Contract No:

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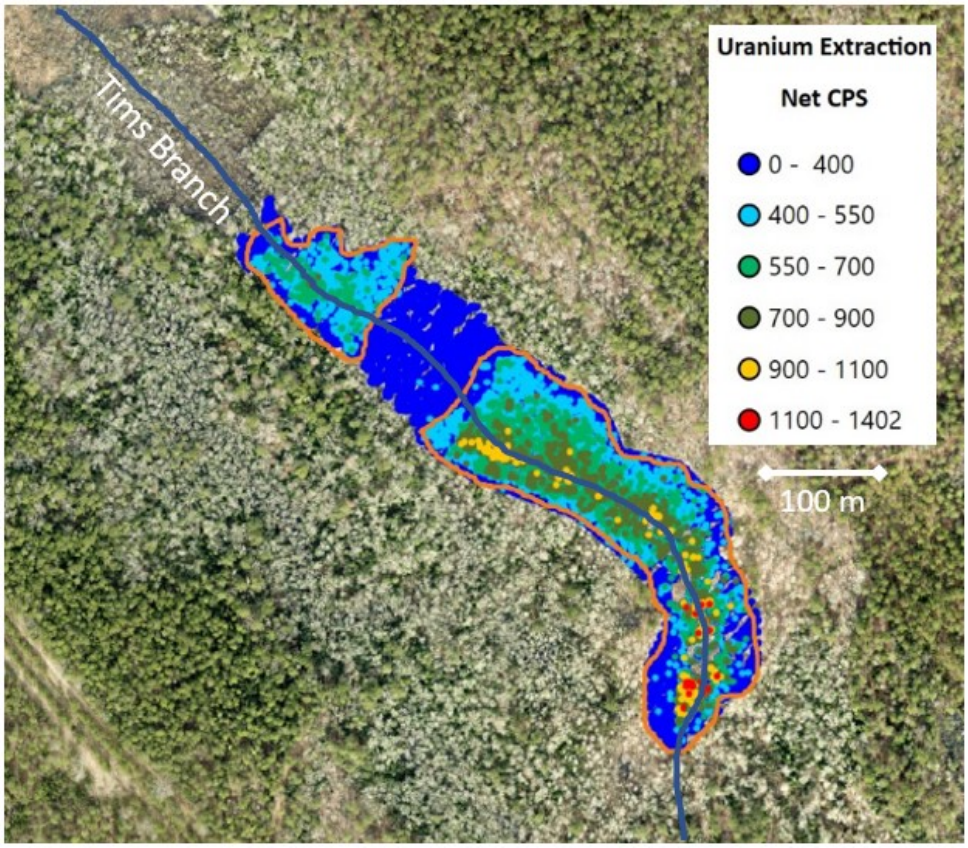
Disclaimer:

Title of Project
Immobilization of Uranium in a Wetland 8-km Downstream from an Industrial Source

Project Start and End Dates
Project Start Date: 10/1/2020
Project End Date: 9/30/2021

Project Highlight
Wetlands can be extremely effective at retaining contaminants for long periods of time. After 50 years, 94% of the uranium released into a stream remains immobilized in downstream wetlands. Hectare-sized uranium hotspots were identified as far as 8 km downstream. A walk-over survey acquiring 97,000 gamma spectra was planned and executed based on previous aerial gamma flights' findings. Walk-over spectra were used as ground-truth measurements and were utilized to create uranium contamination maps.



Project Team
Principal Investigator: Kimberly A. Roberts
Team Members: Daniel I. Kaplan and Dien Li
External Collaborators: Ronald J. Smith (SRNS), Connor J. Parker (Clemson University), Brian A. Powell (Clemson University & SRNL)

Abstract
A three-day walk-over survey with portable gamma detecting equipment was conducted over a uranium-contaminated wetland located 8-km downstream from a former fuel fabrication facility. 97,000 spectra were collected, individually processed to extract uranium activity data, and then integrated with topographical information (LIDAR) to create maps. These maps reveal that 50 years after being released into the environment, 11% of the uranium is retained in the 9-ha wetland area. Combined with measurement collected closer to the source, it was determined that 94% of the released uranium is presently being held in downstream wetlands. This demonstrates that wetlands can be very effective at immobilizing contaminants for long durations. The survey also showed that previous flyover maps overestimated the size of the contaminated areas by 140% but had the advantage of being completed in orders-of-magnitude fewer labor hours. Depending on project needs, the walk-over technique may be useful to include in tandem with flyover measurements to acquire maps with greater sensitivity and spatial resolution.

