

ERDC/EL MP-20-3

Environmental Laboratory



**US Army Corps  
of Engineers®**  
Engineer Research and  
Development Center



## **A Novel Laboratory Simulation System to Uncover the Mechanisms of Uranium Upward Transport in a Desert Landscape**

Qinku Zhang, Steven L. Larson, John H. Ballard, Pohlee Cheah,  
Joseph A. Kazery, Heather M. Knotek-Smith, Fengxiang X. Han

June 2020

**The U.S. Army Engineer Research and Development Center (ERDC)** solves the nation's toughest engineering and environmental challenges. ERDC develops innovative solutions in civil and military engineering, geospatial sciences, water resources, and environmental sciences for the Army, the Department of Defense, civilian agencies, and our nation's public good. Find out more at [www.erdcl.usace.army.mil](http://www.erdcl.usace.army.mil).

To search for other technical reports published by ERDC, visit the ERDC online library at <http://acwc.sdp.sirsi.net/client/default>.

# **A Novel Laboratory Simulation System to Uncover the Mechanisms of Uranium Upward Transport in a Desert Landscape**

Steven L. Larson, John H. Ballard, and Heather Knotek-Smith

*Environmental Laboratory  
U.S. Army Engineer Research and Development Center  
3909 Halls Ferry Road  
Vicksburg, MS 39180*

Qinku Zhang, Pohlee Cheah, Joseph A. Kazery, and Fengxiang Han

*Department of Chemistry and Biochemistry  
Jackson State University  
Jackson, MS 39217*

Final report

Approved for public release; distribution is unlimited.

Prepared for U.S. Army Corps of Engineers  
Washington, DC 20314

Under Project Number 458170, "Depleted Uranium (DU) Clearance from DoD  
Ranges"

## Abstract

After depleted uranium (DU) is deposited in the environment, it corrodes producing mobile uranium species. The upward transport mechanism in a desert landscape is associated with the dissolution/precipitation of uranium minerals that vary in composition and solubility in soil pore water. The objective of this study is to develop the laboratory column simulation to investigate the upward transport mechanism with cyclic capillary wetting and drying moisture regimes. Results showed that evaporation driven upward transport occurred even during the first 2 months of wetting-drying regimes. Evaporation driven upward transport may control the U movement in the soil profile in an arid climate. The new system did not generate any uranium-containing wastewater.

- Simulates the upward transport process of pollutants with different pollution levels and species.
- Simultaneously simulate the transport process of multiple pollutants simultaneously.
- Evaluate the influence of biogeochemical factors on pollutant transport such as various cations and anions (Ca, Mg and carbonates) in water.

**DISCLAIMER:** The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products. All product names and trademarks cited are the property of their respective owners. The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

**DESTROY THIS REPORT WHEN NO LONGER NEEDED. DO NOT RETURN IT TO THE ORIGINATOR.**

## Preface

This study was conducted for the U.S. Army Corps of Engineers under Project 458170, titled, "Depleted Uranium (DU) Clearance from DoD Ranges." The Grant Officer's Technical Representative was Mr. John H. Ballard, Office of the Technical Director for Installations and Operational Environments, ERDC-EL-EZT and the Technical Point of Contact was Dr. Steven L. Larson, Environmental Engineering Branch, ERDC-EL-EPE.

The work was performed by the Environmental Engineering Branch of the Environmental Processes Division, U.S. Army Engineer Research and Development Center, Environmental Laboratory (ERDC-EL). At the time of publication of this Miscellaneous Paper, Ms. Brooke Petery was Acting Branch Chief; Dr. Brandon Lafferty was Acting Division Chief; and Dr. Elizabeth Ferguson was the Technical Director for Installations and Operational Environments. The Acting Deputy Director of ERDC-EL was Dr. Justin Berman and the Acting Director was Dr. Jack Davis.

This report documents a collaborative study conducted under the sponsorship of the U.S. Army Futures Command with FY18 Congressional Program Increase Funds in PE 0603728A in the Fiscal Year (FY) 2018 Department of Defense Appropriations Act. Collaborative work was conducted by the U.S. Army Engineer Research and Development Center and Jackson State University via Cooperative Agreement W912HZ-16-2-0021.

