

Metal extractability from contaminated SRS sediments: Comparison of column and batch results

J. C. Seaman, V. M. Vulava, A. G. Sowder, B. P. Jackson, S. A. Aburime, and P. M. Bertsch

ABSTRACT

Tims Branch, a stream on the U.S. Department of Energy's Savannah River Site located near Aiken, South Carolina, received significant amounts U and Ni as a result of nuclear materials production and refinement. Batch and column experiments were used to evaluate potential remediation scenarios and the migration hazard of U and Ni from flood-plain sediments collected along Tims Branch. Treatment solutions included a low-ionic-strength groundwater surrogate (artificial groundwater), 1 mM ethylenediaminetetraacetic acid (EDTA), 1 mM CaCl₂ (pH 3.0), 1 mM Na-phytate (Na₁₂C₆H₆O₂₄P₆), and 1 mM Ca-phytate (CaC₆H₁₆O₂₄P₆). The two organic phosphate compounds were included in the study because of their potential to serve as in-situ immobilizing agents through the formation of insoluble precipitates in association with the contaminant metals. Repacked columns were leached with a specific treatment solution for 30 pore volumes (PV) at a constant seepage velocity of 8 m day⁻¹ (26 ft day⁻¹). After leaching, solid-phase metal redistribution was evaluated using the toxicity characteristic leaching procedure and sequential extraction methods. For comparison, batch extractions were conducted using a solid-to-solution ratio (1:20) that mimicked the total leaching volume. Despite differences in reaction time, batch and column results were generally consistent. The CaCl₂ and EDTA column treatments removed substantial Ni from the labile fractions, i.e., water soluble and exchangeable, as indicted by subsequent extractions for the residual sediments. The effectiveness of the treatments in removing U and Ni was not evident from digestion of the residual column sediments. Ca-phytate significantly reduced U mobility in columns, with evidence for solid-phase redistribution to more recalcitrant fractions. Na-phytate extracted the most U in batch and columns despite inducing colloid dispersion that clogged the column and precluded further leaching after 8–10 PV.

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AUTHORS

J. C. SEAMAN ~ *Savannah River Ecology Laboratory, University of Georgia, PO Drawer E, Aiken, South Carolina 29802; seaman@srel.edu*

John C. Seaman is an associate research professor with the Savannah River Ecology Laboratory, located on the Savannah River Site and operated for the Department of Energy by the University of Georgia. Seaman received his B.S. (1987) and M.S. (1990) degrees from Texas A&M University in agronomy and soil science, respectively, and his Ph.D. (1994) in environmental soil science from the University of Georgia.

V. M. VULAVA ~ *Savannah River Ecology Laboratory, University of Georgia, PO Drawer E, Aiken, South Carolina 29802*

Vijay M. Vulava is a research associate with the Department of Earth and Planetary Sciences at the University of Tennessee. He has a B. Tech. degree (1992) and an M.S. degree (1994) in civil and environmental engineering from J.N. Technological University, India, and University of Maryland, United States, respectively, and a Ph.D. (1998) in environmental soil chemistry from the Federal Institute of Technology, Switzerland.

A. G. SOWDER ~ *Savannah River Ecology Laboratory, University of Georgia, PO Drawer E, Aiken, South Carolina 29802*

Andrew G. Sowder is a physical scientist with the Office of the Senior Coordinator for Nuclear Safety at the U.S. Department of State. Sowder received his B.S. degree (1990) in optics from the University of Rochester and his Ph.D. (1998) in environmental engineering and science from Clemson University.

B. P. JACKSON ~ *Department of Earth Sciences and Department of Chemistry, HB6105, Dartmouth College, Hanover, NH 03755*

Brian Jackson is Director of the Trace Element Analysis Laboratory in the Center for Environmental Sciences at Dartmouth College, Hanover, New Hampshire. Jackson received his B.S. degree (1989) in chemistry from Oxford University and his Ph.D. (1998) in environmental soil science from the University of Georgia.