Objectives

- Create a map of contaminant uranium concentrations in a wetland located 8-km downstream from its source using a walk-over survey technique with recently improved portable gamma radiation detectors with integrated GPS equipment.
- Compare maps generated from this walk-over survey to previous flyover gamma detection techniques.
- Estimate the fraction of the 43,500 kg of uranium released 50 years ago that remain sequestered in the wetland.

REVIEWS AND APPROVALS

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Kimberly A. Roberts	Date
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Connor J. Parker	Date
Brian A. Powell	Date

2. Technical Review:

James Dyer	Date

3. PI's Manager Signature:

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4. Intellectual Property Review:

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

SRNL Legal Signature

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Ryan Petersen Date

Introduction

Contaminants released to the surface environment or from subsurface disposal facilities may resurface in wetlands or riparian zones. This is true in humid regions, such as the SRS, and arid regions, such as Yucca Mountain or the Hanford Site. Wetlands have several important roles in the hydrological cycle, including maintaining water quality by removing surface water and groundwater contaminants. Our team recently demonstrated for the first time using a recently improved gamma spectroscopy mapping technique that SRS wetlands can be effective at attenuating uranium, retaining approximately 83% of the total uranium released to a stream.[1] It was possible to make this discovery because of the unique attributes of the contaminated area: it had been left undisturbed for over 50 years and included extensive federally mandated, monitoring data. Current models describing the fate of the uranium at this site predict a wide range of outcomes, including that a majority of the uranium was retained in the sediment within 50 m of the source and that the uranium was transported >21 km in the streamwater to the Savannah River. Improving the geochemical conceptual models underpinning these transport models is necessary for estimating human risk more accurately, not just at the SRS, but elsewhere.

Most long-term studies evaluating wetland attenuation of contaminants focus on a wetland's capacity to remove mobile aqueous contaminants by monitoring stream-contaminant concentrations before and after entering a wetland.[2,3] An alternative approach is to compare the soil contaminant concentrations inside and outside the contaminated wetland.[4] Neither approach is intended to provide a spatial estimate of the contamination zone nor to provide a quantitative estimate of the long-term contaminant retention by the wetland.

Contaminant mapping techniques are readily available at the micrometer scale (e.g., Scanning Electron Microscopy/Energy Dispersive X-ray) and millimeter scale (e.g., X-ray computed tomography, wet chemistry/spectroscopy). In order to describe contaminant distributions at larger scales, such as at the landscape scale of kilometer, these types of techniques are used together with transport models. Unfortunately, the selection of assumptions to include in these transport models dictate the predicted contaminant distribution. Analytical techniques providing direct measurements of contaminants at the landscape scale are needed. Such direct measurements will reduce the uncertainty associated with predicting contaminant health risks and will provide better data for developing responsible stewardship and/or remediation strategies of contaminated lands.

Approach

A walk-over survey of Tims Branch was conducted to determine the areal distribution of uranium in the wetland using portable gamma and X-ray spectroscopy equipment. Integration of the gamma spectral data with uranium depth-profile data from soil cores provided an estimate of the uranium inventory in the contaminated area. Three general steps were employed to address the experimental objectives of this study: conduct a walk-over survey, determine uranium concentration profiles in sediment cores, and perform spectral and data analyses.

Walk-Over Gamma Detection Survey: A three-day survey of the contaminated area on Tims Branch was initiated on January 19, 2021. Five students from Clemson University and Augusta University were taught about gamma and X-ray detection and trained to use the field equipment and spectral and data analyses. As many as five surveyors were in the field at one time. Backpacks issued to the surveyors were equipped with a 3.8cm x 6.4cm x 20.3cm NaI detector, integrated GPS unit, and computer tablets (Fig 1). Gamma spectral measurements and positions were saved every second on the computer and backpack control module (multi-channel analyzer). The computer and software provided both

navigation and visualization of the gamma spectral data with one second updates (Fig 1). Detection spot size of each measurement was approximately 2-m diameter. Surveyors walked predetermined paths identified on the GPS system in the tablets. At the end of each survey day, the data stored in each backpack were downloaded and archived. To complete the project, approximately 200,000 gamma and X-ray spectra were collected. Of these, 97,000 provided information about the contaminated area, while the remaining spectra provided information about the limits of the contaminant plume.