The Commander of ERDC was COL Teresa A. Schlosser and the Director was Dr. David W. Pittman.

---

# A Novel Laboratory Simulation System to Uncover the Mechanisms of Uranium Upward Transport in a Desert Landscape

---

## Method details

### *Background*

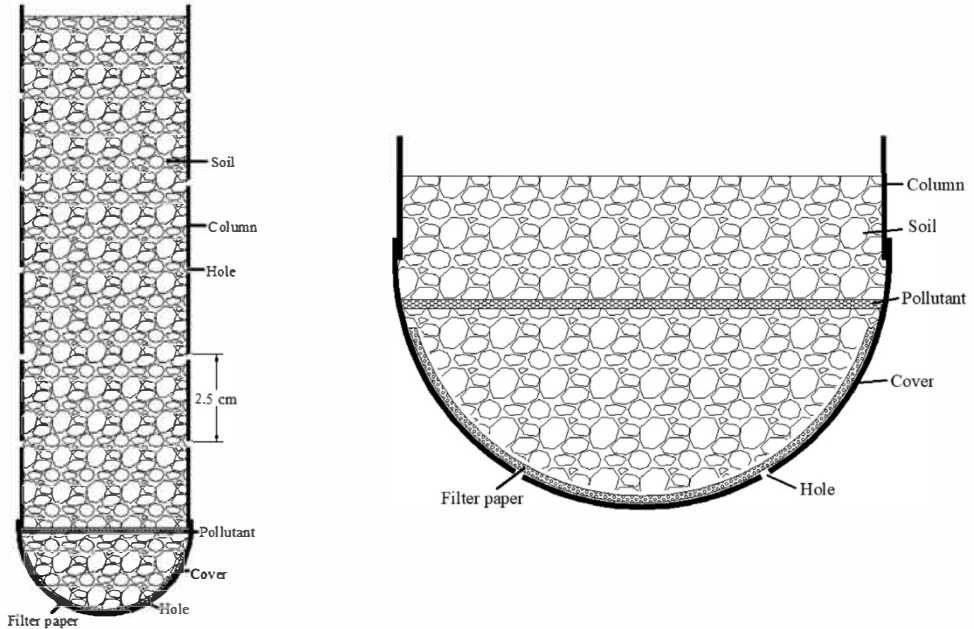
DU is a unique metal (U + Ti alloy) that is used for both military and civil applications that require extremely high density such as kinetic energy penetrators and ballasts. These uses include ammunition armor counterweights drilling equipment, surrogate for fissionable high density materials. DU penetrators are used in weapons system for its self-sharpening, high density and hardness characteristics as a result DU alloy particulates has become distributed in some locations. During the 1991 Gulf War about 321 tons [1] of DU were fired and approximately 170–1700 tons [2] were used in the second Gulf war (2003). DU penetrators have been fired at military testing and training facilities in various countries. Uranium can be a toxic and radioactive contaminant in the environment [3], and an enhanced understanding of mobility of this metal in soils is required in order to support the sustainable use of this material.

When the DU metal is deposited in soil, processes of corrosion and transport occur as the metal allow weathers. Visual observations of autunite group minerals have been made on military testing ranges through its definitive bright yellow coloration on the soil surface and within the soil lying atop buried penetrators. The corrosion and upward transport mechanism over multiple dissolution/precipitation events of U in arid soil had not been studied in controlled conditions. A unique laboratory apparatus was required in order to perform controlled studies of these processes.

The transport of U in soil was affected by various biogeochemical conditions and environmental factors, such as the initial uranium solubility of the corrosion product, the pH values of soil, the soluble ions present in the soil pore water, the mass of organic matter in soil, sizes of soil particles and soil moisture regimes etc. Column experiments were used to simulate the transport of U and other heavy metals in soil, often downward transport with gravity driven of surface/ground water. However, both gravity driven downward transport as well as evaporation driven upward transport influences the U movement through the soil profile. This novel laboratory design of a column system is to simulate capillary-evaporation driven upward transport of U in soil (Fig. 1). This system generated no uranium-containing wastewater.

