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Arsenic Geochemistry of Alluvial Sediments and Pore Waters Affected by Mine Tailings along the Belle Fourche and Cheyenne River Floodplains

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Abstract Gold mining operations in the northern Black Hills of South Dakota resulted in the discharge of arsenopyrite-bearing mine tailings into Whitewood Creek from 1876 to 1977. Those tailings were transported further downstream along the Belle Fourche River, the Cheyenne River, and the Missouri River. An estimated 110 million metric tons of tailings remain stored in alluvial deposits of the Belle Fourche and Cheyenne Rivers. Pore-water dialysis samplers were deployed in the channel and backwaters of the Belle Fourche and Cheyenne Rivers to determine temporal and seasonal changes in the geochemistry of groundwater in alluvial sediments. Alluvial sediment adjacent to the dialysis samplers were cored for geochemical analysis. In comparison to US Environmental Protection Agency drinking water standards and reference concentrations of alluvial sediment not containing mine tailings, the Belle Fourche River sites had elevated concentrations of arsenic in pore water (2570 μg/L compared to 10 μg/L) and sediment (1010 ppm compared to < 34 ppm), respectively. Pore water arsenic concentration was affected by dissolution of iron oxyhydroxides under reducing conditions. Sequential extraction of iron and arsenic from sediment cores indicates that substantial quantities of soluble metals were present. Dissolution of arsenic sorbed to alluvial sediment particles appears to be affected by changing groundwater levels that cause shifts in redox conditions. Bioreductive processes did not appear to be a substantial transport pathway but could affect speciation of arsenic, especially at the Cheyenne River sampling sites where microbial activity was determined to be greater than at Belle Fourche sampling sites.

Keywords Mine tailings · Arsenic transport · Arsenic speciation · Sequential extraction · Iron dissolution

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1 Introduction

The Black Hills of western South Dakota (SD) (Fig. 1) have a long history of gold mining and milling since the late 1800s. The largest mine in this area was the Homestake Mine in Lead, SD, which operated from 1876 to 2002 (Mitchell 2009). The ore produced from this and other mines in this area contained approximately 0.8% arsenopyrite associated with gold (Noble 1950). Arsenopyrite (FeAsS) is a metallic sulfide mineral that is rich in arsenic (As). Prior to 1972, an estimated 110 million metric tons of processed mine tailings were discharged into Whitewood Creek and its tributaries (Marron 1992). An estimated 14.5 million metric tons (13% of the total amount) is stored in alluvial sediment deposited along Whitewood Creek (Marron 1992). In 1983, the US Environmental Protection Agency (EPA) placed a 30-km reach of Whitewood Creek on the National Priority List (NPL of the "Superfund" cleanup program), and subsequently delisted the site in 1996 (EPA 2017). Discharge of tailings into Whitewood Creek ended with completion of the Grizzly Gulch tailings impoundment in 1977 (Goddard 1989). Numerous environmental and ecological assessments have been conducted along these waterways by the EPA, US Geological Survey (USGS), universities, and others to evaluate the effects of mine tailings in floodplain sediment and waters (Bergeland et al. 1977; Cherry et al. 1986; EPA 2005; EPA 2006; Goddard 1989; Horowitz et al. 1988; Kuwabara et al. 2003; Marron 1992; Stamm and Hoogestraat 2012). Approximately 27.9 million metric tons (25%) of tailings are stored along the floodplain of the Belle Fourche River (Marron 1992). The remaining 67.6 million metric tons (62%) of tailings were deposited along the Cheyenne River, discharged into Lake Oahe, or discharged into the Missouri River prior to the construction of Oahe Dam in 1950s. However, the Belle Fourche and Cheyenne Rivers downstream from Whitewood Creek were not listed on the NPL by the EPA.

The Belle Fourche and Cheyenne Rivers are locally incised river systems (Stamm and Hoogestraat 2012; Stamm et al. 2013) that have well-defined point bars, cut banks, and floodplains (Goddard 1989). After discharge of the tailings ceased in 1977, Whitewood Creek and the Belle Fourche River quickly incised as much as 2 m of the previous beds, leaving tailings-enriched sediments perched above the level of average flow at most locations along these rivers (Marron 1992). Concentrations of arsenic (As) were greatest in Whitewood Creek and generally decreased as in the downstream direction from the contaminant source area of the Homestake Mine (Cherry et al. 1986; Goddard 1989). Arsenic concentrations also decreased with distance away from the main river channels, with greater As concentrations being measured in abandoned back channels (EPA 1973; Stamm and Hoogestraat 2012).