S. A. ABURIME ~ *Savannah River Ecology Laboratory, University of Georgia, PO Drawer E, Aiken, South Carolina 29802*

Sunnie A. Aburime is an associate professor in the Department of Engineering at Clark Atlanta University, Atlanta, Georgia. Aburime received both his B.S. (1978) and M.S. (1982) degrees in chemistry from Jackson State University and his Ph.D. (1986) in environmental engineering from Cornell University.

P. M. BERTSCH ~ *Savannah River Ecology Laboratory, University of Georgia, PO Drawer E, Aiken, South Carolina 29802*

Paul M. Bertsch is a professor of environmental soil science and director of Savannah River Ecology Laboratory of the University of Georgia. Bertsch received his B.S. degree in plant and soil science from the University of Connecticut, his M.S. degree in soil chemistry from Virginia Tech, and his Ph.D. (1994) in soil physical chemistry and mineralogy from the University of Kentucky.

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INTRODUCTION

Information regarding the processes by which a given contaminant is sorbed within a system is critical to the design of an effective remediation strategy, particularly when advocating a natural attenuation or intrinsic remediation approach. Numerous reactions control the migration and bioavailability of contaminant metals in the subsurface environment, including ion exchange, specific sorption reactions with mineral surfaces and organic materials, metal chelation and complexation, and mineral solubility reactions. Ecological risk, therefore, is driven largely by solid-phase speciation as controlled by solution chemistry (e.g., pH, ionic strength, composition) and the abundance and type of reactive binding sites, instead of total metal concentrations. Several experimental approaches have been adopted to estimate the mobile and/or bioavailable pool of soil contaminants, for example, (1) simple one-step batch extraction experiments; (2) sequential extraction methods using increasingly more aggressive chemical agents, each targeted at a specific solid phase or partitioning mechanism; and (3) column-leaching experiments (Rigol et al., 1999; Pueyo et al., 2003; Voegelin et al., 2003). In recent years, spectroscopic methods, such as synchrotron x-ray absorption techniques, have been widely used for determining redox state and solid-phase speciation for contaminant metals, including uranium (U) (Duff et al., 1997); however, the utility of spectroscopic techniques in evaluating the most reactive contaminant pool, commonly a small fraction of the total contaminant, is still in question.

Although largely empirical in nature, single-step batch extraction methods are typically used for environmental regulatory purposes because they can be easily standardized and rapidly applied to numerous samples without the need for expensive sample-preparation equipment or specialized technical skills, yielding aqueous samples that can be readily analyzed using one of several instrumental methods. Such methods are generally based on a conceptual understanding of the processes controlling contaminant transport in a given environment. For example, the toxicity characteristic leaching procedure (TCLP) method was designed to mimic the leaching environment present in municipal landfill. Interpreting the results is generally straightforward, limited to a simple comparison with threshold values for a given contaminant in a manner similar to determining drinking water compliance (Buonicore, 1996).

The more involved sequential extraction procedures, such as the widely used Tessier et al. (1979) and Miller et al. (1986) methods, provide additional information concerning contaminant partitioning. As with the single-step methods, sequential extraction methods are operational in nature and suffer from the same limitations associated with the nonspecificity of extractants and problems related to readsorption of metals during the extraction processes. From an environmental remediation standpoint, sequential extractions can provide useful information concerning specific conditions under which a contaminant metal may be mobilized, i.e., acidic,

reducing, etc., and evaluating changes in solid-phase associations resulting from a given remediation treatment (Arey et al., 1999; Seaman et al., 2001b; Voegelin et al., 2003). Still, care must be taken in choosing an extraction procedure and interpreting the results because such schemes are commonly developed for a specific soil or sediment type and may define or extract fractions that are not actually present, e.g., a CaCO_3 fraction when extracting noncalcareous soils.

Column leaching techniques provide another method for evaluating contaminant mobility under physical conditions that better mimic the natural subsurface environment and can be used to assess the efficacy of various treatment technologies that either enhance or reduce the bioavailability and/or mobility of the metals. The experimental design for a contaminant leaching study is far less straightforward, making it difficult to compare results for studies conducted using different leaching solutions, column lengths, and flow rates. Previous studies, however, have clearly demonstrated the utility of evaluating potential remediation strategies using both batch and column techniques to identify possible limitations that are not clearly evident under batch conditions (Seaman et al., 1999, 2001b).