### *Procedures*

- 1 Dry clean soil in the drying oven
- 2 Grind dry soil using ground plate and grinding rod
- 3 Obtain <2 mm fraction using 2 mm screen
- 4 Grind the desired mass of soil metal compounds ( $\text{UO}_2$ ,  $\text{UO}_3$ ,  $\text{UO}_2(\text{NO}_3)_2$ ) into powder with agate mortar
- 5 Drill a series of holes with a diameter of 0.5 cm along the column ( $D \times H = 4 \text{ cm} \times 15 \text{ cm}$ ) from the bottom to the top with the interspace of 2.5 cm between holes



**Fig. 1.** The structure diagram of the column.

- 6 Drill the 3 mm-scale holes in the bottom cover and put one filter paper on the top of the bottom cover
- 7 Place a small layer of soil above the filter paper of the bottom cover
- 8 Weigh the proper amount of solid metal compounds and uniformly spread them on the top surface of the soil
- 9 Connect the column to the bottom section with the bottom cover, filter paper, a thin layer soil and a thin layer of U metal compounds
- 10 Add soil to the column in the heights of 5 cm with packing-packing force (slide hammer 20–25 newtons/cm<sup>2</sup>)
- 11 Place the bottom of the packed column inside the solutions containing water with the desired companion cations/anions in aqueous solution [4,5]. The position of U contaminant inside the column should be higher than the water level in order to the upward transport of U compound dissolved in pore water through capillary force when evaporation occurs
- 12 Place column with wet soil in oven. The temperature of the oven can be set in order to simulate temperature ranges of interest. In the current configuration the temperature was set to 45 °C. The temperature simulated the hot summer in Yuma, AZ desert.
- 13 Repeat the wetting and drying cycles (wetting-drying, Step 12–13) when the soil of the column was completely dry (about 7 days later)
- 14 After repeating “wetting-drying” cycles for 2 months, remove a sample soil from the lowest hole of the column, use X-ray fluorescence spectrometer (XRF) to measure the uranium concentration in soil
- 15 Monitor the upward migration of uranium by sampling from the holes at different soil column heights
- 16 The “wetting-drying” cycles and experiments can discontinued be stopped when the U is detected at the desired study height
- 17 Take the soil out of the column in one piece
- 18 Cut the soil column into 2.5 cm layers and take 2 g mixed soil as a subsample
- 19 Use X-ray power diffraction (XRD) to study the U compounds in the soil
- 20 Run Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) to study the morphology and elemental composition of samples to determine element distribution in the soil

- 21 Measure the fractionation of uranium in each section with the method of selective sequential dissolution (SSD) [6]
- 22 Calculate U transport rate in the soil under wetting-drying cycle moistures

### *Final remarks*

This work presents a novel laboratory uranium upward transport simulation system that provides a capability to evaluate pore water chemistries into the capillary rise uranium transport phenomenon. The procedure consisted of three steps: soil column preparation, operation of U transport driven through soil capillary and evaporation under wetting-drying cycle moistures, and analysis and characterization of stratified soil column. The traditional method required a large amount of uranium-containing solution and a diaphragm pump to feed the water continuously. The traditional column transport system is not adequate to study the mechanism of U upward transport in an arid desert landscape. This method offered systematic “wetting-drying” of the soil moistures, which better simulates the actual upward transport process and mineralogical forms of uranium in natural soil driven by evaporation. This method had the advantages of low energy consumption, low waste production and better representation of uranium transport in a natural arid environment.

### **Procedures for the total uranium and fractionation of uranium in the soil samples**

#### *Total uranium*

- 1 The total U concentrations were detected and monitored in soils, which was taken out from small holes along the column with X-ray fluorescence spectrometer (Bruker).
- 2 After the end of the experiments, total U in soils were also measured with Inductively coupled plasma mass spectrometry (ICP-MS) after acid digestion.
- 3 For acid digestion-ICP-MS, weight 1.0 g soil sample into digesting tube (50 mL) with replicates
- 4 Digest the soil with 25 mL of 4 M HNO<sub>3</sub> in a water-bath at 80 °C for 16 h [7,8]
- 5 The supernatant was decanted and filtered through a 0.45- $\mu$ m filter
- 6 Dilute the digested soil solution
- 7 Measure the metal concentrations in the diluted solution with ICP-MS

#### *Fraction of uranium*

U in soils was fractionated with the selective sequential dissolution (SSD) [6].

