

On the basis of the results of the treatability study, a pilot-scale rhizofiltration system was designed and erected in a small greenhouse at the Ashtabula site. A general water flow diagram of the pilot rhizofiltration system is shown in Figure 1. Inert plastic was used to build the system tanks. The effluent was filtered through a 1-mm screen to prevent root debris from exiting the system. All root debris were collected and added to the roots for analysis. A local nursery was contracted to grow sunflower plants hydroponically until they were ready to be transferred to the rhizofiltration system. Plants were grown hydroponically using  $33.5 \times 43.5$  cm flats with a 2 cm deep feeder layer of Pro-Mix for 6 weeks. Well-established plants were moved to the rhizofiltration system and were used for 2 weeks for water treatment. A portable greenhouse ( $6.00 \times 4.25$  m) with temperature control system, supplementary lighting, and all necessary electrical and water connections (manufactured by Nexus, Inc.) was erected by Phytotech at the site. The pilot rhizofiltration system was assembled in the greenhouse. A surge tank was used for the pretreatment of the source water. The water temperature was maintained at 24 °C, and the pH was automatically adjusted to  $5.5 \pm 0.3$ . The system consisted of two skids. Each of the skids contained five sequentially connected tanks of 150 L each. The system design allowed two circuits of water flow (Figure 1). This design permitted an independent



**FIGURE 1.** Scheme of the commercial rhizofiltration unit with a flow diagram of rhizofiltration system at the Ashtabula site. Six-week-old sunflower plants were placed in the system for 2 weeks. During the operation, plants in skids A and B were alternatively harvested and replaced with a new set of plants from the nursery. Flow circuits were changed weekly to ensure effective removal of U at low concentrations with fresh sunflower roots.

usage of skids, two directions of water flow, and flexibility in flow rates. Water samples were taken at regular intervals from all the tanks in the system.

**Sample Preparation and Analysis.** All water samples were acidified with analytical-grade concentrated  $\text{HNO}_3$ . Roots and shoots were harvested separately, rinsed in deionized water, placed in paper bags, and dried at 70 °C in a forced-air convection oven. The dried material was ground to uniform size ( $< 1$  mm) using a stainless steel grinder. For wet digestion analysis (12), 250 mg of dry plant material was mixed with 5 mL of concentrated  $\text{HNO}_3$  in a Folin Wu digestion tube for at least 6 h at room temperature. The samples were then heated at 180–200 °C until the dense yellow fumes disappeared and were boiled until the volume was reduced by approximately 50%. One milliliter of concentrated  $\text{HClO}_4$  was added to the cooled tubes. The tubes were heated again until the solution was clear (about 60–90 min), then removed from the heating block, and brought to 25 mL with deionized water. The resulting solution was analyzed for metal content by inductively coupled plasma spectrometry (ICP) (Fisons Accuris, Fisons Instruments, Inc., Beverly, MA) or mass spectrometry ICP–MS (Fisons Plasma Quad, Fisons Instruments, Inc., Beverly, MA). Certified National Institute of Standards and Technology plant (peach leaf) standards were carried through the digestion and analyzed as part of the QA/QC protocol. Reagent blanks and spikes were used where appropriate to ensure accuracy and precision in the analysis.

## Results

**Screening of Cultivars.** The following four different plant cultivars were tested for their ability to remove U from the Ashtabula site water with U concentration of 56  $\mu\text{g/L}$ : sunflower (*Helianthus annuus* L.) cv. SF-187 and cv. Mammoth giant, bean (*Phaseolus coccineus* L.) cv. White Half Runner, and Indian mustard (*Brassica juncea* (L.) Czern.) cv.