Previous studies of groundwater in alluvial sediments of Whitewood Creek demonstrated the importance of sediment-water interactions in As mobilization (Cherry et al. 1986; Fuller and Davis 2003). During the spring and early summer, when streamflow is at higher stages, the water table can rise more than 1 m in the alluvial aquifer and tailings materials of Whitewood Creek, whereas when streamflow recedes, the pore water and leached metals in those materials drain back into the stream channel (Cherry et al. 1986). The highest As groundwater concentrations have been reported in alluvial material adjacent to thick (about 1-m) mine-tailings deposits (Cherry et al. 1986). In some locations along Whitewood Creek, mine tailings that overlie the alluvial material appear to be unaltered from the time they were milled (Cherry et al. 1986; Goddard 1989), with lack of weathering being attributed to onset of reducing conditions immediately after sediment burial. Fuller and Davis (Fuller and Davis 2003) described rapid (< 5 min) precipitation/coprecipitation of As and ferrihydrite in bed sediments along Whitewood Creek as iron (Fe)- and As-rich groundwater seeped into oxidized surface water. These results highlight the importance of potential erosional processes in As mobilization in these streams.

The solid-aqueous interactions of As in groundwater are controlled by Fe and As speciation, redox conditions, mineral phases, sulfide availability, and microbial interactions (Dixit and Hering 2003; O'Day et al. 2004; Pedersen et al. 2006; Smedley and Kinniburgh 2002). These factors create complex biogeochemical interactions that can spatially vary and complicate the characterization of the occurrence and distribution of As in large-scale aquifer systems. The physical properties pH and Eh may constrain As mobility and valency. Arsenite is the most common reduced species [As(III), such as in the form H_3AsO_3], and arsenate is the most common oxidized species

