



# The impact of biostimulation on the fate of sulfate and associated sulfur dynamics in groundwater

Ziheng Miao<sup>a,b</sup>, Concepcion Carreón-Diazconti<sup>c</sup>, Kenneth C. Carroll<sup>d</sup>, Mark L. Brusseau<sup>a,b,\*</sup>

<sup>a</sup> Department of Soil, Water and Environmental Science, University of Arizona, 429 Shantz Building #38, P.O. Box 210038, Tucson, AZ, USA

<sup>b</sup> Department of Hydrology and Water Resources, University of Arizona, Harshbarger Building #11, Tucson, AZ, USA

<sup>c</sup> Engineering Institute, Autonomous University of Baja California, Mexicali, Baja California, Mexico

<sup>d</sup> New Mexico State University, Las Cruces, NM, USA

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## ABSTRACT

The impact of electron-donor addition on sulfur dynamics for a groundwater system with low levels of metal contaminants was evaluated with a pilot-scale biostimulation test conducted at a former uranium mining site. Geochemical and stable-isotope data collected before, during, and after the test were analyzed to evaluate the sustainability of sulfate reducing conditions induced by the test, the fate of hydrogen sulfide, and the impact on aqueous geochemical conditions. The results of site characterization activities conducted prior to the test indicated the absence of measurable bacterial sulfate reduction. The injection of an electron donor (ethanol) induced bacterial sulfate reduction, as confirmed by an exponential decrease of sulfate concentration in concert with changes in oxidation–reduction potential, redox species, alkalinity, production of hydrogen sulfide, and fractionation of  $\delta^{34}\text{S}$ -sulfate. High, stoichiometrically-equivalent hydrogen sulfide concentrations were not observed until several months after the start of the test. It is hypothesized that hydrogen sulfide produced from sulfate reduction was initially sequestered in the form of iron sulfides until the exhaustion of readily reducible iron oxides within the sediment. The fractionation of  $\delta^{34}\text{S}$  for sulfate was atypical, wherein the enrichment declined in the latter half of the experiment. It was conjectured that mixing effects associated with the release of sulfate from sulfate minerals associated with the sediments, along with possible sulfide re-oxidation contributed to this behavior. The results of this study illustrate the biogeochemical complexity that is associated with in-situ biostimulation processes involving bacterial sulfate reduction.

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## 1. Introduction

Approximately 160,000 abandoned hardrock mines are estimated to exist in the 12 western states and Alaska on state, private, or federal lands (GAO, 2008). Of these, approximately 20% are reported to have environmental degradation issues such as surface water or groundwater contamination. An analysis of

156 hardrock mining sites listed or in consideration for listing on the federal Superfund National Priorities List (NPL) as of 2004 indicated that remediation operations will last from 40 years to in perpetuity at a majority of the sites (EPA, 2004). The average cost to remediate a mining site on the NPL is estimated to range from approximately \$20 to \$150 million (EPA, 2004; Probst and Konisky, 2001). Approximately \$5 billion has been expended by federal agencies for cleanup of hardrock mining sites (GAO, 2008), and estimated total costs for the current 156 NPL-related sites range from 7 to 24 billion dollars (EPA, 2004). It is likely that additional sites will require some form of cleanup, with attendant additional costs, given that, for example, 77% of the

\* Corresponding author at: Department of Soil, Water and Environmental Science, University of Arizona, 429 Shantz Building #38, P.O. Box 210038, Tucson, AZ, USA.

E-mail address: [brusseau@email.arizona.edu](mailto:brusseau@email.arizona.edu) (M.L. Brusseau).

sites on the Bureau of Land Management's abandoned mine lands inventory require further investigation and/or remediation (BLM, 2013).

Acid rock drainage and its potential impact on surface and groundwater quality is generally considered to be the primary environmental concern for many hardrock mining sites in the U.S.A. and elsewhere (INAP, 2013; ITRC, 2008; MEND, 2013; NRC, 1999, 2002). Groundwater contamination serves as one of the primary risk drivers for human health exposure at many hardrock mining sites. For example, approximately two thirds of the 129 mining sites currently listed on or proposed for the Superfund NPL or being remediated under the Superfund alternative approach framework have groundwater contamination (EPA, 2013). The most common groundwater contaminants reported for these sites are arsenic, selenium, uranium, sulfate, and heavy metals. A survey of federal and state Superfund mining sites in Arizona revealed that the most common constituents present as contaminants in groundwater are sulfate, arsenic, and uranium, with selenium and perchlorate also present at some sites.

Extensive groundwater contaminant plumes containing constituents such as arsenic, selenium, uranium, and sulfate often form at mining sites because of the relatively high aqueous solubilities of the constituents (in comparison to regulatory standards), their limited retardation (due to generally anionic speciation), and generally low (or very site dependent) attenuation potential. In many cases, the plumes are hundreds of meters to several kilometers long. These large plumes are very expensive to contain and remediate using pump and treat (NRC, 2013), the standard method for treating contaminated groundwater at such sites (EPA, 2002, 2013).