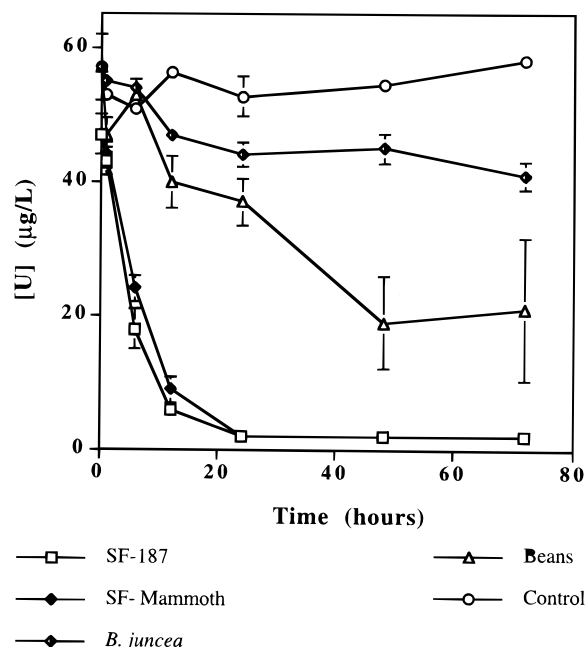


FIGURE 2. Rhizofiltration of Ashtabula site water. Four-week-old hydroponically grown plants were used to treat 750 mL of the Ashtabula site water. Plant cultivars: sunflower cv. SF-187 (root DW  $1.81 \pm 0.15$ ), sunflower cv. Mammoth giant (root DW  $2.93 \pm 0.19$ ), beans (root DW  $1.93 \pm 0.15$ ), *Brassica juncea* (root DW  $1.38 \pm 0.19$ ). Vertical bars denote SE ( $n = 3$ ).

426308. Experiments were conducted in the growth chamber using plastic jars containing 750 mL of the site water. Both sunflower cultivars removed greater than 95% of U from the solution in 24 h (Figure 2). Beans and Indian mustard were less effective in U removal. After 48 h of treatment, however, beans also reduced U concentration to the proposed drinking water limit at 20 µg/L. Analysis of U distribution in the sunflower (cv. SF-187) system showed that practically all of the U was concentrated in the roots. The amount of U transported to shoots was negligible. Uranium concentration in shoots did not significantly differ from the U concentration in the shoots of the untreated plants.

**Metal Removal from Water by Sunflower Roots.** Four-week-old sunflower plants were used to treat water that contained added metals. Each replicate contained 750 mL of water and 200 µg/L Cs, 200 µg/L Sr, or 600 µg/L U. Ten-milliliter samples were taken periodically to monitor metal concentrations. The treatment of Cs, U, or Sr solution with sunflower roots reduced dramatically the concentration of metals within a few hours (Figure 3).

Different types of removal kinetics were found for metals tested (Figure 3). The plants were most effective in removing U from water. Uranium concentration decreased 10-fold to 63 µg/L in 1 h. After 48 h, an equilibrium was reached at 10 µg/L. For Cs there was no reduction in concentration within the first hour of treatment. However, after 6 h a noticeable reduction in Cs concentration was measured. Within 24 h, almost all of the Cs was removed, leaving a final concentration of less than 3 µg/L. Strontium concentration was reduced to 35 µg/L within 48 h. The concentration of Sr continued to decline for the next two days, reaching a level of 1 µg/L. The concentration of each metal in the controls remained constant for the duration of the experiment.

**Effect of Concentration and pH on Uranium Uptake by Sunflower Plants.** Three-week-old hydroponically grown sunflower plants were transferred to miniature batch rhizofiltration systems containing U concentrations of either 10, 30, 90, 810, or 2430 µg/L. The experiment was conducted simultaneously at pH levels of 5.0 and 7.0. The plants were