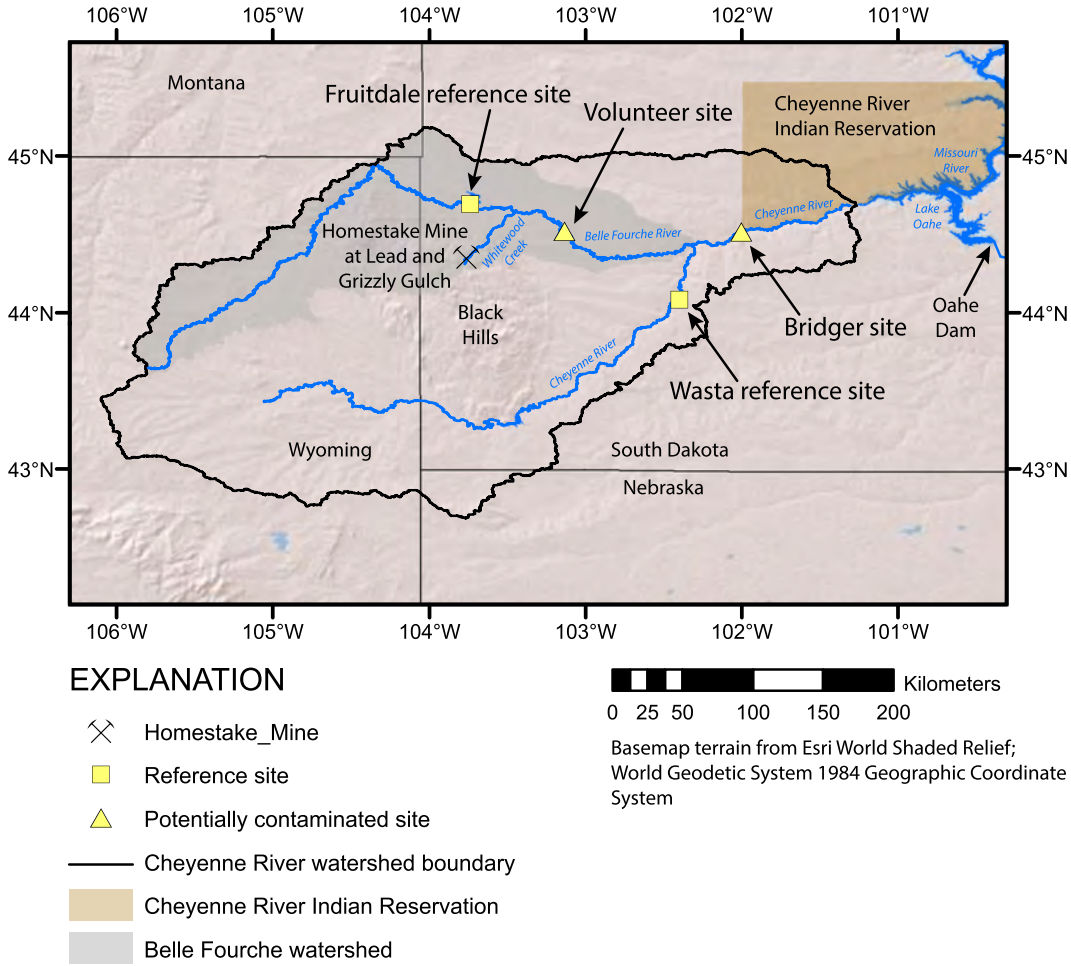


Fig. 1 Study area of the Cheyenne and Belle Fourche Rivers

[As(V), such as in the form H_3AsO_4] in water. Arsenite is considered to be more mobile and toxic than arsenate (Fendorf et al. 2010; Morton and Dunnette 1994). The presence of Fe, sulfur (S), and other ions coupled with microbial reduction may affect the accumulation of As in sediment pore waters (Fendorf et al. 2010).

There are two causes of large-scale As dissolution into water in soil or groundwater (Smedley and Kinniburgh 2002). One cause is high pH (> 8.5), which may result in desorption of As and other metals from soil and sediment particles. The second cause is strongly reducing conditions at neutral pH, which causes As desorption from Fe and other oxides on soil and aquifer particles. In most systems, Fe is the predominant sorbent for As and other trace elements, and dissolved As will adsorb to either amorphous or crystalline Fe minerals during the transition from reducing to oxidizing conditions, and desorb during the transition from oxidizing to reducing transitions (Dixit and Hering 2003; Fendorf et al. 2010; Ford 2002; Smedley and Kinniburgh 2002). Arsenite has a stronger binding affinity to Fe hydroxides than arsenate and in turn is also more easily desorbed from Fe hydroxides (Dixit and Hering 2003; Kocar et al. 2010). Sorption site availability related to changes in Fe mineralogy and anion competition may affect As sorption and release (Ford 2002; O'Day et al. 2004; Pedersen et al. 2006). Highly crystalline Fe and Fe sulfide mineral structures provide fewer sorption sites than amorphous Fe oxides but have a tendency to create stronger bonds in their crystal lattice that prevent As release (O'Day et al. 2004; Pedersen et al. 2006). Therefore, release of As occurs when sorption sites are no longer available and when large concentrations of competitive ions for sorption sites are present. Conversely, recrystallization of Fe oxides could

be retarded and high total dissolved solids (TDS) could persist in pore waters if flow rates are low in the associated aquifers (O'Day et al. 2004; Pedersen et al. 2006). Precipitation of sulfides via abiotic or biotic sulfate reduction can cause decreases of As(III) and Fe concentrations in soil pore water and groundwater through (co)precipitation. With time, As can be incorporated into metallic sulfide crystal lattices (Bostick and Fendorf 2003; Kirk et al. 2004; Saunders et al. 2008). In sulfur-rich systems, thioarsenate $(AsS_4)^{3-}$ compounds are thought to be important chelating agents for solid/aqueous As. In hydrologic systems lacking reactive Fe, precipitation of As sulfides can be enhanced through thioarsenate formation (Wilkin et al. 2003). The role of thioarsenic compounds in As cycling is not well understood but is thought to be important in systems with changing redox conditions in As- and sulfide-rich environments at near-neutral pH.

To minimize the effect of As on humans and aquatic biota, investigation of redox conditions, pH, and biogeochemistry in these hydrologic systems is integral to understanding the fate and transport of As in the environment (Fendorf et al. 2010; Kocar et al. 2010; O'Day et al. 2004; Pedersen et al. 2006; Root et al. 2007; Smedley and Kinniburgh 2002). The objective of the study described in this paper was to determine geochemical and biological factors controlling As fate and transport processes in alluvial sediment of the floodplain backwaters and channel along the Belle Fourche and Cheyenne Rivers of South Dakota, and in associated pore water in those alluvial sediments.

2 Methods

2.1 Location and Site Descriptions

The Belle Fourche River watershed (18,700 km^2) is a sub-basin of the Cheyenne River watershed (62,800 km^2) (Fig. 1). Whitewood Creek, which drains the area of the Homestake Mine, is a tributary to the Belle Fourche River. Land use along the Belle Fourche and Cheyenne Rivers is typically agriculture (hay production) and range land. For this study, two sites were selected where alluvial deposits, particularly those exposed on floodplains, had characteristics typical of mine tailings (Fig. 1; (EPA 1973; Goddard 1989)): the Volunteer site along the Belle Fourche River, and the Bridger site along the Cheyenne River. There were two independent sampling locations at each of these sites: one in the active channel and one in abandoned back channels of these rivers (Table 1; Figs. S1–S4). In addition, two reference sites were selected along reaches upstream from sources of mine tailings: the Fruitdale reference site along the Belle Fourche River, and the Wasta reference site along the Cheyenne River. The Fruitdale reference site is upstream from Whitewood Creek, and the Wasta reference site is upstream from its confluence with the Belle Fourche River (Fig. 1). Reference sites had one sampling location at each site, and sites with characteristics typical of mine tailings had two sampling locations at each site (Table 1; Figs. S1–S4).