Developing cost-effective methods to treat mining-impaired waters is deemed a critical research need for remediation of mining sites (EPA, 2004; NRC, 1999, 2002, 2005). Very few alternatives to pump and treat are available for remediation of large groundwater contaminant plumes containing arsenic, uranium, sulfate, or similar constituents. Permeable reactive barriers (PRBs) have been demonstrated to be an effective method for treating waters containing inorganic contaminants (e.g., Hashim et al., 2011; ITRC, 2011) and, for example, can be a robust alternative for controlling acid rock drainage at the source, thereby preventing or reducing contamination of groundwater (e.g., Benner et al., 1997; ITRC, 2011). However, PRBs are impractical for the large, deep contaminant plumes common to mining sites in the western U.S. Monitored natural attenuation (MNA) has become a popular option to consider as a green, lower-cost alternative to pump and treat for metal-contaminated sites (e.g., EPA, 2007a, 2007b). Heavy metals and acidity in acid rock drainage are generally effectively attenuated near the source. Unfortunately, rates of natural attenuation are insufficient to prevent the migration of arsenic, uranium, sulfate, or similar constituents at many mining sites (e.g., EPA, 2007c; Moncur et al., 2005), as evidenced by the very large contaminant plumes that typically develop. This is reflected in the fact that MNA is being used at only a very small number of the current Superfund-related mining sites (EPA, 2013). Methods to enhance the rates of natural attenuation and improve the feasibility of MNA for metal-contaminated sites are a current focus of research and development (ITRC, 2010).

In-situ bioprecipitation or biosequestration is one enhanced-attenuation alternative that has potential for remediation of large, deep groundwater contaminant plumes containing arsenic, uranium, selenium, sulfate, and similar constituents (e.g., DOE, 2003; EPA, 2000; Hashim et al., 2011; Miao et al., 2012). This technology entails injection of a reagent solution into the treatment zone to generate reducing conditions, which induces sequestration (via precipitation and/or enhanced adsorption) of the target contaminants. This sequestration in turn reduces bioavailability of the contaminant, thereby reducing risk. A number of laboratory experiments have been conducted to investigate microbially induced precipitation of uranium, arsenic, selenium, and technetium (e.g., Abdelouas et al., 1998, 2000, 2002; Gu et al., 2005; Jong and Parry, 2003; Kauffman et al., 1986; Keimowitz et al., 2007; Kirk et al., 2010; Lovley and Phillips, 1992; Omeregic et al., 2013; Rittle et al., 1995; Sun et al., 2009; Teclu et al., 2008; Uhrig et al., 1996). In addition, a small number of in-situ bioprecipitation pilot tests have been conducted at field sites, primarily for uranium (e.g., Anderson et al., 2003; Istok et al., 2004; Saunders et al., 2008; Williams et al., 2011; Wu et al., 2006).

Bacterial sulfate reduction (BSR) is one of the primary processes involved in most in-situ biosequestration efforts. A critical component of BSR processes is the disposition of hydrogen sulfide. Ideally, the sulfide will be fully sequestered via, for example, formation of metal-sulfide precipitates, such as occurs for treatment of acid rock drainage wherein concentrations of heavy metals are typically relatively high. However, concentrations of arsenic, uranium, selenium, etc. are often significantly lower than sulfate concentrations in groundwater contaminant plumes at mining sites, and heavy metals are typically present at only trace levels. Under such conditions, it is likely that iron-sulfide precipitates formed through interaction with indigenous iron oxides associated with the sediment will exert a significant control on sequestration of sulfide (Bottrell et al., 1995; Knoller and Schubert, 2010; Rickard, 1995, 1997) and possibly co-contaminants (O'Day et al., 2004; Root et al., 2009; Saalfeld and Bostick, 2009). Minimal research has been conducted to evaluate the impact of BSR for systems with higher sulfate and lower metals concentrations, particularly for conditions representative of mining sites in the SW US.

A pilot-scale ethanol-injection test was conducted to investigate the efficacy of biostimulation for remediation of nitrate and sulfate contaminated groundwater at a former uranium mining site (Borden et al., 2012). The objective of the research reported herein is to investigate the impact of the biostimulation test on the fate of sulfate and associated sulfur dynamics. Geochemical and stable-isotope data collected before and after the test were analyzed to evaluate the sustainability of sulfate reducing conditions induced by the test, the fate of hydrogen sulfide, and the impact on aqueous geochemical conditions.

## 2. Materials and methods

### 2.1. Site background

The Monument Valley site is a former uranium mining site located at Cane Valley, Arizona, 24 km south of Mexican Hat, UT (Fig. 1). Uranium mining at the site occurred from 1943 to 1968. From 1964 to 1968, batch and heap leaching with sulfuric acid

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