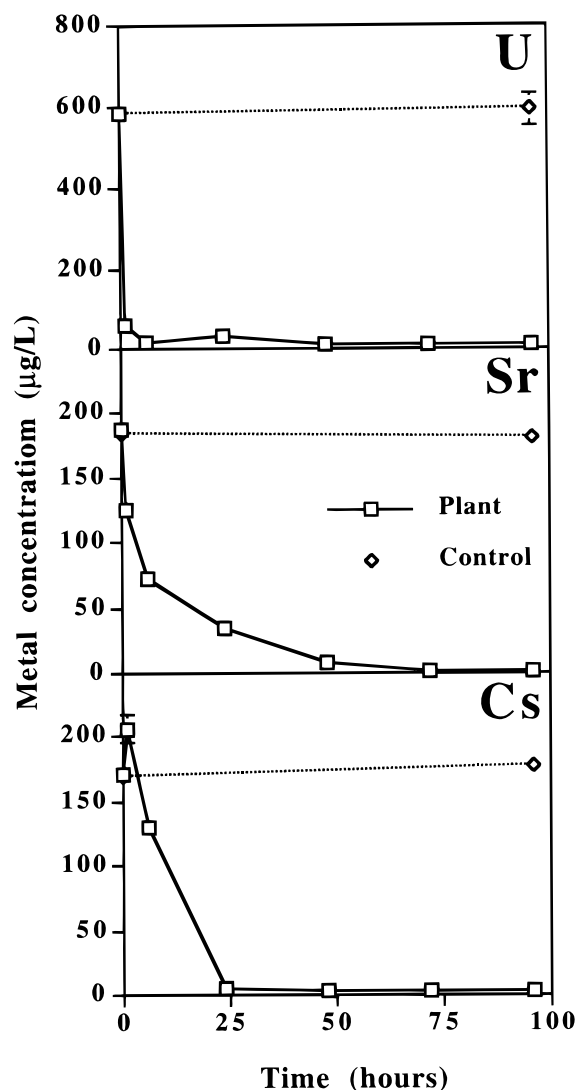


FIGURE 3. Rhizofiltration of U, Sr, and Cs. Four-week-old sunflower plants (cv. 187) were used to treat 750 mL of solution. Roots DW was respectively  $1.21 \pm 0.20$  g for U,  $1.13 \pm 0.08$  g, for Sr, and  $0.94 \pm 0.21$  g for Cs. Vertical bars denote SE ( $n = 3$ ).

grown for 1 week in the U solution. No signs of phytotoxicity were observed. The plants approximately doubled their biomass during the week (data not shown).

Uranium levels in the sunflower shoots generally remained below 2 µg/g dry weight (DW). Slightly elevated U concentrations in shoots were observed only at the highest concentration of U (2430 µg/L) and low pH (Figure 4), reaching 5 µg/g. The U concentrations in roots increased linearly with increasing solution concentration. Sunflower roots adsorbed more U at pH 5 as compared to pH 7. The shoots to roots ratio of U concentration (Figure 4) clearly shows that there is no significant transport of U to the above-ground matter.

The bioaccumulation coefficient was expressed as a ratio of metal concentration in the plant tissue (µg/kg DW) to the metal concentration in the solution (µg/L). Bioaccumulation coefficient for sunflower shoots were low (Table 1); however, sunflower roots concentrated uranium from solution up to 10 000-fold. No dramatic difference was found in bioaccumulation coefficients for different U concentrations used; however, lower pH resulted in a significant increase of U bioaccumulation. In the range of concentrations from 10 to 2430 µg/L, an average bioaccumulation coefficient for U in sunflower roots was  $6624 \pm 870$  and  $3379 \pm 430$  for pH 5 and pH 7, respectively.

