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Uranium delivery and uptake in a montane wetland, north-central Colorado, USA

R. Randall Schumann [a, *], Robert A. Zielinski [a], James K. Otton [a], Michael P. Pantea [a], William H. Orem [b]

[a] U.S. Geological Survey, P.O. Box 25046, Denver Federal Center, Denver, CO 80225–0046, United States
[b] U.S. Geological Survey, 12201 Sunrise Valley Dr., Reston, VA 20192, United States

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ABSTRACT

Comprehensive sampling of peat, underlying lakebed sediments, and coexisting waters of a naturally uraniferous montane wetland are combined with hydrologic measurements to define the important controls on uranium (U) supply and uptake. The major source of U to the wetland is groundwater flowing through locally fractured and faulted granite gneiss of Proterozoic age. Dissolved U concentrations in four springs and one seep ranged from 20 to 83 ppb (μg/l). Maximum U concentrations are ~300 ppm (mg/kg) in lakebed sediments and >3000 ppm in peat. Uranium in lakebed sediments is primarily stratabound in the more organic-rich layers, but samples of similar organic content display variable U concentrations. Post-depositional modifications include variable additions of U delivered by groundwater. Uranium distribution in peat is heterogeneous and primarily controlled by proximity to groundwater-fed springs and seeps that act as local point sources of U, and by proximity to groundwater directed along the peat/lakebeds contact. Uranium is initially sorbed on various organic components of peat as oxidized U(VI) present in groundwater. Selective extractions indicate that the majority of sorbed U remains as the oxidized species despite reducing conditions that should favor formation of U(IV). Possible explanations are kinetic hindrances related to strong complex formation between uranyl and humic substances, inhibition of anaerobic bacterial activity by low supply of dissolved iron and sulfate, and by cold temperatures.

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1. Introduction

Wetlands function as efficient filters that trap suspended particles, incorporate excess dissolved nutrients, and fix dissolved metals (Cu, Pb, Zn, Cr, Hg, U) and metalloids (As, Se) of environmental concern (Shotyk, 1988; Reddy and Delaune, 2008). Organic-rich, microbially active wetland soils and sediments provide ideal substrates for metal uptake by a variety of mechanisms including ion exchange, metal-organic complexing, adsorption, and precipitation of metal sulfides and oxides (Walton-Day, 2003). Important controlling variables include pH, Eh, water/sediment chemistry, and the type, diversity, and activity of resident microorganisms. Interplay of the various uptake mechanisms is complex and site specific. For example, wetlands that receive sulfate-rich waters can support active bacterially mediated sulfate reduction that is indicated by H_2S generation and precipitation of metal sulfides and reduced oxides (Machemer and Wildeman, 1992; Groudev et al., 1999). In contrast, wetlands that receive sulfate-poor waters may fix metals by one or more mechanisms in which sulfate reduction plays a lesser role. The observed distribution of metals within a wetland is the net result of spatial and temporal variations in these uptake mechanisms and variations in metal supply from source rocks and sediments.

Uranium-bearing wetlands are a relatively well-documented subclass of metal-enriched wetlands. Reported occurrences are from a variety of geologic, hydrologic, and climatic settings, mostly in North America and Europe (Armands, 1967; Halbach et al., 1980; Toens, 1984; Zielinski et al., 1987, 1988; Culbert and Leighton, 1988; Shotyk, 1988; Shotyk et al., 1992; Read et al., 1993; Owen and Otton, 1995; Tixier and Beckie, 2001; Gonzalez-Acevedo et al., 2006). Many of the reported wetlands are removed from obvious sources of pollution, but some are located near U mines and deposits of U-bearing mining/milling wastes (Akber et al., 1992; Groudev et al.,

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* Corresponding author.
E-mail address: rschumann@usgs.gov (R.R. Schumann).

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1999; Schöner et al., 2009). This suggests that in some settings, U-bearing wetlands might be used as indicators of concealed ore deposits, or as pollution controls.

Studies of U-bearing peat and organic-rich lakebeds are of scientific interest because they describe the first stage of U-organic matter associations that, after burial and diagenesis, may form U-bearing coal or shale, respectively. These studies also contribute to broader topics such as the role of metals in soil-forming processes and the environmental controls on contaminant migration. Knowledge gained from natural wetlands can inform the design of engineered wetlands (Hammer, 1989) and improve the design of commercial facilities for the biologically based removal of dissolved U (Lovley, 1995; Kalin et al., 2005). Results also aid land managers who must understand the important controls on U fixation and mobility in order to predict the environmental impacts of wetland disturbances (Owen and Otton, 1995).

Identification of U-rich wetlands is hampered by their generally low radioactivity, because emplacement of uranium is often too recent to permit significant ingrowth of the more radioactive U decay products (Culbert and Leighton, 1988). This means that physical sampling and chemical analyses, rather than ground-based or aerial radioactivity surveys, are needed to locate and characterize these types of deposits. However, uranium remains a preferred element for study because it is amenable to a variety of specialized measurements such as radiography and U decay-series dating that provide unique spatial and temporal information.

