

VECTORS FOR METAL TRANSPORT IN THE TIMS BRANCH/STEED POND WATERSHED ON THE SAVANNAH RIVER SITE

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Abstract. Following construction of the Department of Energy's Savannah River Site (SRS) near Aiken, SC in 1954, over 44,000 kg of depleted uranium (U), a similar amount of nickel (Ni), and other metal contaminants were released into the Tims Branch-Steed Pond (TBSP) system. Failure of the Steed Pond dam in the 1990s facilitated significant transfer of U to downstream ecosystems largely in association with particulates suspended during rainfall events. Since that time Steed Pond has become much more densely vegetated and the affect of this landcover shift on U and Ni mobilization is currently unknown. Recent monitoring efforts below Steed Pond suggest that during base flow mobilized Ni predominately occurs in soluble or nanoparticulate ($<0.2 \mu\text{m}$) form, while significant portions of U are mobilized as filterable particulates ($>0.2 \mu\text{m}$). To evaluate the current impact of rainfall events, we have installed an automated stream monitoring system below the outlet of Steed Pond. This monitoring system is triggered by turbidity measurements to capture peaks in suspended particulates during episodic rain events. In addition, we are conducting laboratory studies that probe the influence of pH, ionic strength and redox status on the remobilization of colloid-bound U within the TBSP system.

HISTORICAL CONTEXT

Environmental releases of uranium (U) and other contaminants at the Department of Energy's Savannah River Site (SRS), near Aiken, SC, occurred shortly after construction of the facility in 1954 (Figure 1). Most of the U releases occurred just north of Tims Branch/Steed Pond area (TBSP) from the nuclear fabrication facility, known as M Area. Fuel and target assemblies used in the SRS reactors were fabricated onsite from aluminum (Al) and U metal

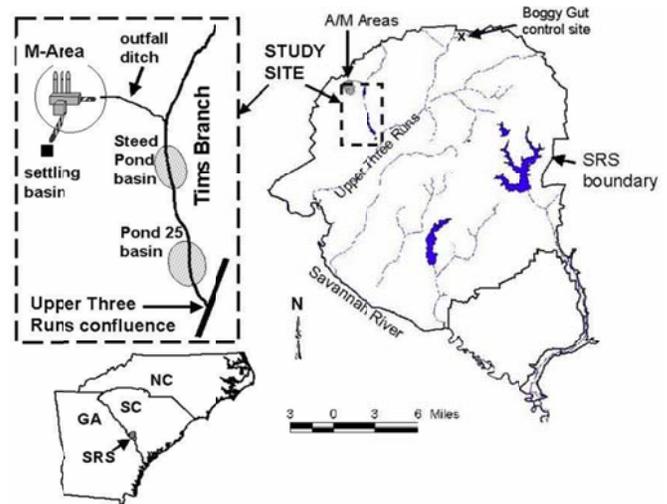


Figure 1. Regional location of the SRS, M Area, and Tims Branch/Steed Pond (Adapted from Sowder et al., 2003).

(Evans et al., 1992). Significant releases to Tims Branch waters finally ended in 1979 with the diversion of the primary U release streams to the settling basin (Figure 2). Furthermore, all releases of untreated process waste water were diverted to the settling basin in May 1982 (Evans et al., 1992). The peak release years occurred in the late 1960's and early 1970's with releases declining since that time. The Tims Branch-Steed Pond (TBSP) system is located within the M Area watershed, and was estimated to have received approximately 44,000 kg of depleted U between 1954 and 1985. The total recorded U release is 23.7 curies (Evans et al., 1992). However, stream sediment studies have shown that the U is largely associated with Steed Pond sediments (Jackson et al. 2005).

1954:
SRS Constructed

Early 1970s:
Dam Repaired

1982:
Relases to Tims
Branch cease

Early 1960s:

1979:

1984:

The conditions for deposition of U in Tims Branch are influenced by stream morphology. The discharges from M Area entered a drainage ditch and flowed down a steep slope that intersects Tims Branch (Figure 3). Steed Pond acted as a settling basin for Tims Branch. Water entering the pond had a residence time of around 3 days (Hayes, 1984), which was sufficient to reduce the activity of alpha radiation to <1 pCi/L in the downstream waters based on aerial surveys (Evans et al., 1992). Much of this reduction of radioactivity resulted from an accumulation of ~ 0.9 m of sediment behind the Steed Pond wooden dam (Evans et al., 1992).

mitigation was its function as a sediment trap for the Tims Branch river, with trapping efficiency based on the pond water stage and pond residence time.

PREVIOUS STUDIES

Monitoring efforts in the 1990s indicated that suspended sediment loading in the stream was influenced by episodic erosion events during rainstorms resulting in up to 2800% increase in U transport compared to baseflow (Batson et al., 1996; Batson, 1994).