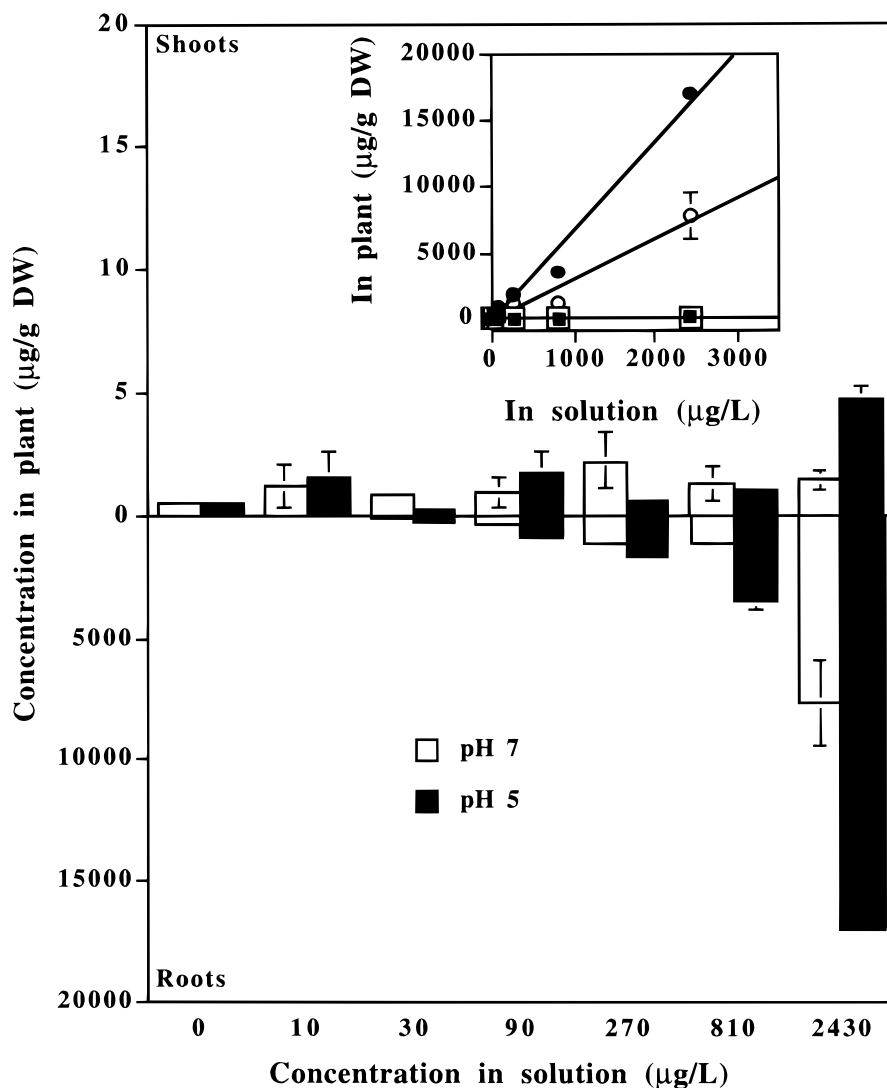


FIGURE 4. Uranium concentrations in 4-week-old sunflower plants treated for 1 week in 60-L miniature batch rhizofiltration systems. Initial concentration of U in solution is shown on the X axis. The regression analysis for roots (●, pH 7; ○, pH 5) and shoots (■, pH 7; □, pH 5) is displayed in the inset. The solution pH was adjusted daily using 1 M KOH or 1 M HNO<sub>3</sub>. Vertical bars denote SE ( $n = 3$ ).

TABLE 1. Bioaccumulation Coefficients for Sunflower Plants (Cultivar SF-187)<sup>a</sup>

U (µg/L)	bioaccumulation coefficient			
	pH 7		pH 5	
	shoots	roots	shoots	roots
10	119 ± 83	3721 ± 144	150 ± 114	4227 ± 252
30	28 ± 5	3786 ± 572	9 ± 3	8438 ± 536
90	11 ± 7	3903 ± 342	19 ± 11	9480 ± 846
270	8 ± 4	4316 ± 193	2 ± 0	6243 ± 116
810	2 ± 1	1360 ± 57	1 ± 0	4336 ± 342
2430	1 ± 0	3186 ± 719	2 ± 0	7021 ± 47

<sup>a</sup> The plants were grown in a miniature batch rhizofiltration systems with different U concentrations. For each experiment roots of three sunflower plants were immersed in 60 L of solution.

**Rhizofiltration System Operation.** *Ashtabula Site Water Characteristics.* Uranium-contaminated water from a former uranium processing facility in Ashtabula, OH, contained treated process water with pH from 6.8 to 7.9. Water temperature was changing seasonally from 13 to 20 °C. The uranium concentration in the water fluctuated from 21 to 874 µg/L (24.6–304 pCi/L) with <sup>238</sup>U as the major isotope. The concentration of major elements in the contaminated water stream is presented in Table 2. The water contained

relatively high concentrations of Ca, K, Mg, Na, and S. The remaining tested elements had concentrations ≤1 mg/L. Traces of As, Mn, and Ni were also detected.