### **Verifying the validity**

Uranium compounds (UO<sub>2</sub>, UO<sub>3</sub>, UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>) were placed at the bottom of the column. Total uranium concentration in soils of the column by height was measured with XRF after “wetting-drying” cycles periodically (Fig. 2). There was no uranium detected above the initial level in the columns constructed using UO<sub>2</sub> and UO<sub>3</sub>. The transport distance of uranium reached up to 7.5 cm after 4 months in the column of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>. There was no significant difference ( $p=0.05$  level) in the concentration of uranium at 2.5 cm and 5 cm height after 2 and 4 months.

To illustrate the usefulness of the method for simulations varied soil types and conditions, UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> was placed at the bottom of the column which were contacted with aqueous solution containing different cations (tap water, 1 mmol/L CaCl<sub>2</sub>-NaHCO<sub>3</sub> solution, 1 mmol/L MgCl<sub>2</sub>-NaHCO<sub>3</sub> solution or 1 mmol/L CaCl<sub>2</sub>-MgCl<sub>2</sub>-NaHCO<sub>3</sub> solution). These aqueous solutions were used as capillarity solution to study the effect of different cations/anions on U upward transport. Total uranium concentration was measured with XRF after “wetting-drying” cycles for every 2 months (Fig. 3). After 4 months, the transport distances of uranium in the MgCl<sub>2</sub>-NaHCO<sub>3</sub> and CaCl<sub>2</sub>-NaHCO<sub>3</sub> column were 7.5 cm and 5 cm in height, respectively. However, uranium was undetected in the CaCl<sub>2</sub>-MgCl<sub>2</sub>-NaHCO<sub>3</sub> column. For the column of MgCl<sub>2</sub>-NaHCO<sub>3</sub>

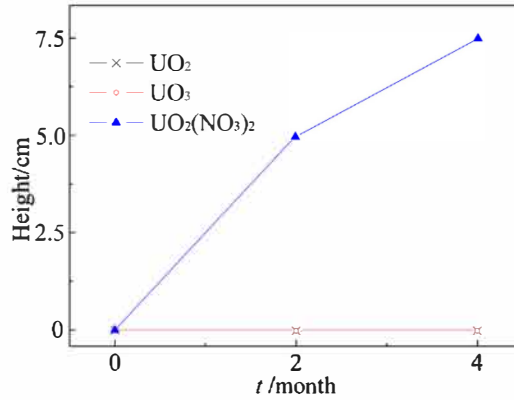


Fig. 2. The transport of different uranium species in H<sub>2</sub>O.

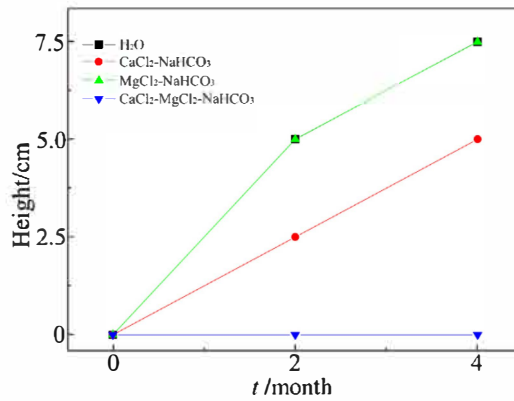


Fig. 3. Transport of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> in different aqueous solutions containing CaCl<sub>2</sub>-NaHCO<sub>3</sub>, MgCl<sub>2</sub>-NaHCO<sub>3</sub> and CaCl<sub>2</sub>-MgCl<sub>2</sub>-NaHCO<sub>3</sub> solution.