Fig. 1: (**Left**) Surveyor with tablet and gamma backpack equipped with NaI gamma detector and telemetry. (**Right**) Example of tablet screen showing walking lines and measured radiation.

Uranium Concentrations in Sediment Cores: Results from the survey were used to identify locations with elevated uranium concentrations for determining the distribution of uranium in the sediment profile. Seven 2.5-cm diameter by ~30-cm long cores were collected along a transect through the most contaminated portion of the study site. The cores were shipped to Clemson University, where they were sectioned into 2-cm long segments. Including background samples collected adjacent to the contamination zone, there was a total of 98 samples. The samples were digested using heated, concentrated nitric and hydrofluoric acids; the digestates were subsequently analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The uranium concentration in all samples was well above the instrument's detection limit.

Spectral and Data Analysis: Analysis of some 200,000 spectra was accomplished with the software AVID. High Purity Germanium field measurements identified two isotopes, ^{238}U and ^{235}U, at a location ~2-km downstream from the source as well as at the study site, 8-km downstream from the source (Fig. 2). The similar spectra support the contention that the uranium contamination at both locations originates from the same source, which simplified interpretation of the gamma spectra. The peak intensities of ^{238}U and ^{235}U were extracted from each spectrum and assigned to the corresponding GPS coordinates. Both isotopes' activities were well above the activities of the primordial uranium and its decay products.

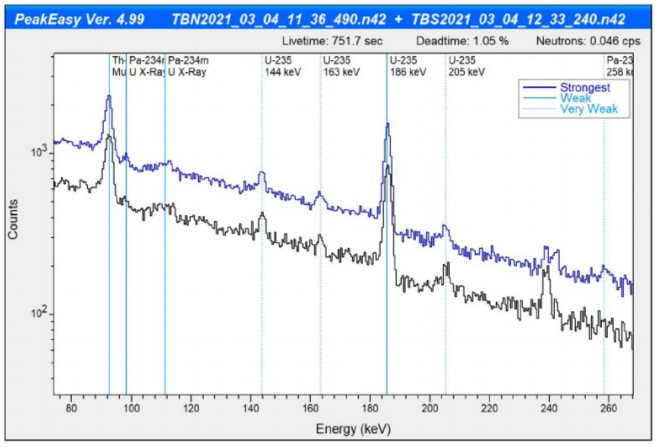

Fig. 2. Example of High Purity Germanium spectra taken from two locations: Black spectrum = Tims Branch North (2-km downstream) and Blue spectrum = Tims Branch South (8-km downstream). The two near-identical spectra indicate that the two areas have similar contamination sources. (Note that ^{234m}Pa is a decay daughter of ^{238}U and is used to estimate ^{238}U activity.)

To estimate the uranium inventory, it was necessary to account for not only the near-surface uranium measured by the gamma spectral measurements, but also the deeper uranium observed in the core samples. To accomplish this, a Gamma Correction Factor was developed that was used with the gamma spectral activity data to account for the underlying U, whose emissions were shielded by the soil. Additional details of this complicated calculation are provided by Kaplan et al.[1]

To put these mapping results into a larger context, they were also:

- layered over LIDAR ground elevation data to evaluate the relative importance of ground elevation on uranium distribution,
- combined with uranium mapping results by Kaplan et al. [1] from another section of Tims Branch to provide an estimate of the fraction of released uranium (43,500 kg) remaining in the downstream wetlands, and
- compared to maps generated from flyover data collected with helicopters.

Accomplishments

Uranium Transport: The results from the three-day survey are presented in Figure 3. Examples of the uranium depth profiles are presented in Table 1. Finally, integrating the uranium mapping results on the X-Y plane with the uranium depth-profile data from the sediment soil cores allowed for an estimate to be made of the mass of uranium in the surveyed area (Table 1).