**Flow Rate Test.** To evaluate the dynamic characteristics of the pilot system, different initial flow rates were used. The system U concentration profile for a flow rate of 0.15–1.60 L/min is shown in the Figure 5. The pilot-scale rhizofiltration system reduced the U concentration from several hundred micrograms per liter to below the regulatory discharge level of 20 µg/L. By increasing the flow rate and thus reducing the residence time in the tanks, the highest flow rate giving desirable system operation was found to be approximately 1 L/min. Reductions in soluble U concentrations correlated with the increased concentration of U in the roots (Figure 6). As expected, the highest U concentration in roots was observed in the first tank of the system. Under continuous flow, roots were able to accumulate more than 1.0% of U on DW basis, producing a bioaccumulation coefficient of 30 000.

**Uranium Removal at High Concentrations.** To test the ability of the rhizofiltration system to treat high inlet concentrations of U, the influent was spiked for 1 week with UO<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> stock solution (350 mg U/L) to bring the concentration to over 1000 µg/L at a flow rate of 1.05 L/min. Under these conditions, the U concentration was reduced by 95% with the effluent concentration ranging from 40 to 70 µg

TABLE 2. Major Element Concentrations in Source Water at Ashtabula Site<sup>a</sup>

sample no.	concentration ( $\mu\text{g/L}$ )											
	Al	Ca	Co	Cu	Fe	K	Mg	Na	S	Sr	U	Zn
1	73	34 239	85	94	104	6 975	2 344	24 340	26 608	100	100	223
2	92	50 317	53	103	94	5 519	13 622	36 549	22 694	110	21	163
3	364	60 155	44	78	1096	4 513	14 215	50 394	28 489	175	325	143
4	79	85 087	59	239	91	5 614	11 977	27 988	16 477	664	634	197
5	139	49 320	87	111	169	6 329	15 368	19 438	19 346	95	874	137
6	96	98 376	112	136	52	7 692	19 332	32 994	27 319	507	209	103
7	78	78 780	73	89	42	6 526	18 648	31 994	23 806	311	196	112

<sup>a</sup> Samples were taken at different times during the rhizofiltration system operation.

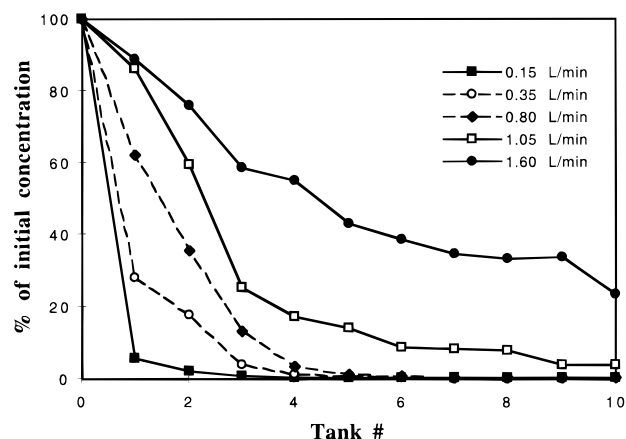


FIGURE 5. Uranium concentration profile in the pilot rhizofiltration system at different flow rates. The concentration in the surge tank was used for a 0 point. The tank's position is shown in Figure 1. Circuit 1 flow was used for all experiments.

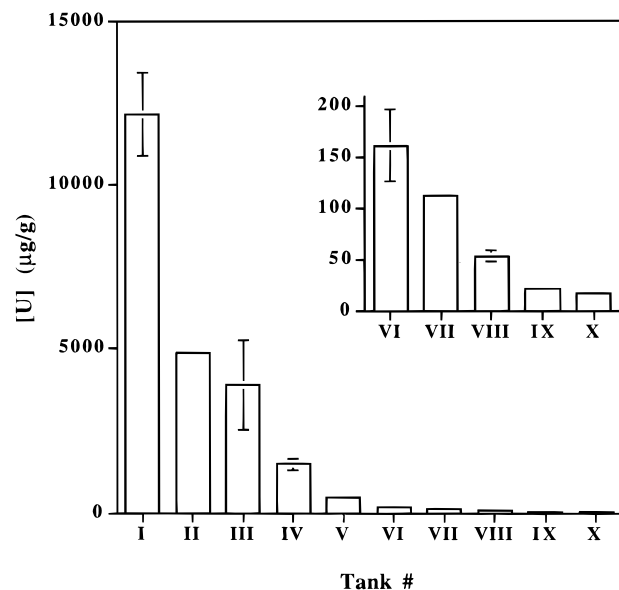


FIGURE 6. Uranium concentration in roots after 2 weeks of continuous operation of the pilot rhizofiltration system at the flow rate of 1.05 L/min. Inset displays the U concentration in last five tanks. Vertical bars denote SE ( $n = 4$ ).