and CaCl<sub>2</sub>-NaHCO<sub>3</sub>, no significant difference ( $p=0.05$  level) was observed in the concentration of uranium in soil at 2.5 cm and 5 cm height after 2 and 4 months. Liu et al. [9] used chitosan/polyaniline as solid-phase extractant for adsorbing U from bicarbonate-buffer solution containing Ca<sup>2+</sup> and Mg<sup>2+</sup>, and found that the adsorption affinity was in the sequence of U-CO<sub>3</sub><sup>2-</sup> > Ca-U-CO<sub>3</sub><sup>2-</sup> > Mg-U-CO<sub>3</sub><sup>2-</sup>. Meanwhile, some similar phenomenon occurred in previous research reports [10–12]. This could be caused by the complexes of Ca(UO<sub>2</sub>)(CO<sub>3</sub>)<sub>3</sub><sup>2-</sup> and Ca<sub>2</sub>(UO<sub>2</sub>)(CO<sub>3</sub>)<sub>3</sub> which tends to be adsorbed on the soil in neutral to weak alkaline solution.

### Conclusion

The present method offers a systematic “wetting-drying” of the soil moisture through evaporation driven capillary movement in the arid environment. This system better simulates the actual upward transport process and mineralogical forms of uranium in natural soil in a desert climate. The traditional column method often uses a peristaltic pump to feed water, requires high energy consumption and generates a large amount of contaminated wastewater. The present method has the advantages of low energy consumption, low U wastewater production, and better similarity to the uranium transport in the natural arid environment.

## References

- [1] S. Handley-Sidhu, N.D. Bryan, P.J. Worsfold, D.J. Vaughan, F.R. Livens, M.J. Keith-Roach, Corrosion and transport of depleted uranium in sand-rich environments, *Chemosphere* 77 (2009) 1434–1439.
- [2] United Nations Environment Programme, **Technical Report on Capacitybuilding for the Assessment of Depleted Uranium in Iraq**, UNEP, Geneva, 2007.
- [3] M. Gavrilescu, L.V. Pavel, I. Cretescu, Characterization and remediation of soils contaminated with uranium, *J. Hazard. Mater.* 163 (2009) 475–510.
- [4] A.S. Saleh, J.Y. Lee, Y.H. Jo, J.I. Yun, Uranium(VI) sorption complexes on silica in the presence of calcium and carbonate, *J. Environ. Radioact.* 182 (2018) 63–69.
- [5] J. Liu, C.S. Zhao, G.Y. Yuan, Y. Dong, J.J. Yang, F.Z. Li, J.L. Liao, Y.Y. Yang, N. Liu, Adsorption of U(VI) on a chitosan/polyaniline composite in the presence of Ca/Mg-U(VI)-CO<sub>3</sub> complexes, *Hydrometallurgy* 175 (2018) 300–311.
- [6] F.X. Han, W.L. Kingery, J.E. Hargreaves, T.W. Walker, Effects of land uses on solid-phase distribution of micronutrients in selected vertisols of the Mississippi River Delta, *Geoder* 142 (2007) 96–103.
- [7] F.D. Meng, K. Jin, S.L. Guo, J.H. Larson, L.M. Chen, Z. Arslan, G. Yuan, Y.H. Ma, C.A. Waggoner, F.X. Han, Influences of U sources and forms on its bioaccumulation in Indian Mustard and Sunflower, *Water Air Soil Pollut.* 229 (2018) 1–11.
- [8] F.X. Han, A. Banin, Long-term transformations and redistribution of potentially toxic heavy metals in arid-zone soils incubated: I. Under saturated conditions, *Water Air Soil Pollut.* 95 (1997) 399–423.
- [9] J. Liu, C.S. Zhao, G.Y. Yuan, Y. Dong, J.J. Yang, F.Z. Li, J.L. Liao, Y.Y. Yang, N. Liu, Adsorption of U(VI) on a chitosan/polyaniline composite in the presence of Ca/Mg-U(VI)-CO<sub>3</sub> complexes, *Hydrometallurgy* 175 (2018) 300–311.
- [10] A.S. Saleh, J.Y. Lee, Y.H. Jo, J.I. Yun, Uranium (VI) sorption complexes on silica in the presence of calcium and carbonate, *J. Environ. Radioact.* 182 (2018) 63–69.
- [11] B.D. Stewart, M.A. Mayes, S. Fendorf, Impact of uranyl-calcium-carbonate complexes on uranium (VI) adsorption to synthetic and natural sediments, *Environ. Sci. Technol.* 44 (2010) 928–934.
- [12] A. Meleshyn, M. Azeroual, T. Reeck, G. Houben, B. Riebe, C. Bunnenberg, Influence of (calcium-)uranyl-carbonate complexation on U(VI) sorption on Ca- and Na-bentonites, *Environ. Sci. Technol.* 43 (2009) 4896–4901.
- A. Meleshyn, M. Azeroual, T. Reeck, G. Houben, B. Riebe, C. Bunnenberg, Influence of (Calcium-)Uranyl-Carbonate Complexation on U(VI) Sorption on Ca- and Na-Bentonites, *Environmental Science and Technology*, 43 (2009) 4896–4901.