Table 1 Site names, abbreviations for sampling locations, and associated geomorphic setting. Geochemical analysis for sites are available from the US Geological Survey (USGS) National Water Information System (U.S. Geological Survey 2018), and are archived by USGS site number

River/site name and number, and USGS site number	Abbreviated sampling location name	Geomorphic setting
Belle Fourche/Fruitdale reference, USGS 06436000	BF-F	Bank erosion/bar deposition
Belle Fourche/Volunteer 1, USGS 443013103081100	BF-V-1	Downstream end of submerged bar on river right
Belle Fourche/Volunteer 2, USGS 443051103075500	BF-V-2	Sediment filled back channel on river left; seasonal ponding and sediment accumulation at high flow
Cheyenne/Wasta reference, USGS 0642359	CR-W	Bank erosion/ bar deposition
Cheyenne/Bridger 1, USGS 443044102001000	CR-B-1	Seasonally flooded back channel on river left; bank sediment contributes to sediment load
Cheyenne/Bridger 2, USGS 443043102001000	CR-B-2	Seasonally flooded back channel on river left; active sediment deposition from main channel

2.2 Pore Water Samples

Pore water samples were collected by South Dakota School of Mines and Technology (SDSM&T) personnel from pore water dialysis samplers (PWDSs) installed at all four sites (Volunteer, Bridger, Fruitdale reference, and Wasta reference sites; Table 1). Herein, pore water will refer to groundwater in alluvial sediments. Sampling of pore water used methods similar to those described in Hesslein (Hesslein 1976), Larson et al. (Larson et al. 2012), and Urban et al. (Urban et al. 1997). The PWDSs were constructed from a 76.2-cm × 45.7-cm × 2.54-cm plexiglass "core," two 0.45-μm Whatman® dialysis membranes, two 0.3175-cm plexiglass "covers" (to hold membranes in place), and nylon screws; the system was held in place by nylon screws. A total of 576 circular cells, or chambers, (18 rows by 32 columns), each 1.5 cm in diameter were drilled through the plexiglass core and covers. The dialysis membrane and covers were placed on either side of the core to retain water in the chambers. Covers allowed flow in and out of the chamber through the dialysis membrane, with a resulting recovery of 80 mL per row (32 chambers). Two rows of chambers were collected as one composite sample for the analyses; thus, a total of nine composite samples were analyzed per PWDS. The rows at or above the sediment surface (at least the top two rows) were considered surface water samples. Nylon screws and bolts were used to affix the cover plates, dialysis membranes, and chambers, thus minimizing potential metallic interactions with the samples. The chambers were submerged in a deionized distilled water bath, and nitrogen gas was bubbled for 12 h in the water bath immediately prior to field deployment to minimize oxygen entrainment. The PWDSs were inserted vertically into saturated sediments, perpendicular to the surface water flow direction. Alluvial sediments were unconsolidated, allowing the PWDSs to be driven into the sediment deposits. As many as four rows of chambers were exposed to the water column in the channel (indicated by negative or zero depth from sediment surface). The PWDSs were deployed for 12 days during June and July 2010 at sampling locations BF-F (Fruitdale reference site) and CR-W (Wasta reference site), 13 days at sampling locations BF-V-1 and BF-V-2 (Volunteer site), and 18 days at sampling locations CR-B-1 and CR-B-2 (Bridger site), allowing for equilibrium between the PWDS chambers and the local environment to be established. After those time periods, the PWDSs were removed and the contents in the individual pore-water chambers extracted using 10-mL syringes within 1 h of removal. All surface and pore water samples were collected in 250-mL acid rinsed bottles and preserved with 2 mL of nitric acid. Exposure of samples to direct sunlight was avoided to prevent As(III) oxidation by ultraviolet light while extracting samples from chambers (Emett and Khoe 2001).