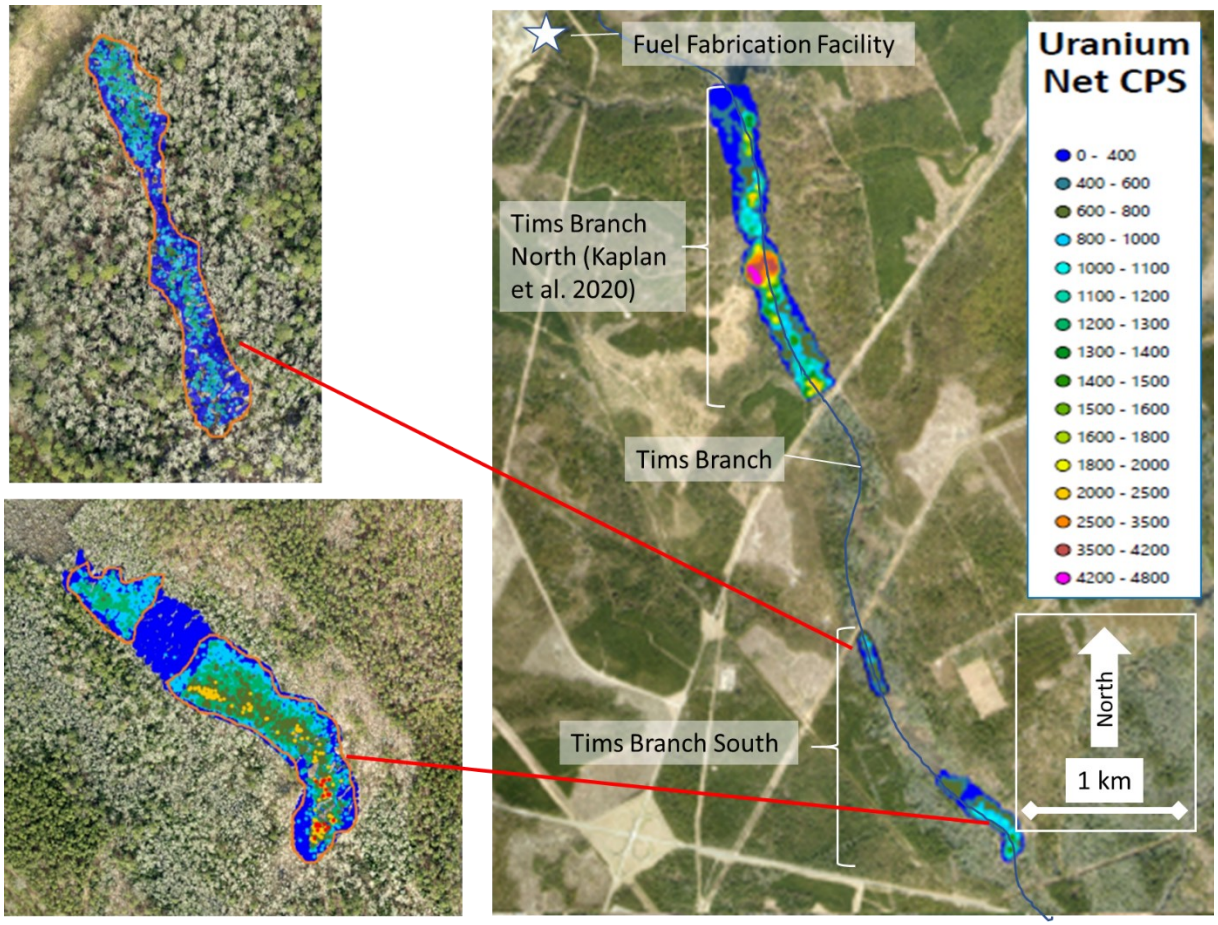

Fig. 3: (**Left**) Map of uranium activity (units are counts per second (CPS)) in Tims Branch South. (**Right**) Map of uranium concentrations of Tims Branch South and Tims Branch North (as reported by Kaplan et al.[1]). Map also locates the original source of the uranium contamination: the M-Area Fuel Fabrication Facility.

