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## In situ mobility of uranium in the presence of nitrate following sulfate-reducing conditions



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### ABSTRACT

Reoxidation and mobilization of previously reduced and immobilized uranium by dissolved-phase oxidants poses a significant challenge for remediating uranium-contaminated groundwater. Preferential oxidation of reduced sulfur-bearing species, as opposed to reduced uranium-bearing species, has been demonstrated to limit the mobility of uranium at the laboratory scale yet field-scale investigations are lacking. In this study, the mobility of uranium in the presence of nitrate oxidant was investigated in a shallow groundwater system after establishing conditions conducive to uranium reduction and the formation of reduced sulfur-bearing species. A series of three injections of groundwater (200 L) containing U(VI) (5  $\mu$ M) and amended with ethanol (40 mM) and sulfate (20 mM) were conducted in ten test wells in order to stimulate microbial-mediated reduction of uranium and the formation of reduced sulfur-bearing species. Simultaneous push-pull tests were then conducted in triplicate well clusters to investigate the mobility of U(VI) under three conditions: 1) high nitrate (120 mM), 2) high nitrate (120 mM) with ethanol (30 mM), and 3) low nitrate (2 mM) with ethanol (30 mM). Dilution-adjusted breakthrough curves of ethanol, nitrate, nitrite, sulfate, and U(VI) suggested that nitrate reduction was predominantly coupled to the oxidation of reduced-sulfur bearing species, as opposed to the reoxidation of U(IV), under all three conditions for the duration of the 36-day tests. The amount of sulfate, but not U(VI), recovered during the push-pull tests was substantially more than injected, relative to bromide tracer, under all three conditions and further suggested that reduced sulfur-bearing species were preferentially oxidized under nitrate-reducing conditions. However, some reoxidation of U(IV) was observed under nitrate-reducing conditions and in the absence of detectable nitrate and/or nitrite. This suggested that reduced sulfur-bearing species may not be fully effective at limiting the mobility of uranium in the presence of dissolved and/or solid-phase oxidants. The results of this field study confirmed those of previous laboratory studies which suggested that reoxidation of uranium under nitrate-reducing conditions can be substantially limited by preferential oxidation of reduced sulfur-bearing species.

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## 1. Introduction

Uranium-contaminated groundwater is a human and environmental health concern due to releases associated with the mining, milling and processing of uranium ore as well as those from natural sources (Brugge et al., 2005). The mobility of uranium in groundwater is highly dependent on groundwater pH, redox potential and the mineralogy of the solid-phase subsurface media. In circumneutral pH groundwater, uranium primarily exists as soluble U(VI)-bearing species under oxidizing conditions or as less soluble U(IV)-bearing species under reducing conditions (Goodwin, 1982; Grenthe et al., 1992; O'Loughlin et al., 2011). Under oxidizing conditions and circumneutral pH, U(VI)-bearing species can be immobilized by adsorption to iron-bearing minerals (Li and Kaplan, 2012). Under reducing conditions, U(VI) can be reduced to immobile U(IV) chemically by reduced iron- or sulfur-bearing species (Chakraborty et al., 2010; Hyun et al., 2012, 2014; Jeon et al., 2005) and/or biologically by native anaerobic microbial communities (Wall and Krumholz, 2006). Microbial-mediated uranium reduction in particular, has been the predominant mechanism utilized for enhancing in situ uranium immobilization (Newsome et al., 2014). However, reoxidation of previously reduced uranium in the presence of dissolved- and/or solid-phase oxidants can result in remobilization of uranium, which poses a significant challenge for remediating uranium-contaminated groundwater (Singh et al., 2014).

