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In situ porewater uranium concentrations in a contaminated wetland: Effect of seasons and sediment depth☆

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ABSTRACT

Previous studies have shown that Tims Branch wetlands on the Savannah River Site in South Carolina, USA is an effective environmental sink for sequestering the 44 tons of uranium (U) released into the system. The objective of this study was to evaluate over the course of a year, the fluctuations in sediment porewater U concentrations as a function of sediment depth, and the conditions and the extent that the contaminated wetlands acted as an environmental source for U. Sediment desorption tests indicated that U was strongly bound (K_d values were 2100–6900 L/kg), and sequential extraction experiments indicated that a majority of the U was associated with the readily oxidizable fraction (presumably, organic matter fraction). *In situ* porewater samples were collected using diffusion samplers that were placed in the contaminated wetlands and their uranium concentrations indicated that as much as 3×10^{-5} wt-% of the system U was in the mobile aqueous phase (federal maximum contaminant levels (MCL) = 0.03 μg/L U). Aqueous U concentrations were correlated to *Eh* ($r = 0.422$; $n = 113$; $p \leq 0.001$). These data also suggested that there may be a critical *Eh* at ~400 mV, above which aqueous U concentrations increased significantly ($p \leq 0.01$) by more than an order of magnitude. These results have implications on the long-term stewardship of this contaminated system; sediment organic matter concentrations and wetland hydrology and plant vegetation need to be maintained in a manner that does not permit strong reoxidation of the system. This could be achieved by minimizing land-use changes or the occurrences of forest fires and ensuring that the system's hydrology is not greatly altered.

1. Introduction

Wetlands have been described as the kidneys of the earth (Brix, 1994). This analogy stems from the fact that wetlands contain several biogeochemical processes that promote removing contaminants from subsurface and surface waters. The unique hydrological regimes of wetlands create an environment that often has dense plant populations and sediments with elevated natural organic matter concentrations, microbial activity, and chemical gradients that can provide a wide range of mechanisms for binding contaminants. This cleansing characteristic of wetlands has been studied for decades and is utilized in agricultural and urban systems to remediate groundwater contaminants. It is also utilized by environmental engineers to create artificial wetlands to remediate contaminated streams.

Tims Branch on the Savannah River Site (SRS) in South Carolina US received 44 tons of uranium (U) waste between 1954 and 1989 from a facility that manufactured fuel and target assemblies for nuclear reactors (Evans et al., 1992; Pickett, 1990). This release of U accounted for greater than 97% of the gross alpha activity introduced to the environment from SRS operations (Evans et al., 1992). It has been estimated that over 80% of the released U remains in Tims Branch wetlands, of which 70% resides in Steed Pond, an abandoned farm pond predating the SRS (Evans et al., 1992; Pickett, 1990). Tims Branch aqueous U concentrations are at or below regulatory limits of 0.03 μg/L (SRNS, 2015), indicating that these wetlands are effective at sequestering this large mass of U.

Previous studies conducted at the SRS have shown that most wetland U was associated with sediment organic matter (Bertsch

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et al., 1994; Li et al., 2015; Sowder et al., 2005). Also, the U in the wetlands existed primarily in the oxidized form, uranyl (UO_2^{2+}), but between 0 and 20% also existed in the less mobile U(IV) oxidation state (Bertsch et al., 1994; Li et al., 2015). Greenhouse mesocosm studies simulating Tims Branch conditions demonstrated that U concentrations near plant roots were as much as an order of magnitude greater than in root-free soils (Koster van Groos et al., 2016). Furthermore, it was shown that U greatly concentrates on plant roots, co-associated with root phosphate (Chang et al., 2014).

Gilson et al. (2015) conducted mesocosm studies to elucidate the effect of moisture regimes on the biogeochemical conditions leading to the release of U from wetland sediments. They noted that porewater U concentrations increased after drying and rewetting, but the cumulative amount of U released following the dry period constituted less than 1% of the total U immobilized in the sediment. This low level of remobilization suggested, and XANES analyses confirmed, that microbial reduction was not the primary means of U immobilization, as the U immobilized was primarily U(VI) rather than U(IV). Drying followed by rewetting caused a redistribution of U downward in the soil profile. They demonstrated that short periods of drought conditions may cause an otherwise reducing wetland to redistribute sediment U without causing large U releases into the mobile aqueous phase.

There is an increasing concern that these wetland “sinks” for contaminants may eventually become environmental “sources” for contaminants. Understanding the biogeochemistry of these systems is needed to provide information that can be used to make long-term sustainable management decisions in response to changes in hydrology, rainfall, fires, and urban development. The objectives of this Tims Branch field study were: 1) to quantify fluctuations of porewater U concentrations, and 2) to identify important biogeochemical factors that may be responsible for the release of sediment bound U. Our approach was to measure porewater chemical concentrations over the course of a year through the use of depth-discrete diffusion samplers placed in two locations within the U-contaminated wetland and to relate these results to sediment U desorption properties.