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

<b>1. REPORT DATE (DD-MM-YYYY)</b> June 2020			<b>2. REPORT TYPE</b> Final		<b>3. DATES COVERED (From - To)</b>	
<b>4. TITLE AND SUBTITLE</b> A Novel Laboratory Simulation System to Uncover the Mechanisms of Uranium Upward Transport in a Desert Landscape					<b>5a. CONTRACT NUMBER</b>	
					<b>5b. GRANT NUMBER</b>	
					<b>5c. PROGRAM ELEMENT NUMBER</b> 633728 03F	
<b>6. AUTHOR(S)</b> Qinku Zhanga, Steven L. Larson, John H. Ballard, Pohlee Cheah, Joseph A. Kazery, Heather M. Knotek-Smith, Fengxiang X. Han					<b>5d. PROJECT NUMBER</b> 458170	
					<b>5e. TASK NUMBER</b> 5	
					<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> U.S. Army Engineer Research and Development Center Environmental Laboratory 3909 Halls Ferry Road Vicksburg, MS 39180					<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>  ERDC/EL MP-20-3	
<b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> Budget and Programs Div Department of the Army USACE 441 G Street NW Washington, DC 20314					<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>  USACE	
					<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b>	
<b>12. DISTRIBUTION / AVAILABILITY STATEMENT</b> Approved for public release; distribution is unlimited.						
<b>13. SUPPLEMENTARY NOTES</b> Originally published in MethodsX Journal, online 3 December 2019. Collaborative work was conducted by the U.S. Army ERDC and Jackson State University via Cooperative Agreement W912HZ-16-2-002.						
<b>14. ABSTRACT</b> <p>After depleted uranium (DU) is deposited in the environment, it corrodes producing mobile uranium species. The upward transport mechanism in a desert landscape is associated with the dissolution/precipitation of uranium minerals that vary in composition and solubility in soil pore water. The objective of this study is to develop the laboratory column simulation to investigate the upward transport mechanism with cyclic capillary wet-ting and drying moisture regimes. Results showed that evaporation driven upward transport occurred even during the first 2 months of wetting-drying regimes. Evaporation driven upward transport may control the U movement in the soil profile in an arid climate. The new system did not generate any uranium-containing wastewater.</p> <ul style="list-style-type: none"><li>• Simulates the upward transport process of pollutants with different pollution levels and species.</li><li>• Simultaneously simulate the transport process of multiple pollutants simultaneously.</li><li>• Evaluate the influence of biogeochemical factors on pollutant transport such as various cations and anions (Ca, Mg and carbonates) in water.</li></ul>						
<b>15. SUBJECT TERMS</b> Contaminant, Uranium, Transport, Radioactive, Soil, Fraction						
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>	
<b>a. REPORT</b> Unclassified	<b>b. ABSTRACT</b> Unclassified	<b>c. THIS PAGE</b> Unclassified			<b>19b. TELEPHONE NUMBER (include area code)</b>	
			SAR	9		