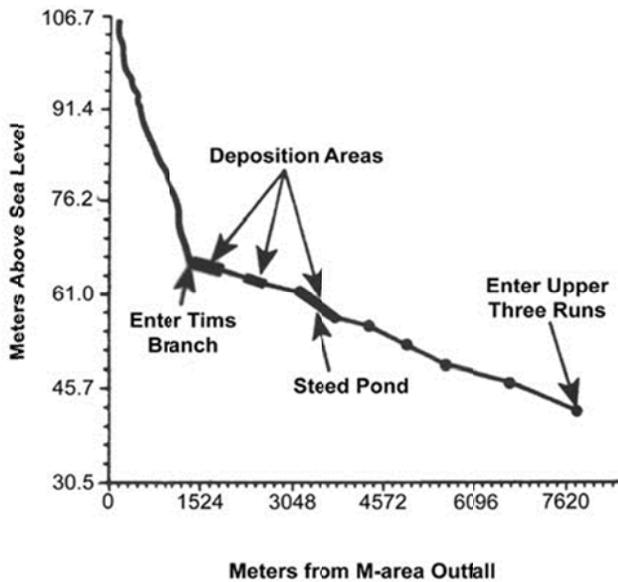


Figure 3. Elevation of Tims Branch System from the M-Area outfall to Upper Three Runs Creek (Evans et al., 1992).

Steed Pond originally had an area of about 14 acres until part of the wooden dam collapsed in the early 1960's and the pond was partially drained. Ten years later, the wooden dam was repaired and the pond returned to a surface area of 11 acres (Evans et al., 1992). In 1984, however, the wooden dam collapsed again and the pond was emptied (Evans et al., 1992). It remains dry at present with many braided streams flowing throughout. It appears one of Steed Pond's primary mechanisms of contaminant

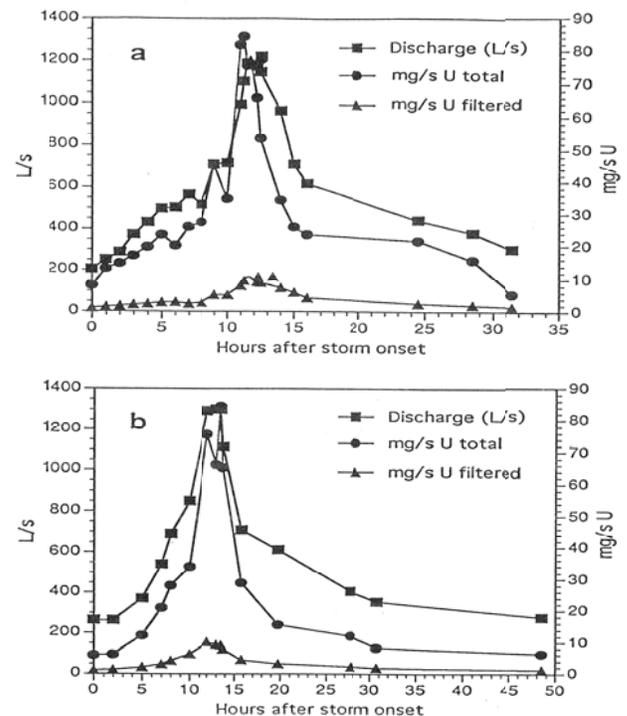


Figure 4. Hydrograph of U mass flux vs. discharge for March 23, 1993 (a), and March 26, 1993 (b) (Redrawn from Batson et al., 1996).

The results of Batson et al. (1994, 1996) indicated that what was thought to be a stable depositional area within Steed Pond was instead subject to significant erosion sending massive amounts of suspended soil particles

downstream. They showed that as little as 16 mm of rainfall was needed to cause significant increase in stream turbidity and associated increases in U flux (Batson et al., 1996). By carefully measuring filtered (<0.45µm) and unfiltered samples, Batson et al (1996) observed most of this U was associated with suspended particulates rather than dissolved (Figure 4).