2. Materials and methods

2.1. Field sampling

Two diffusion samplers were placed in Steeds Pond along the edge of Tims Branch at #1 Contaminated site and #2 Contaminated site shown in Fig. 1. This stretch of Tims Branch was previously shown to have the greatest sediment U concentrations (Pickett, 1990). The diffusion samplers used in this study were described by MacDonald et al. (2013) (Fig. 2). Briefly, two of these 0.8-m long PVC samplers were placed along the banks of Tims Branch at the #1-Contaminated and #2-Contaminated sites (Fig. 1). The diffusion sampler consisted of 20 60-mL chambers (3.5 × 1.2 × 0.9 cm) stacked on top of one another with a polyethersulfone membrane (0.22 μm pore size) stretched over the front of the chamber openings to separate the sediment from the chambers. Two 0.16-cm (1/16 inch) Tygon tubes were embedded in the side of the PVC structure to connect each sampling chamber to above ground. The tubes were used to add deoxygenated, deionized water to the chambers. This water was permitted to equilibrate passively with the sediment pore water for three months before withdrawing the water samples from the 20 chambers. The diffusion samplers were emplaced such that the uppermost chamber was ~5 cm below Tims Branch water level on the day of deployment. The diffusion samplers were collected four times by drawing porewater into a syringe attached to the 0.16-cm tubing. While sampling, the second tube leading into the chamber withdrew N_2 from a Tevlar bag in an effort

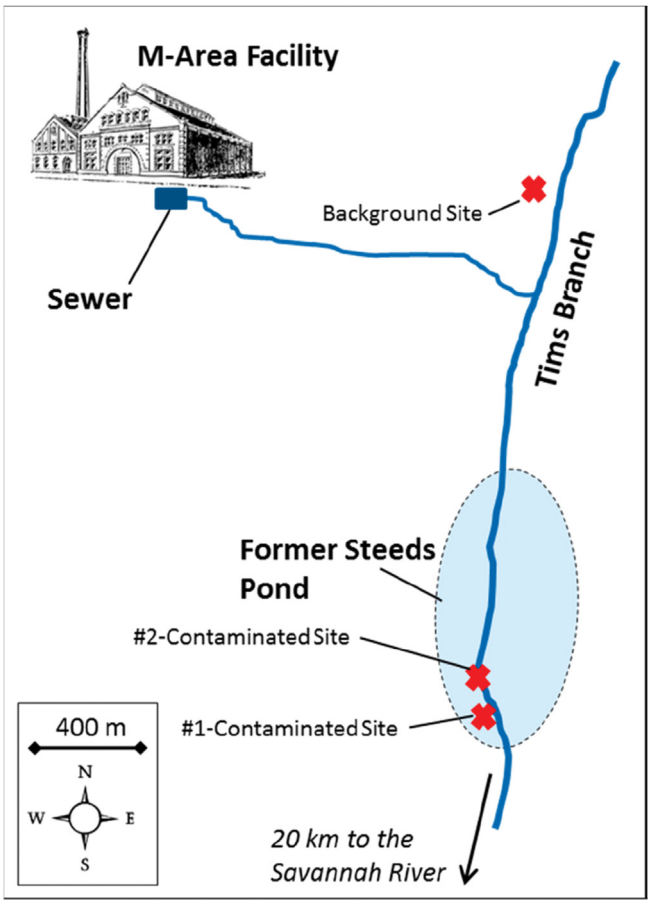

Fig. 1. Schematic representation of sampling locations at the Tims Branch study site.

to minimize reoxidation of the system. pH and *Eh* were measured in the field, while all other analyses were measured in the laboratory as described in Section 2.2.

Three sediment samples were collected: two near the diffusion samplers (#1-Contaminated and #2-Contaminated), and the third from a minimally contaminated area just upstream of the M-Area discharge tributary (Background Sample) (Fig. 1). The Background sediment sample was used to provide an uncontaminated analogue of the contaminated samples and is expected to be minimally impacted by SRS operations. The location of the Background sample was selected based on its similar vegetative, hydraulic, and topographic characteristics with the two contaminated samples. At each location, the surface biological debris was scraped away and then the surface 10 cm depth of sediment was recovered with a hand trowel. The samples were placed in zip lock bags, and stored in an ice chest. Once at the Savannah River National Laboratory, the sediment samples were placed in three zip lock bags; the space between each bag was filled with N_2 gas, forming a double-N_2 gas envelope around the samples. A second sediment sample at the #1-Contaminated site was collected at 10–20 cm depth, where a dark gleyed layer was observed, suggesting the presence of a highly reducing zone (this corresponds to approximately 22–32 cm depth of the diffusion samplers). This sediment sample was only analyzed for qPCR, described in Section 2.2.4.

2.2. Sediment and porewater characterization

2.2.1. General soil characterization

All storage, testing, and characterization of the sediments were