U/L (Figure 7). Thus, the desired discharge concentration of 20  $\mu\text{g/L}$  was not achieved under the tested conditions.

**Routine Pilot-Scale System Operation.** To simulate commercial operating conditions, the pilot rhizofiltration system was operated continuously for 3–8 weeks using several flow rates. At the beginning of this period, the rhizofiltration system was filled with clean tap water, and 6-week-old sunflower plants were placed in both skids. The water flow direction was set by using flow circuit 1 (Figure 1). After the

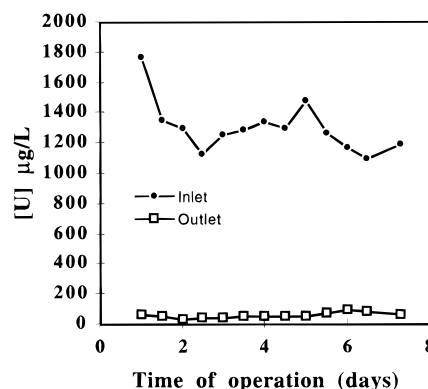


FIGURE 7. Pilot rhizofiltration system performance at the high level of U concentrations in influent. The influent was spiked for 1 week with  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$  stock solution (350 mg U/L) to bring the concentration over 1000  $\mu\text{g/L}$  at a flow rate of 1.05 L/min.

first week, sunflower plants loaded with U in skid A were harvested and replaced with a fresh set of plants. The water flow direction was changed to circuit 2 (Figure 1). This way plants in skid B were exposed to the high concentration of U in the system. During the operation, plants in skids A and B were alternately harvested and replaced with new sets of 6-week-old sunflower plants from the nursery. The plants were exposed to U-contaminated water for 2 weeks. At the end of the operating period, plants in both skids were harvested simultaneously. Plant biomass was dried and analyzed for U content. Shoots of the sunflower plants contained negligible amounts of U ( $<5 \mu\text{g/g}$ ).

Results of the pilot-scale rhizofiltration system operation showed that, from an average influent U concentration of 207  $\mu\text{g/L}$  (Figure 8), the effluent concentration was generally reduced below 20  $\mu\text{g/L}$ . Several spikes with the influent U concentration over 500  $\mu\text{g/L}$  did not significantly effect rhizofiltration system performance.

## Discussion

The greenhouse experiments and performance of the pilot-scale rhizofiltration system clearly demonstrated that it is possible to use hydroponically grown terrestrial plants to remove uranium from contaminated water. Using the rhizofiltration system based on sunflower plants, a total of more than 200 000 L of wastewater was treated at Ashtabula, OH, resulting in U concentrations below the regulatory discharge level of 20  $\mu\text{g/L}$ .

Uranium was removed much faster from the contaminated water as compared to Cs and Sr. The mechanism of U uptake and translocation in plants is still largely unknown. In terrestrial plants, the concentration of U in the above-ground parts was reported to be in the range from 0.005 to 8 mg/kg DW (6). In the growth chamber experiments, more than 99% of U associated with plant matter was found in the roots. Sunflower plants used in the pilot-scale rhizofiltration system were able to accumulate  $>1\%$  of U in their roots. In hydroponic experiments, the ability of the roots to remove