In this study, batch and column methods were used to evaluate the impact of various leaching solutions on contaminant mobility, more specifically, U and nickel (Ni). Tims Branch, a second-order stream draining 16 km² (6.1 mi²) in the watershed basin of the Savannah River, was contaminated with U, Ni, lead (Pb), chromium (Cr), copper (Cu), thorium (Th), and other metals resulting from nuclear materials production on the Savannah River Site (SRS) (Pickett, 1990; Evans et al., 1992). From the early 1950s to the late 1960s, the stream received about 44,000 kg of U from fuel fabrication operations. Significant deposition occurred in Steed Pond, a former farm pond on Tims Branch, because of the longer residence times and reduced flow velocities (Batson, 1994; Batson et al., 1996). The wooden dam ruptured in 1984, draining the pond and exposing the contaminated sediments to erosion (Pickett, 1990). No attempt was made to rebuild the dam, and revegetation has been hampered somewhat by metal toxicity that continues to limit plant growth (Batson, 1994; Punshon et al., 2003). Most of the contamination appears to be restricted to Steed Pond, but wide areas of the Tims Branch stream system have elevated levels of contaminants as well (Punshon et al., 2003), the ecological impact of which is still uncertain.

Several chelating agents have been evaluated for use in extracting contaminant metals, such as citric acid,

ethylenediaminetetraacetic acid (EDTA), diethylenetriamine pentaacetic acid (DTPA), and carboxy-methyl cyclodextrins (Palmer and Fish, 1992; National Research Council, 1994; Vulava and Seaman, 2000; Neilson et al., 2003; Tandy et al., 2004). Unfortunately, chelating agents may complex strongly with soil components such as Fe-oxides and Al-oxides instead of the targeted metal, e.g., Pb, Cd, etc. (Kedziorek et al., 1998; Kedziorek and Bourg, 2000). If so, substantial amounts of complexing agents must be added to extract the contaminant while potentially mobilizing Fe, Al, and other metals and radionuclides, drastically altering the soil-aquifer matrix.

In-situ immobilization offers an alternative to various extraction schemes for reducing the migration potential and bioavailability of the contaminants so they remain in place. For example, the addition of hydroxyl-apatite (HA; $\text{Ca}_5(\text{PO}_4)_3\text{OH}$) is quite effective at reducing the solubility of U and other metals in contaminated sediments from the Tims Branch watershed through the formation of secondary phosphate (PO_4) precipitates (Arey et al., 1999; Seaman et al., 2001a). However, the deployment of in-situ immobilization agents is generally limited to surficial areas of contamination where relatively insoluble reactants can be readily mixed with the contaminated material of interest, a practice that would drastically disturb a functioning, albeit contaminated, watershed. To overcome such limitations, researchers have investigated a range of soluble PO_4 -containing materials with limited success, including phytate (the hexaphosphoric acid of myo-inositol), depending on the material's compatibility with the geology and groundwater chemistry of a given site (Nash et al., 1998a, b). For example, Seaman et al. (2003) observed that Na-phytate increased the solubility of several contaminants when added to Steed Pond/Tims Branch sediments in a series of batch experiments, whereas Ca-phytate reduced the solubility of several metals to a degree similar to HA.

The primary objective of the current study was to compare the use of batch and column techniques to evaluate changes in the mobility of U and Ni from Tims Branch sediments under various leaching conditions that include commonly used extracting agents and phytate-based contaminant-immobilizing agents.