This study documents the conditions and processes controlling the efficient uptake of U in a relatively remote, natural wetland that is absent of reported U occurrences, mining impacts, or other obvious sources of pollution. Unlike previous studies of U-rich wetlands, this study is distinguished because it provides an exceptionally detailed three-dimensional view of the distribution of uranium in as much as 3.7 m of Holocene peat, underlain by organic-rich lacustrine silt and clay (gyttja) and organic-poor clay and silt of a precursor post-glacial lake, with a combined thickness of as much as 8.5 m. The hydrologic characteristics of the entire sedimentary package from surface to bedrock were investigated with an extensive array of installed piezometers and water-table monitoring wells. Mechanisms of U uptake were investigated by a variety of techniques that utilize analyses of waters and of core and auger samples collected from depths as great as 11 m. Results of this study provide new insights regarding the spatial association of U with organic matter in peat and, unlike previous studies of metal delivery to wetlands, identify several pathways for the delivery of U to specific areas and horizons in the wetland. The techniques used in this broad-scope investigation can be readily applied to other U-rich or metal-rich wetlands.

2. Physical setting

The study area is located approximately 13 km north of Rocky Mountain National Park in north-central Colorado, USA, within the upper reaches of the Laramie River valley (Fig. 1). We informally refer to this wetland as the Boston Peak (BP) wetland after the U.S. Geological Survey 7.5' topographic quadrangle in which it is located, and because this name was informally given to the wetland when the occurrence of elevated uranium and trace metal concentrations were first documented there by Sarnecki (1983). The study area lies within the Roosevelt National Forest, in an area that is largely used for recreational activities such as camping, fishing, and hunting. The wetland occupies an area of approximately 3.9 ha at an altitude of approximately 2700 m above sea level. It is separated from the Laramie River to the west by a low, elongate, north-trending bedrock ridge (Fig. 1). To the east, the wetland is flanked by a steep bedrock slope thinly mantled with glacial deposits, colluvium, and talus. The north (downstream) margin of the wetland is bordered by a large landslide (Fig. 1).

Annual precipitation in the area is typically 50–64 cm, with most falling as snow during the months October-May (Khun et al., 1983). Snowmelt occurs primarily in May-June and is the primary source of water to the area. During the summer months, rain is delivered in the form of occasional afternoon thundershowers (Dougherty et al., 1987). Surface runoff enters the wetland via a small intermittent stream that is sourced by a seep zone at the contact between bedrock and the overlying landslide deposits, which enters the wetland at its northeastern edge. During spring snowmelt and following heavy rains, surface runoff also enters the wetland via overland flow that runs down the valley side slopes to the east and west of the wetland, through an intermittent surface drainage from the south, and from melting snow on the wetland surface during late spring. Surface water exits the northwestern corner of the wetland via a gap between the bedrock ridge to the west and the landslide to the north (Figs. 1 and 2).

The primary source of water to the wetland is groundwater from springs and seeps that are sourced in fracture systems in the surrounding crystalline bedrock. The springs and seeps enter the wetland at the edges and from beneath, and form spring pools on the wetland surface (Fig. 2) where the upwelling water is forced through the peat overlying the margins of the lake sediments.

The elevation of the wetland places it in the upper montane life zone, which supports mature forests of spruce/fir, lodgepole pine, and aspen (Willard and Foster, 1990). The dominant vegetation types in the wetland include sedges (*Carex*), spike rush (*Eleocharis rostellata*), mosses (primarily *Sphagnum*), and grasses. Shrubs of willow (*Salix planifolia*) and birch (*Betula glandulosa*) are located primarily at the northern end and margins of the wetland. These hydrologic and vegetative characteristics classify the BP wetland as a minerotrophic fen-carr complex (Mitsch and Gosselink, 1986; Cooper, 1988). The southern half of the wetland (fen) is dominated by dwarf-shrub, sedge, and grass plants. The northern half (carr) primarily hosts grasses, tall shrub, and tree species. Peat comprising the southern (fen) part of the wetland contains very little or no mineral matter. In contrast, peat underlying the northern part is mixed with alluvial sediments derived from the drainage to the northeast, and from slope wash (till, landslide deposits, and weathered crystalline bedrock) from the adjacent valley sides, resulting in deposits that range from a mucky peat to organic-rich mineral soil in composition.

3. Geologic setting

Bedrock in the study area consists of two-mica granite gneiss, mafic gneiss, and amphibolite, all of Proterozoic age (Fig. 3). Locally these units are overlain by poorly lithified volcaniclastic sediment and tuff of Tertiary age, and by Pleistocene glacial till. A kilometer-wide, north-trending zone of variably sheared and shattered bedrock underlies the study area. This zone represents the trace of the Green Ridge fault, a high-angle reverse fault exhibiting evidence of probable Laramide movement (McCallum et al., 1983). This fault provides some of the structural control of the previously glaciated, north-trending Laramie River valley. Chemical analyses of rock samples and a gamma spectrometric survey of the area indicate that some of the sheared and altered rocks are anomalously uraniferous. Seventeen specimens of crystalline bedrock collected within a ~0.5 km radius surrounding the wetland contain from 0.4 to 119 ppm U. Higher concentrations of uranium in these samples were associated primarily with iron-oxide stained, granitic and amphibolitic rocks in mineralized shear and fracture zones (F.A. Hills, USGS, written communication, 1992). The source of U is speculative, but highly fractured granite gneiss shows evidence of