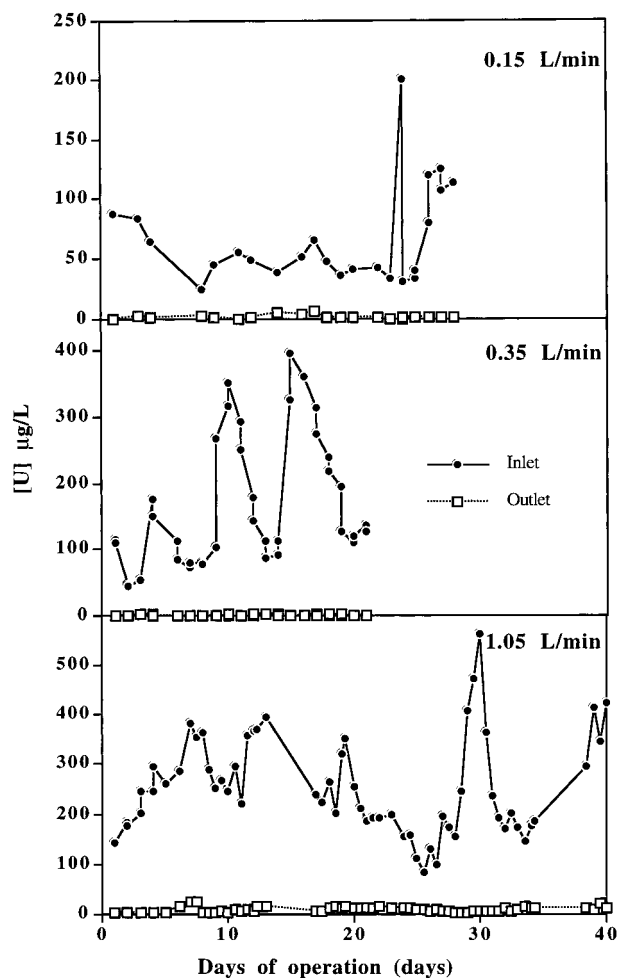


FIGURE 8. Pilot rhizofiltration system performance at the Ashtabula, OH, site. Sunflower plants were grown hydroponically for 6 weeks and then were transferred to the rhizofiltration system for 2 weeks. Plants were periodically harvested and replaced with fresh plants from the nursery. The pilot rhizofiltration system was assembled in the greenhouse. A surge tank was used for the pretreatment of the source water. The water temperature was maintained at  $24\text{ }^{\circ}\text{C}$ , and the pH was automatically adjusted to  $5.5 \pm 0.3$ . System performance at three different flow rates is shown in this figure.

U from solution is species dependent. The specially selected cultivars of sunflower plant proved to be more effective in uranium removal from water than beans or Indian mustard.

The best environment for uranium removal using rhizofiltration was at moderate acidic pH. This correlated with biosorption data (13, 14). The MINTEQA2 PC program (V 3.10, courtesy of W. Lindsay) was used to simulate uranium speciation in the Ashtabula site source water. At pH 5.5, uranium was mostly present as  $\text{UO}_2\text{OH}^+$  (56%) and  $\text{UO}_2^{2+}$  (27%) cations. The results obtained during treatability study and the pilot-scale rhizofiltration unit operation also match the current understanding of uranium chemistry (15). The majority of the uranium associated with plant material was found in the roots. Precipitation on the root surface and compartmentalization in root cells could prevent uranium movement along the vascular system to above-ground matter. The chemical structure and architectonic of the plant cells differs significantly from the properties of bacterial and fungus cells used for biosorption. That is why several suggested mechanisms of uranium biosorption (16, 17) could be only of a limited application to the rhizofiltration process.

Plant roots are functionally and morphologically divided in several zones (18), and each zone could play a particular role in U removal from the solution. Kinetics of U removal from solution in the growth chamber experiments suggest

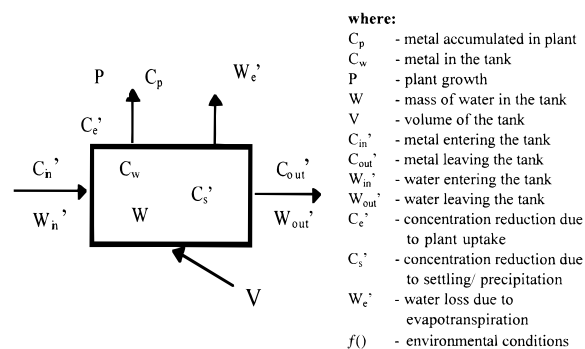


FIGURE 9. Variables of the rhizofiltration process in a single tank. All variables could have direct or indirect effect on the kinetics of U removal from the contaminated water. The metal concentration available to the plants [ $C_a = f(C_w, C_{in}^*)$ ] was introduced as an integrated variable for modeling purposes.

that U absorption by roots could be a mechanism for the initial rapid phase of U concentration reduction. Surface absorption is a combination of such physical and chemical processes as chelation, ion exchange, and chemical precipitation. Positively charged U ions may interact with carboxyl groups of polygalacturonic acid and other negatively-charged binding sites within plant cell walls.