2.3 Sediment Cores

Sediment was cored by SDSM&T personnel within 2 m of each PWDS location immediately after the PWDSs were removed. Sediment samples were collected using a polypropylene sleeved, stainless steel, 30.5-cm length, 5-cm diameter split core sampler using a slide hammer. Three sediment cores were collected from each of the four sampling sites (total of six sampling locations), although not to the entire depth extent of the PWDS. Immediately after coring, the sleeve containing the sediment was removed, capped, sealed with wax, and stored at 4 °C to preserve in situ conditions. One of the three cores collected from each sampling location was stored at − 17 °C for microbial analysis.

2.4 Analytical Methods

Analytical methods are described for pore water and surface water analyses, sediment analyses, microbial analyses, sequential extraction and ethanol wet sieve, and elemental analysis using X-ray diffraction and scanning electron microprobe.

2.4.1 Pore Water

Samples collected from two rows of chambers from each PWDS (~ 160 mL) were composited in a 1000-mL beaker, shaded from sunlight throughout the sampling procedure to minimize ultraviolet oxidation of As, and minimizing intersample contamination. Field measurements performed on each sample included temperature, TDS, specific conductivity, oxidation/reduction potential (ORP), pH, and aqueous ferrous iron [Fe(II)] concentration. The TDS, pH, and specific conductivity were measured using an EXTECH® ExStik® II pH/conductivity multiprobe, and ORP was measured using an OAKTON® Waterproof ORPTestr® 10 probe. All field instruments were calibrated in the field prior to sample analysis.

The Fe(II) concentration was determined using UV-Vis spectrometric methods described by Stookey (Stookey 1970). Approximately 40 mL of composited water sample was filtered using an ion-exchange As speciation cartridge containing an aluminosilicate medium, which retains As(V) (Meng and Wang 1998). The filtrate was stored in a separate 250-mL polyurethane sample bottle and analyzed for As concentration, which because of filtration was assumed to contain only As(III). The remaining composited sample (~ 120 mL) was placed in a separate 250-mL sample bottle and analyzed for element concentrations. Two milliliters of concentrated nitric acid was added as preservative prior to laboratory analysis. Concentration of selected elements [aluminum (Al), As, calcium (Ca), Fe, potassium (K), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), and selenium (Se)] for pore waters were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) at the US Geological Survey (USGS) National Water Quality Laboratory (NWQL) in Lakewood, CO, using an Agilent 7500ce ICP-MS instrument with an octopole reaction system (Garbarino et al. 2006). Geochemical analyses are available from the USGS National Water Information System (U.S. Geological Survey 2018), archived by USGS site numbers as listed in Table 1. Concentration of As(V) was estimated as the concentration of arsenic in the unfiltered water sample [~ 120 mL; As(V) and As(III)], minus the concentration of the As in the filtered water sample [40 mL; assumed to be As(III)].

2.4.2 Sediment

Each of the three sediment cores from each of the four sampling sites (six sampling locations) were subsampled into five equal-length segments, each representing ~ 6-cm depth intervals. Core subsamples were dried at 60 °C for 24 h, and subsequently broken apart using mortar and pestle or by hand to disaggregate individual sediment grains. One core sample was used for microbial analysis. The second core was wet sieved for the sequential extraction procedure. Elemental concentrations in the third cores were analyzed using X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscope (SEM) analyses, loss on ignition (LOI) ((Heiri et al. 2001)), carbon (C), and nitrogen (N).

2.4.3 Microbial Analysis

Microbial community activity in the first core samples was determined by SDSM&T personnel using Biolog EcoPlate (Hayward, CA) microbial analysis, with 96 individual substrate wells being analyzed in triplicate similar to methods used in other sediment studies (Chaerun et al. 2011; Leflaive et al. 2008) to best represent in situ conditions in the field. Sediment samples weighing approximately 3 to 6 g were extracted from each of the five subsamples of each frozen sediment core, and vortexed with 25 mL of deionized water prior to centrifuging at 3000 rpm. Sample of 100-μL centrate was pipetted into each EcoPlate plate well, and samples were incubated either aerobically or anaerobically (depending on incubation goal) at 25 °C for 7 days. Substrate utilization was determined using an optical density Biolog plate reader ($\lambda = 590$ nm) after 4 h of incubation and every 24 h thereafter. Substrate utilization was indicative of changes in optical density in each individual substrate well and changes with time were used to calculate average substrate well color development (AWCD) profiles (Eq. 1) using methods and procedures described by Garland and Mills (Garland and Mills 1991) and Zhou et al. (Zhou et al. 2008).

$$AWCD = \sum(C-R)/n \quad (1)$$

where

C absorbance per well
R absorbance of control well
n total number of substrates.