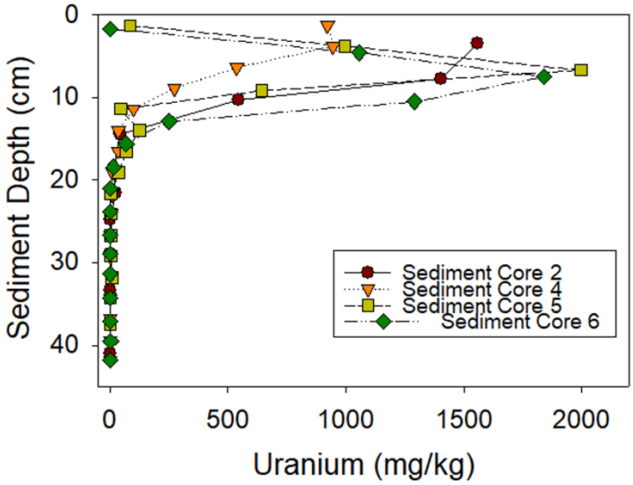

Fig. 4. Examples of uranium depth profiles from four sediment cores collected along a transection through the most contaminated area of Tims Branch South.

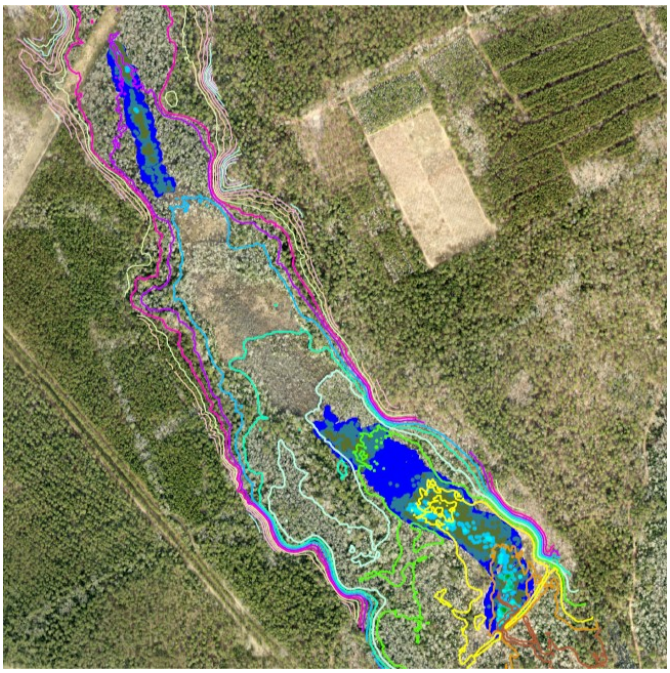

Fig. 5. 1-m-resolution LIDAR ground elevation map layered over the uranium gamma map. Elevation generally decreases from North (top) to South and from the edges to the center of the wetland study area.

The key results related to uranium transport are:

- There were two contamination areas separated by almost a kilometer that had a total area of 47,400 m^2. The contamination areas were characterized by 97,000 spectra (Figure 3).
- The highest uranium concentration detected was 2000 mg/kg. For reference, background levels are closer to 5 mg/kg uranium on the Savannah River Site (Figure 4).
- In general, the highest uranium concentrations were buried beneath about 4 to 8 cm of deposited cleaner stream sediment. Negligible contamination was found below ~18 cm (Fig. 4).
- A strong inverse correlation existed between ground elevation and uranium distribution (Fig. 5).

Table 1. Uranium mass balance based on walk-over survey gamma measurements and mass spectroscopy measurements of uranium concentration in sediment cores.

	Metric tonnes uranium	**% of added uranium detected 50 years after release**	**Source**
Total uranium released into Tims Branch during operations	43.5	– –	Evans et al. (1984)[5]
Tims Branch North	36.2	83%	Kaplan et al. (2020)[1]
Tims Branch South	4.8	11%	This study
Total uranium detected in Tims Branch Wetland		94%	This study

- The total mass of uranium in these two sites were 4.8 metric tons U, or 11% of the total uranium released by the Fuel Fabrication Facility into Tims Branch.
- This is the first report of such large masses of uranium (as opposed to gram quantities) being transported kilometer distances.

Walk-over vs. Flyover Gamma Mapping:

Previously unpublished results from a helicopter flyover campaign that included Tims Branch South was completed in 2020. A comparison of the maps and equipment are presented in Figure 6 and Table 2.