In oxic waters, U is present as a linear, hexavalent oxo-cation UO_2^{2+} (Uranyl). Uranyl has 4 to 6 free coordination sites around the equator of the linear molecule that form strong complexes with hydroxide or carbonate ligands (Hudson et al., 1999). Oxygen bearing functional groups on the surface of mineral or organic solids can bind to these equatorial coordination sites and facilitate the removal of U from the aqueous phase. Laboratory studies using Steed Pond sediments have shown that both organic matter and iron (Fe) redox chemistry play a strong role in controlling U solubility and distribution (Sowder et al., 2003; Arey et al., 1999). Uranium solubility is apparently governed by dissolved organic carbon (DOC) concentration. Sowder et al. (2003) also established the sediments contain high levels of short-range-ordered (SRO) Fe phases that are known to have high surface areas and high densities of surface hydroxyl groups (Liu et al., 2005). Seasonal variations in redox accompanied by high concentrations of organic matter and aluminum in Steed Pond likely contribute to the enrichment and persistence of SRO Fe in the sediments (Thompson et al., 2011). Field Flow Fractionation (FFF) and Size Exclusion Chromatography (SEC) of Steed Pond sediments by Jackson et al. (2005) indicated that a significant amount of U was associated with nanometer-size colloids rich in Fe. As a result of these studies, more laboratory experiments focusing on sediment manipulation are essential to understand the dynamic processes controlling colloidal migration in the TBSP system.

METHODS

The goal of this project is to determine the role Fe reduction, DOC, and pH have on U mobilization during episodic rain events. In the summer of 2010, we collected samples from Tims Branch during base-flow conditions just downstream from Steed Pond at the same stream sampling location monitored by Batson et al. (1994, 1996). These samples were divided into subsamples of filtered (<0.2 µm pore size) and unfiltered acidified aliquots and analyzed for Ni and U inductively coupled plasma – mass spectrometry (ICP-MS) (EPA Method 6020A, 2007).

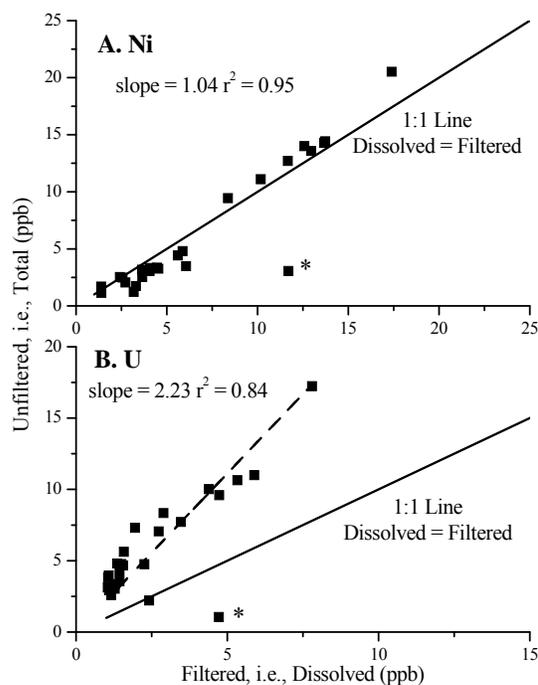


Figure 5. Total and dissolved Ni (A) and U (B) concentrations in Tims Branch stream samples collected in 2010. Starred (*) samples were excluded from the regression analysis.

Analysis of this data indicates that Ni concentrations (Figure 5a) in filtered and unfiltered samples are the same (high r^2 and slope of ≈ 1), suggesting that Ni was present either as a free aquo-ion or in nanoparticulate or other complexes that are smaller than 200 nanometers. While a slope >1 for the U correlation (Figure 5b) indicates that much of the U was associated with a filterable colloidal phase (>200 nm). These recent U measurements are comparable to measurements made by Batson et al. (1994, 1996) during base flow conditions (≈ 2 -6 µg/L of U). This heightens the need to elucidate the key vectors for U mobilization in this system, which we will address by coupling field monitoring and laboratory experiments with particle-sensitive analysis. Stream samples will be collected using an automated stream monitoring system, while our laboratory experiments will focus on establishing the influence of dynamic redox conditions on U and Ni mobilization.

In order to test whether there is currently significant export of U-associated colloids during rain events, we will take stream samples during the rising and falling limb of the hydrograph. Stream samples will be collected by an automated Isco water sampler in combination with a flow

meter and turbidity sensor to monitor particulate levels and trigger sampling within Tims Branch just below Steed Pond. This data, in combination with pH, electrical conductivity (EC), and dissolved oxygen (DO) will be transmitted via VHF (very high frequency) radio telemetry to a base site and displayed via the internet for real time monitoring. Once collected, water samples will be transported to lab for metals and colloid analysis via ICP-MS and transmission electron microscopy (TEM) and/or X-ray diffraction (XRD).

In addition, we will perform various sediment incubations under anoxic and oxic conditions across a range of pH and DOC concentrations to assess the potential for sediment mobilization. We will utilize flow field flow fractionation (FFF) in combination with ICP-MS in order to separate particles based on size and elemental composition.

We hypothesize that our automated water sampling during periodic rain events will yield results similar to Batson et al (1996) at base flow, but provide new descriptions of the colloidal composition across the hydrograph. Our aspiration is to describe the environmental controls on colloid interactions in TBSP as they pertain to U mobilization.

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