Profiles having sigmoid shaped growth patterns were fit to a logistic growth equation (Salomo et al. 2009) using equation Eq. 2 to determine the asymptote (K) and exponential rate of AWCD change (p) and other parameters.

$$Y = \frac{K}{1 + e^{-p(t-s)}} \quad (2)$$

where

Y AWCD fit to the logistic growth equation
K asymptote/carrying capacity
p exponential rate of AWCD change
s time (h) when $Y = K/2$
t incubation time (h)

The values of p indicate how fast the substrates are being metabolized; values of p greater than 0.02 indicate rapid substrate utilization and values smaller than 0.02 indicate slower substrate utilization. The K value is the predicted carrying capacity that describes the point at which the AWCD (substrate utilization) reaches a maximum for a microbial population. If the AWCD was minimal for the entire incubation, then values of K, s, and p may be negative, and correlation coefficient (R^2) values are likely to be small due to inability to conform to the model expressed in Eq. 2.

2.4.4 Sequential Extraction and Ethanol Wet Sieve

Sequential extraction techniques performed by SDSM&T personnel, which are the sequential ordering of extraction techniques on the basis of the mobility of elements, were used for sediment analysis of As and Fe generally following methods described by Hochella et al. (Hochella et al. 2005). The ethanol wet sieve was conducted to determine binding affinities, simulated by the sequential extraction, associated with each size fraction. The sediment cores designated for ethanol wet sieve and sequential extraction were subsampled and dried as previously described. Initial dry weights of each core section were recorded prior to the sieving process and after sieving. Polycarbonate sieve rings and screens were used to avoid introducing additional elements into the sediment samples. Four sieve sizes were used: 1000, 500, 250, and 125 μm.

Each size fraction acquired from the sieving process was subjected to a series of sequential chemical extractions modified from the methods described by Root et al. (Root et al. 2007; Root et al. 2009) and Keon et al. (Keon et al. 2001). The extractants and their associated procedures are provided in Table S1. Extractions 1 through 4 used a ratio of 1:100 (0.3 g solid/30 mL extractant) to prevent extractant exhaustion (Keon et al. 2001). The sediment samples were placed in 50-mL polypropylene centrifuge tubes with the extractant and agitated for the specified time with an Eberback reciprocal shaker. Next, samples were centrifuged for 25 min at 4000 rpm, and the supernate was decanted into polypropylene sample bottles. The samples then were rinsed with distilled deionized (18.2 Milli-Q®) water, centrifuged as above and decanted into corresponding sample bottles. The 40-mL total sample volume (extractant + rinse) was then filtered using 0.45-μm filter membranes and preserved with 100 μL of concentrated nitric acid (NHO_3). The residual sediment was used for the next sequential extraction. Extraction 5 followed EPA method 200.7, in which 1.2 mL of 1 + 1 HNO_3/H_2O solution plus 3 mL 1 + 1 HCl/H_2O solution were added to the sediments, and then collectively heated to 115 °C for 30 min in a graphite digestion block (EPA 2001). Centrifuging and filtering proceeded as described previously and the supernatant was diluted to a total volume of 30 mL. All extractants were analyzed via Teledyne-Leeman Labs Prodigy dual view ICP-AES by SDSM&T personnel for As and Fe concentrations.

2.4.5 Elemental, XRD, SEM Analyses

The third cores from each site were used for the remaining analyses: XRD, ICP-AES (sediments), SEM, LOI, C, and N analysis. These cores were sectioned, dried, ground, and homogenized as previously described. Mineralogy was analyzed using a Rigaku Ultima Plus XRD on a split sample ground to a homogenous size (~ 10 μm). The ground sediment samples were scanned at angles ranging from 3° to 60° at a continuous rate of 2°/min. The diffraction peaks detected from the scan were analyzed with Jade 7.5 software. A separate split was analyzed for elemental concentration via ICP-AES analysis, and sulfur analysis using a LECO Induction Furnace by SGS Minerals Services (Toronto, Canada).

Sediment samples were prepared for SEM analysis by adhering to carbon tape and were carbon coated to minimize charging of the sample. The SEM analysis was completed by SDSM&T personnel using a Zeiss SUPRA40 Variable-Pressure Field-Emission SEM. To analyze energy-dispersive spectroscopy (EDS) output, Spirit software by Princeton Gamma-Tech was used to create spectrums and spectrum reports. All ground sediment samples were analyzed using a 20-kV accelerating voltage, 60-μm (high) aperture size and high vacuum.