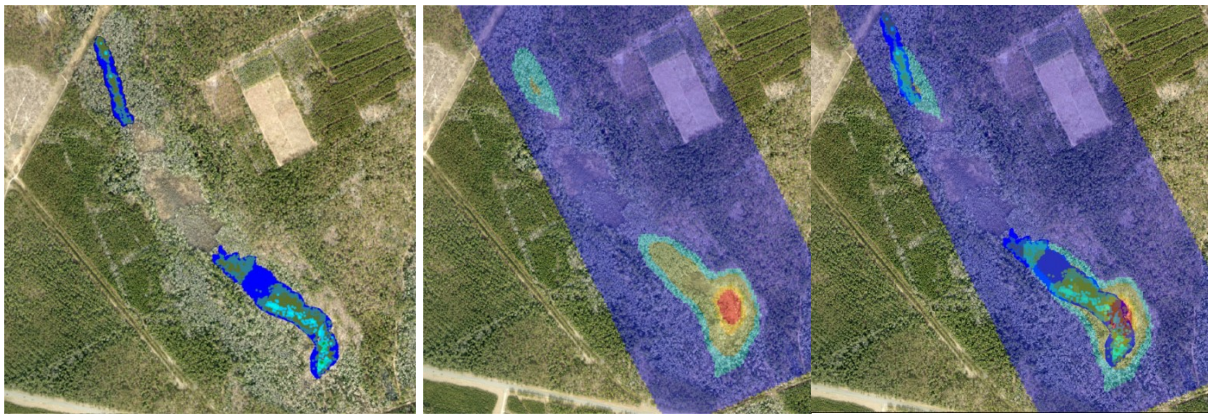

Fig. 6. (**Left**) Walk-over map, (**Middle**) flyover map, and (**right**) walk-over map layered over flyover map.

Table 2. Comparison between Walk-over and Flyover gamma detection techniques.

	Walk-Over	**Flyover**
Spot size (m^2)	0.8	180
Data acquisition time (sec)	1	1
Number spectra in contaminated area	97,000	760
Detector height from ground (m)	1	30
Spacing between survey lines (m)	3	45
Ground speed (km/hr)	1	70
NaI detector (W × H × L; cm)	one 6×4×20	three 5×10×40
Approximate Minimum Detectable Activity ($\mu Ci/m^2$)	1.18	0.99
Survey acquisition time (person-hr)	55	1.5
Estimated contamination area (m^2)	47,400	114,000
Aerial overestimation of contamination area ((Fly – Walk)/Walk) × 100		140%

The key results from the comparison of these two gamma measurements mapping techniques are:

- This is the first time that aerial remote sensing was ground truthed using a data-intensive technique (Figure 6).
- The flyover survey identified uranium hot-spots; however, it overestimated the contaminated area by 140% due to limitations associated with physics and geometry (Table 2).
- Depending on project needs, the much slower walk-over technique may be coupled with aerial measurements to acquire maps of greater sensitivity and spatial resolution (Table 2).

FY 2021 Peer-reviewed/Non-peer reviewed Publications

Ramírez-Guinart, O., **Kaplan, D. I.**, Rigol, A., and Vidal, M. (2021). Deriving probabilistic soil distribution coefficients (K_d). Part 1: General approach to decreasing and describing variability and example using uranium K_d values. *Journal of Environmental Radioactivity* 222:106362.

Future Plans

- Complete technical journal article for *Environmental Science and Technology*
- In discussion with program manager to apply technology to ^{137}Cs-contaminated site

Intellectual Property
None

Total Number of Post-Doctoral Researchers
None

Total Number of Student Researchers
5 students
Michael Laird – B.S. Physics; August University
James Foster – M.S. student in Environmental Engineering and Earth Sciences; Clemson University
Saran Donaher – Ph.D. student in Environmental Engineering and Earth Sciences; Clemson University
Connor Parker – Ph.D. student in Environmental Engineering and Earth Sciences; Clemson University
Kelli Trotter – M.S. student in Environmental Engineering and Earth Sciences; Clemson University

References

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3. Dean, A. P.; Lynch, S.; Rowland, P.; Toft, B. D.; Pittman, J. K.; White, K. N., Natural wetlands are efficient at providing long-term metal remediation of freshwater systems polluted by acid mine drainage. *Environmental science & technology* **2013,** *47* (21), 12029-12036.
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5. Evans, A. G.; Bauer, L. R.; Haselow, J. S.; Hayes, D. W.; Martin, H. L.; McDowell, W. L.; Pickett, J. B. *Uranium in the Savannah River Site Environment*; WSRC-RP-92-315; Westinghouse Savannah River Company, Aiken, SC, 1992.