MATERIALS AND METHODS

Field-moist sediments collected along Tims Branch, located on the Department of Energy's SRS, Aiken, South Carolina, were sieved (2 mm) to remove stones

and large organic debris, i.e., stems, roots, and leaves. Soil aggregates were gently crushed by hand to pass through the sieve. The uniform bulk material was then air-dried and subsequently stored in a cool dark place for further use. Typical of the soils from the SRS, the Tims Branch sediment is acidic in nature, with a somewhat higher organic carbon content and finer texture, indicative of deposition in the stream flood plain (Table 1). As determined by x-ray diffraction (Whittig and Allardice, 1986), the clay fraction is dominated by kaolinite, hydroxy-interlayered vermiculite (HIV), and gibbsite, with lesser amounts of goethite and quartz. The U and Ni contents are several times higher than the values reported for nonimpacted soils on the SRS and South Carolina coastal plain, in general (Pickett et al., 1985; Canova, 1999).

BATCH EXTRACTIONS

Samples of 1 g (dry weight) of Tims Branch sediment were placed in three replicate 50-mL centrifuge tubes with 20 mL of one of the following extracting solu-

tions: artificial groundwater (AGW), EDTA (1 mM NaEDTA), 1 mM Na-phytate ($\text{Na}_{12}\text{C}_6\text{H}_6\text{O}_{24}\text{P}_6$), 1 mM Ca-phytate ($\text{Ca}_9\text{C}_6\text{H}_{16}\text{O}_{24}\text{P}_6$), or CaCl_2 (1 mM, adjusted to pH 3.0). All chemicals used in the study were of analytical grade. Analytical grade Na and Ca salts of phytic acid, hereafter referred to as Na-phytate and Ca-phytate, respectively, were purchased from Sigma Chemicals. The AGW, based on routine groundwater-monitoring data for nonimpacted water table wells located on the SRS (Strom and Kaback, 1992), contained the following (mg L^{-1}): 1.00 Ca^{2+} , 0.37 Mg^{2+} , 0.21 K^+ , 1.40 Na^+ , and 0.73 SO_4^{2-} . The batch soil-to-solution ratio (1 g soil in 20 mL⁻¹ extractant) was chosen to mimic the total solution collected in the column-leaching studies described below. After equilibrating overnight, the suspensions were centrifuged at 10,000 rpm ($11,952 \times g$) for 30 min using a Sorvall RC2-B supercentrifuge and passed through a nylon membrane filter (0.22 μm pore size). The filtered supernatants were acidified (1% HNO_3) and analyzed for metals by inductively coupled plasma-mass spectrometry (ICP-MS) (Elan 6000, Perkin-Elmer Corp., Norwalk, Connecticut).

Table 1. Physical and Chemical Properties of Sediment Collected from the Tims Branch Flood Plain on the SRS

		Mean and Standard Deviation
$\text{pH}_{\text{water}}^*$		4.45 ± 0.01
pH_{KCl}		3.86 ± 0.01
EC		71.4 ± 14.9
Total Levels	Average for SRS Soils/Sediments** (mg kg^{-1})	Tims Branch
U	2	290 ± 4
Ni	10	91.6 ± 1.4
Total organic carbon [†]		3.94 ± 0.04 g/100 g
Particle Size Distribution ^{††}		g/100 g
Sand (%)		42
Silt (%)		49
Clay (%)		9

*2:1 solution/soil ratio.

**Pickett et al. (1985).

[†]Total organic carbon, dry combustion method (Nelson and Sommers, 1982).

^{††}Micropipette method (Miller and Miller, 1987).

Dynamic Leaching Experiments

Leaching experiments were performed in 1-cm inner diameter glass chromatography columns equipped with Teflon end pieces. The columns were packed in small incremental steps with the air-dried sediments to obtain a uniform bulk density of 1.06 (± 0.05) g cm^{-3} , which corresponds to a porosity of 0.60 (± 0.02). The ends of the soil columns were packed with small quantities of acid-washed sand to uniformly distribute flow entering and exiting the column. Preliminary experiments indicated negligible sand interaction with the extractants or metals. The repacked soil columns were oriented vertically and slowly saturated in an upflow direction with the extractant solution at a constant pore water velocity of 7.8 ± 0.1 m day^{-1} (25.5 ± 0.3 ft day^{-1}) for approximately 30 pore volumes. Column effluents were filtered (0.22- μm pore size filters) and acidified (1% HNO_3) prior to analysis for metals by ICP-MS, with method detection limits for U and Ni in the column effluents at 0.59 and 2.62 $\mu\text{g L}^{-1}$, respectively. One repacked column was leached with 0.5 M NaHCO_3 , also known as the heap leach method, which has been used for in-situ U mining and evaluated as a possible soil-washing agent.