The LOI was determined by SDSM&T personnel from split ground sediment samples following methods described by Heiri et al. (Heiri et al. 2001) in which mass loss represented the percent weight of organic carbon in each sample. The ground sediment samples were placed in a muffle furnace at 550 °C for 3 h and then allowed to cool. The differences in sample weights from before and after heating to 550 °C were recorded, and the respective LOI at 550 °C (LOI_{550}) was determined using Eq. 3:

$$LOI_{550} = ((DW_{105} - DW_{550})/DW_{105}) \times 100 \quad (3)$$

where

DW_{105} dry sample weight after heating in 105 °C oven

DW_{550} sample weight after heating in muffle furnace at 550 °C

The carbon content in each sediment sample was determined by SDSM&T personnel using Thermo Scientific Flash EA 1112 Series N/C plus CHNS/O analyzer. The sediment samples were heated to 1800 °C, converting the samples into gaseous form. This gas was then passed through a chromatograph column that separated the gasses, which were measured by a thermal conductivity detector. These measurements were analyzed with Thermo Scientific Eager 300 software.

2.5 Data Analysis

Concentration of elements in soils and pore water were analyzed by the Pearson product-moment correlation, or "Pearson's *r*" (Helsel and Hirsch 2002), to compare results between core sections (sediments) or depth intervals (pore water) at each sampling location. Concentrations of As and Fe determined in sequentially extracted sediment samples were compared between size fractions and core sections using the Mann-Whitney rank-sum test (Helsel and Hirsch 2002). Differences in substrate utilization from the Biolog microbial analysis were analyzed by principal component analysis (PCA) using Microsoft® Excel XLSTAT statistical add-on software (Addinsoft, New York, NY).

3 Results

Results are discussed in relation to geochemistry of the pore water as sampled from the PWDS and geochemistry of mineral matter in sediment from cores. Pore waters were analyzed for pH, TDS, redox state, and selected elements. Minerals in sediment were analyzed for a more complete suite of elements. Results of analyses are provided in the supplemental material for this report (Tables S2–S3). Sediment in cores at sites were also analyzed for effects of substrate on the function of aerobic microbial communities (Table S4), and mineralogy of cores was also described (Table S5).

3.1 Pore Water

Pore water pH ranged from 7.0 to 9.0 for all sampling locations due to the alkaline nature of the regional soils and circumneutral conditions common to shallow aquifers in this area (Smedley and Kinniburgh 2002). Concentrations of TDS were similar between water samples collected at reference sites and their respective potentially contaminated sites, ranging from 0.87 to 13 g/L (Fig. 2, Table S2). The largest TDS concentration (13 g/L) was measured at sampling location CR-B-1 on the Cheyenne River at Bridger (from a PWDS in the active channel) above the sediment-water interface (sample collected within the PWDS located several cm above the sediments), similar to other sites. Large TDS concentrations near the sediment-water interface can be explained by the presence of high concentrations of Na, Ca, Mg, and K within the surface water (i.e., "filtered water" from the top rows of the PWDS representing surface-water conditions; Fig. 2, Table S2). Reducing conditions (based on ORP) were measured at all sites below the sediment-water interface, the transition from oxidizing to reducing environment being measured generally at 22 cm below the sediment-water interface, and remained reducing with greater depth. The only exception to that pattern was measured at site BF-V-2, a backwater channel on the floodplain of the Belle Fourche River at Volunteer, which was oxidized throughout the entire depth (Fig. 2c). It should be noted that pore water Al concentration could have been affected by leaching from the As speciation cartridges used during analysis (Table S2).

Dissolved As concentration (i.e., As that passed through membrane filter of the sampler) at the Fruitdale reference site on the Belle Fourche River (BF-F) reached a maximum of 135 μg/L at a subsurface depth of 10 cm. Elevated As concentrations coincided with release of Fe and Mn near the redox boundary into the pore waters at 2 cm below the sediment-water interface (Fig. 2, Table S2). Total As concentration gradually decreased with depth in the remainder of that core. The Fe(II) concentration reached a maximum of greater than 48 mg/L at 22 cm depth in that core, whereas Mn concentrations were greater than 5700 μg/L at depths from 6 to 42 cm, with a maximum Mn concentration of 7080 μg/L being measured at 30 cm depth (Fig. 2, Table S2). The pH remained between 7.15 and 7.5 throughout the pore water in that core with little change at the redox boundary.