Microbial-mediated reduction of uranium can be stimulated by the in situ addition of an electron donor such as ethanol, glucose, acetate, lactate, formate, or emulsified vegetable oil (Senko et al., 2002; Anderson et al., 2003; Istok et al., 2004; Vrionis et al., 2005; Wu et al., 2006, 2007, 2010; Dullies et al., 2010; Campbell et al., 2011; Sharp et al., 2011; Watson et al., 2013). In the presence of an added electron donor, uranium reduction can proceed following depletion of higher energy yielding terminal electron acceptors (TEAs) such as oxygen, nitrate, manganese, and concurrent with ferric-iron reduction (Newsome et al., 2014) which may result in the production of insoluble minerals such as uraninite (UO<sub>2</sub>) (Wall and Krumholz, 2006). However, natural recharge of dissolved-phase oxidants such as oxygen and nitrate into previously reduced groundwater zones can result in reoxidation and subsequent remobilization of uranium (Wu et al., 2007, 2010; Watson et al., 2013). Although the presence of solid-phase oxidants such as Mn(IV)-oxides and/or Fe(III)-oxides can also result in reoxidation of uranium, their abundance is likely limited following uranium-reducing conditions (Vrionis et al., 2005). In order to actively maintain uranium-reducing conditions, the continuous or periodic addition of an electron donor can effectively prevent uranium reoxidation (Wu et al., 2007, 2010; Watson et al., 2013). However, active remediation systems can also be expensive to design, build, and operate. Therefore, creating groundwater conditions which can sustain uranium-reducing conditions after in situ electron donor addition has been terminated and depleted is of critical interest to remediation practitioners.

The importance of reduced sulfur-bearing minerals, formed by sulfate-reducing bacteria, has been recognized as a predominant factor contributing to maintaining uranium-reducing conditions in natural uranium-rich groundwater systems (Iwatsuki et al., 2004; Arthur et al., 2006; Noseck et al.,

2012). This is likely due, in part, to preferential oxidation of common reduced sulfur-bearing minerals such as pyrite (FeS<sub>2</sub>), mackinawite (FeS<sub>0.9</sub>) and alabandite (MnS) by oxygen and nitrate, which are thermodynamically favorable reductants when compared to uraninite (Dean, 1999). This suggests that creating in situ groundwater conditions that are conducive to the formation of reduced sulfur-bearing minerals following uranium reduction may lead to greater stability of immobilized uranium in the presence of oxidants. The importance of preferential oxidation of reduced sulfur-bearing minerals following uranium reduction has been demonstrated experimentally in numerous laboratory studies (Abdelouas et al., 1999, 2000; Moon et al., 2009; N'Guessan et al., 2010; Bi et al., 2013; Bi and Hayes, 2014a, 2014b; Carpenter et al., 2015; Luan et al., 2015). For example, in a flow-through sediment column study, Moon et al. (2009) demonstrated that microbial-mediated uranium reduction followed by enhanced sulfate reduction resulted in the formation of iron sulfides which limited the extent of uranium reoxidation by oxygen and nitrate when compared to a previous study where uranium reduction was not followed by sulfate reduction (Moon et al., 2007). However, in both laboratory studies, the rate and extent of uranium reoxidation were greater when nitrate, as opposed to oxygen, was the oxidant. The relative importance of nitrate as a predominant oxidant for in situ uranium reoxidation has also been recognized at numerous uranium-contaminated sites where nitrate is a common co-contaminant due to activities associated with the processing of uranium ore (Spain and Krumholz, 2011; Lloyd and Renshaw, 2005; Smith et al., 2015). Although nitrate alone does not abiotically oxidize U(IV) to an appreciable extent, dissimilatory nitrate reduction intermediates, such as nitrite, nitric oxide, and nitrous oxide, as well as microbial-mediated nitrate-dependent U(IV) oxidation, have been shown to reoxidize uranium in numerous laboratory and in situ studies (Singh et al., 2014).

Despite the importance of nitrate as an oxidant under field conditions and sulfide-bearing minerals as reductants under laboratory conditions, relatively few studies to date have investigated uranium reoxidation by nitrate following sulfate-reducing conditions in the field. Therefore, a substantial knowledge gap currently exists as to the in situ feasibility of such an approach in terms of limiting the extent of uranium reoxidation. The objective of this study was to test the in situ mobility of uranium in the presence of nitrate following uranium- and sulfate-reducing conditions. Based on the results of previous studies and thermodynamics, we hypothesized that preferential oxidation of reduced sulfur-bearing species, as opposed to reduced uranium-bearing species, can substantially limit the extent of uranium mobilization in the presence of nitrate.

## 2. Materials and methods

### 2.1. Study site

The study site is located in Area 2 of the Oak Ridge Integrated Field Research Challenge (OR-IFRC) site in Oak Ridge, Tennessee. A typical geologic profile of Area 2 would consist of approximately 6 meters of reworked fill and saprolite at the surface underlain by 2 meters of intact saprolite with weathered bedrock below the saprolite (Watson et al., 2004).

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