Based on the information obtained from the rhizofiltration system experiments, a mathematical model of the rhizofiltration process was developed (19). The key component of the model is an expression describing the concentration reduction due to plant uptake in a rhizofiltration tank. To obtain this expression, potential variables involved within a single tank in the rhizofiltration system were identified (Figure 9). A strong relationship was found between the observed concentration reduction due to plant activities ( $C_e^*$ ) and the metal concentration available to the plants [ $C_a = f(C_w, C_{in}^*)$ ]. Subsequent experiments confirmed that the Michaelis-Menten equation was an appropriate choice to describe this relationship (data not shown). The model incorporates the Michaelis-Menten equation for  $C_e^*$  into the mass balance of the rhizofiltration system. This approach allowed prediction of tank concentrations for any part of the rhizofiltration system and days of operation. The model is suitable for tank concentrations ( $C_w$ ) below  $600\text{ }\mu\text{g/L}$ . For tank concentrations above  $600\text{ }\mu\text{g/L}$ , modification by a tuning factor is required for accurate predictions.

Conventional technologies such as ion exchange, reverse osmosis, microfiltration, precipitation, or flocculation are widely used to remove heavy metals from aqueous streams (20, 21). These methods, however, may be ineffective for large water volumes and low metal concentrations. In recent years, more emphasis has been placed on applications using microorganisms in metal removal processes (22) and treatment of various radioactive wastes (23). The ability of immobilized microbial biomass to biosorb uranium has been intensively evaluated (24, 25). Nakajima and Sakaguchi (14) listed 46 basidiomycetes species capable of accumulating uranium. Using immobilized microbial biomass as a biosorbent reduces toxicity problems but at the same time lacks the potential benefits of a metabolism-dependent metal removal process.

In natural waters, uranium is usually complexed with carbonate, hydroxide, sulfate, phosphate, fluoride, and possibly silicate (15). These complexes increase the solubility of uranium and make uranium precipitation more challenging. For this reason, uranium is one of the best candidates for a biological removal process. Byproducts of microbiological industry (26, 27) and vegetable composts (28) were successively tested to extract uranium. It was also recently suggested that aquacultured seedlings of Indian mustard could be used for treatment of various metal-contaminated waste streams

(29). During the evaluation of the rhizofiltration system performance, the efficiency of the same amount of Indian mustard seedlings, dried roots, and live sunflower plant roots was compared (data not shown). Only the live sunflower plants produced satisfactory results, decreasing U concentration below the discharge limit of 20  $\mu\text{g/L}$ .

The actual inlet concentrations at Ashtabula ranged from 21 to 874  $\mu\text{g/L}$  without a discernible effect on the performance of the system (Figure 8). However, the rhizofiltration system certainly has its limitations. In the experiment with the influent U concentration over 1000  $\mu\text{g/L}$ , a desirable low concentration of U in effluent was not achieved. For purposes of performance evaluation, a constant inlet concentration of 350  $\mu\text{g/L}$  of uranium was assumed at a flow rate of up to 1.05 L/min per trough. The capacity for the full-scale system was assumed to be 3800 L/min, at 365 days per year, treating annually a total volume of 2000 million L of uranium-contaminated water. At the specified parameters, 25 kg/day of U-loaded biomass would require treatment and disposal. The roots of the plants at harvest contained up to 90% water, and the mass of the dried roots can be reduced by up to an additional 90% by roasting or other thermal treatment or by advanced composting processes. The roots can also be extracted by an acid solution to render a non-radioactive biomass and a concentrated acid solution of uranium. Results of the experiments and performance of the pilot-scale system propound employing rhizofiltration as an alternative technology for U removal from waste streams.

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