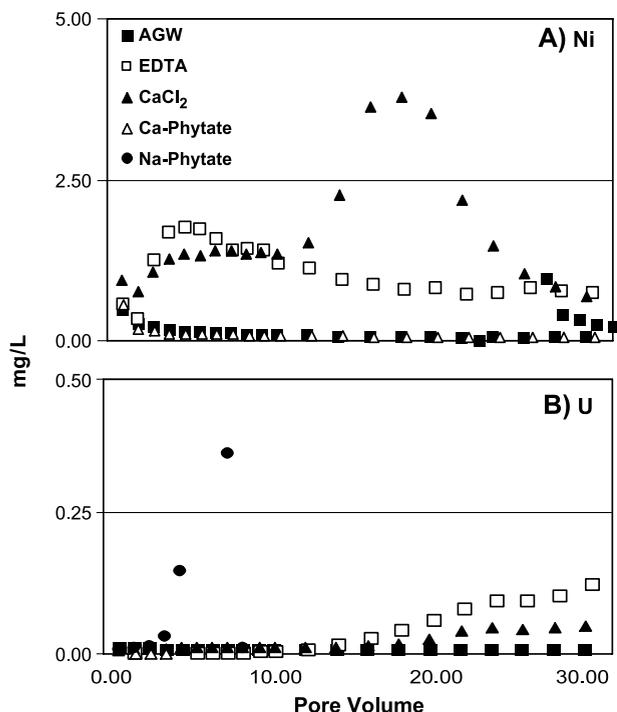


Figure 1. Effluent Ni (A) and U (B) concentrations during leaching with various extracting solutions.

TCLP and Sequential Extraction

After completion of the leaching treatments, the columns were drained, and the residual sediments were extracted using the Environmental Protection Agency (EPA) standardized TCLP (40 CFR, chapter 1, part 268, Appendix 1). The TCLP leaching solution comprises 0.1 M glacial acetic acid and 0.0643 M NaOH, with a final pH of 4.93. After equilibration on a reciprocating shaker for 18 hr at 25°C, the samples were centrifuged, the resulting supernatants were filtered through 0.22- μm -pore-size nylon filters and acidified to 2% HNO_3 prior to analysis for metals using ICP-MS.

Sequential extractions were performed on the bulk soil and residual soil material from each leached column using a modified procedure based on the method of Miller et al. (1986). Each extraction step and the target phase are listed in procedural order from least to most chemically aggressive: (1) deionized water = water soluble; (2) 0.5 M $\text{Ca}(\text{NO}_3)_2$ = exchangeable; (3) 0.44 M glacial acetic acid + 0.1 M $\text{Ca}(\text{NO}_3)_2$ = acid soluble; (4) 0.01 M $\text{NH}_2\text{OH}-\text{HCl}$ + 0.1 M HNO_3 = Mn occluded; (5) 0.1 M $\text{Na}_4\text{P}_2\text{O}_7-10\text{H}_2\text{O}$ = organically bound; (6) 0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4-\text{H}_2\text{O}$, 0.1 M $\text{H}_2\text{C}_2\text{O}_4$ in the dark = amorphous Fe oxides; (7) reduction with 0.5 g Na-dithionite in 0.15 M

$\text{Na}_3\text{H}_5\text{C}_6\text{O}_7 + 0.05 \text{ M H}_8\text{C}_6\text{O}_7$ (sodium-citrate buffer) = crystalline Fe oxides; and (8) 3 mL of HF and 9 mL of HNO_3 and heated at 120 psi in a digestion microwave for 30-min intervals until residual digestion was complete = residual fraction (EPA method 3052). Total U and Ni remaining in the column samples were determined using the residual digestion method described above without the prior sequential extraction steps. Extracted metals in each fraction were quantified by ICP-MS. Batch equilibration and residual soil column extraction results were analyzed as a single-factor ANOVA in SAS using Proc ANOVA and Tukey's test for multiple comparisons.

RESULTS AND DISCUSSION

The effluent concentration histories for Ni and U are presented in Figure 1A and B, respectively, and the total masses recovered for each column treatment is summarized in Table 2. In general, the mobility of Ni (1.76 mg kg^{-1}) and U (0.15 mg kg^{-1}) was quite low for the low-ionic-strength pore solution (AGW) used as a control to simulate mild leaching conditions, accounting for approximately 1.9% and 0.05% of the total Ni and U, respectively. However, a peak in effluent Ni was evident for the EDTA and CaCl_2 treatments (Figure 1A), which also extracted significantly more Ni than the other treatments in the batch trials (approximately 13% of the total Ni), with CaCl_2 being somewhat more effective than EDTA with continued leaching, suggesting that cation exchange is important in controlling Ni partitioning and migration (Table 2). Significant Ni extraction by these treatments was also

Table 2. Cumulative U and Ni Release from Columns and Corresponding Batch Extraction Results

Extractant	Column Ni (mg kg^{-1})	Batch Ni (mg kg^{-1})*	Column U (mg kg^{-1})	Batch U (mg kg^{-1})*
AGW**	1.76	3.14 (A)	0.15	0.63 (A)
CaCl_2 (pH 3)	27.6	12.8 (B)	0.35	0.73 (A)
EDTA	15.7	11.8 (C)	0.60	3.52 (A)
Na-phytate	0.73	1.78 (D)	0.84	10.5 (B)
Ca-phytate	1.35	2.11 (D)	0.00	0.57 (A)

*Letters represent treatment means that are statistically different at the 95% confidence level.

**Artificial groundwater (AGW): surrogate composition based on routine groundwater monitoring of nonimpacted wells screened within the water-table aquifer on the SRS (Strom and Kaback, 1992).

evident in subsequent TCLP extractions, along with the sum of water-soluble plus exchangeable fractions for the residual column materials (Table 3). In general, the total fraction of Ni extracted by all of the treatments was considerably more than U regardless of the batch or column treatment, suggesting that Ni is inherently more mobile and possibly more bioavailable than U in these materials, as has been demonstrated in previous studies (Seaman et al., 2001a; Punshon et al., 2003). Despite clear indications that the CaCl₂ and EDTA treatments extracted significant amounts of Ni from the most labile fractions, the effectiveness of the treatments was not statistically evident in the total residual Ni extractions, presumably because of the high variability in the residual digest data (Table 3). The phytate treatments appeared to reduce Ni solubility in both the initial batch and column experiments, but this was not reflected in subsequent extractions, with the exception of TCLP-extractable Ni for the Na-phytate treatment.

With the exception of the Na-phytate treatment, U extraction appeared to be increasing throughout the course of leaching for the CaCl₂ and EDTA treatments, suggesting that extraction efficiency for U would improve with continued leaching (Figure 1B). As expected, the 0.5 M NaHCO₃ (i.e., heap leach method) was highly effective at extracting U during leaching tests, removing approximately 50% in the 30 PV (data not presented). Except for NaHCO₃, only Na-phytate extracted significant amounts of U during the batch (Table 2) and column treatments, despite severe colloid dispersion and column plugging that precluded

further leaching after approximately 8 PV. In addition, a large amount of humic material appeared to be solubilized by the Na-phytate treatment, which may be responsible for the enhanced U migration. Aside from potentially enhancing the contaminant migration through complexation (Seaman et al., 2003), the Na-phytate treatment could severely alter the hydraulic conductivity of the contaminated zone of interest, further complicating remediation, a factor that is commonly overlooked in laboratory-scale contaminant extraction and immobilization studies.

As seen in the current study, phytate can act as a dispersing agent by solubilizing organics and reversing the positive charge on amphoteric oxide surfaces (Celi et al., 1999, 2001), especially in the presence of high Na levels. Uranyl (UO₂²⁺), the predominant free aqueous U species under aerobic, acidic conditions (pH < 5) (Langmuir, 1997), forms stable complexes with dissolved organic carbon (DOC) (Li et al., 1980). Previous batch experiments have demonstrated the importance of DOC in controlling the solubility of U and other metal contaminants in Steed Pond sediments (Arey et al., 1999; Seaman et al., 2001a). In addition, the EDTA treatment is second only to Na-phytate with respect to U extraction in both the batch and column experiments. Under less acidic conditions (pH > 5), various U(VI)-carbonate complexes tend to predominate, enhancing U(VI) solubility (Langmuir, 1997), as seen in the NaHCO₃ treatment.

Remarkably for the Ca-phytate leaching treatment (Figure 1B), U was essentially at or below the method detection limit for all but a few of the first effluent

Table 3. Batch Extraction Results and Cumulative U and Ni Release from Column Leaching Experiments

	Column Ni (mg kg ⁻¹)	Seq. Ex. Ni (Water Soluble + Exchangeable) (mg kg ⁻¹)**	TCLP* Ni (mg L ⁻¹)**	Total Residual Ni (mg kg ⁻¹)**	Column U (mg kg ⁻¹)	Seq. Ex. U (Water Soluble + Exchangeable) (mg kg ⁻¹)**	TCLP* U (mg L ⁻¹)**	Total Residual U (mg kg ⁻¹)**
Control [†]	–	0.24 (A)	19.0 (A)	91.6 (A)	–	0.80 (A)	5.84 (A, D)	290 (A)
AGW ^{††}	1.76	0.27 (B)	26.1 (B)	78.6 (A)	0.15	0.96 (A)	3.74 (B)	256 (A)
CaCl ₂ (pH 3)	27.6	0.09 (C)	9.4 (C)	65.1 (A)	0.35	0.94 (A)	4.38 (B, C)	273 (A)
EDTA	15.7	0.15 (D)	13.0 (C)	78.9 (A)	0.60	0.93 (A, B)	4.92 (C)	306 (A)
Na-Phytate	0.73	0.20 (E)	18.6 (A)	78.8 (A)	0.84	0.86 (A, B)	6.35 (A)	253 (A)
Ca-Phytate	1.35	0.25 (A, B)	23.4 (B)	73.1 (A)	0.00	0.50 (C)	5.67 (D)	237 (A)

*TCLP: EPA toxicity characteristic leaching procedure, results reported in mg L⁻¹ by convention.

**Letters represent treatment means that are statistically different at the 95% confidence level.

[†]Control represents Tims Branch sediment that was not subjected to any of the column treatments prior to extraction.

^{††}Artificial groundwater (AGW): surrogate composition based on routine groundwater monitoring of nonimpacted wells on the SRS (Strom and Kaback, 1992).

samples. Subsequent batch extraction data indicated that Ca-phytate leaching resulted in significant U solid-phase redistribution to more recalcitrant forms that were not solubilized in the TCLP extraction or the water-soluble and exchangeable fractions of the sequential extractions (Table 3). No significant difference was observed in the total residual U extracted from the column sediments presumably because of the relatively small percentage of U initially present in the soluble and exchangeable fractions and the high analytical variability observed in the residual digest results.

The current study clearly demonstrates the utility of both column and batch techniques for evaluating contaminant migration and redistribution behavior in response to various chemical leaching scenarios, including in-situ chemical immobilization strategies. Reasonable agreement for Ni and U extractability and immobilization treatments was observed between batch and column methods. Sequential extraction results demonstrated changes in solid-phase distribution resulting from the column-leaching treatments, either selective extraction of more labile fractions or a shift to recalcitrant fractions, which likely impact contaminant bioavailability without significantly altering total residual metal loadings. In addition, practical observations made during the column-leaching studies, such as the dissolution and transport of soil humics, and colloid dispersion and the resulting decrease in hydraulic conductivity, may be critical to the effective field deployment of a given remediation strategy.

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