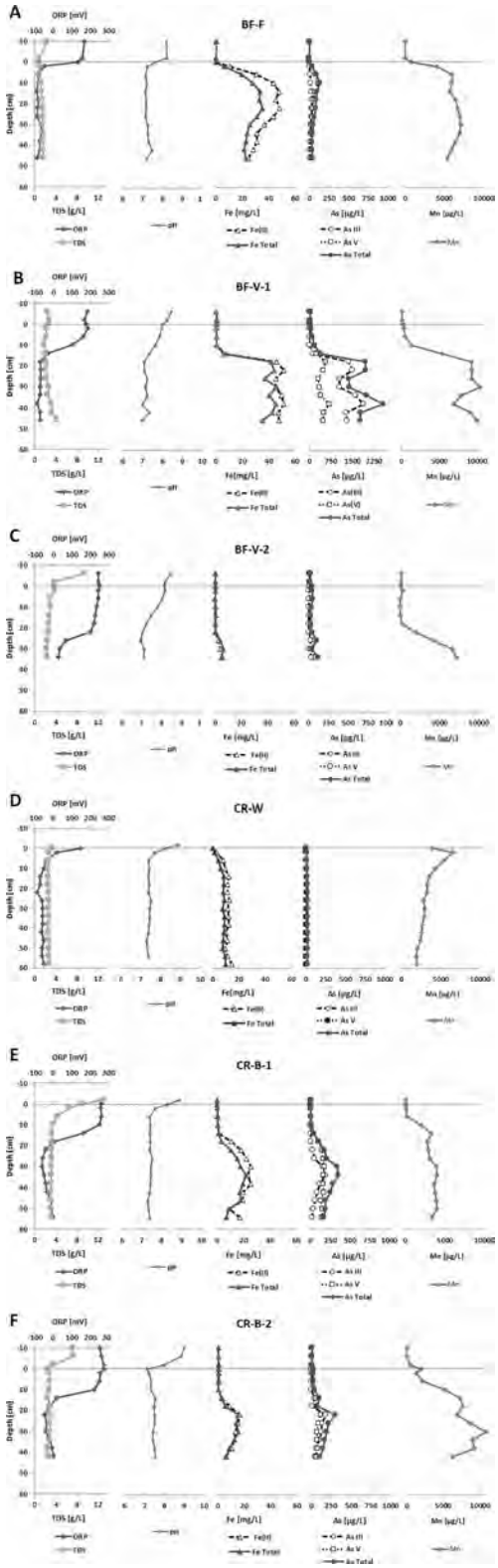


Fig. 2 Selected pore water results for the Belle Fourche River (BF) and Cheyenne River (CR) sampling locations with horizontal line indicating the sediment-surface water interface [**a** Fruitdale reference site, sampling location BF-F; **b** Volunteer site, sampling location BF-V-1; **c** Volunteer site, sampling location BF-V-2; **d** Wasta reference site, sampling location CR-W; **e** Bridger site, sampling location CR-B-1; and **f** Bridger site, sampling location CR-B-2]. Each data point shown represents one analytical result from a composited sample collected at the specified depth

Downstream from the Fruitdale reference site (BF-F) is the Belle Fourche Volunteer site, which is potentially contaminated with mine tailings. At this site, samples were collected at two locations, BF-V-1 and BF-V-2. The BF-V-1 sampling location (in the active channel of the Belle Fourche River, Fig. 2b) had elevated concentrations of dissolved As, Fe(II), and Mn measured under reducing conditions. The channel (as opposed to backwater channel, BF-V- 2) sediments at that sampling location contained the highest pore water As concentration (2570 μg/L) of all samples analyzed, with As(III) being the dominant As species. Reducing conditions were measured below 14 cm at that sampling location (Fig. 2). The Fe(II) and As concentrations averaged 14 mg/L and 74 μg/L in the oxidized zone, respectively, whereas reducing conditions coincided with higher average Fe(II) and As concentrations (43 mg/L and 1683 μg/L respectively). Iron was primarily reduced, in the form of Fe(II), whereas As(III) concentrations were more than 2.5 times greater than As(V) concentrations [As(III) ~ 1300 μg/L and As(V) ~ 500 μg/L, Fig. 2, Table S2]. Total As concentrations were greater by a factor of 19 than the maximum total As concentrations at the reference site, with maximum Fe(II) concentrations being similar (~ 50 mg/L) to Fe(II) concentrations at the reference site. There were significant ($p < 0.05$ based on Pearson product-moment correlations; results not shown) positive correlations between Fe and Mn concentrations, and between Fe and As concentrations, indicating that reducing conditions were associated with the release of redox-sensitive elements into pore water solution.

The second sampling location at the Volunteer site on the Belle Fourche River, BF-V-2, was an abandoned back channel where oxidized conditions were prevalent throughout the sediment pore-water column (Fig. 2c), although Mn profile indicates onset of reducing conditions. Oxidized conditions appeared to limit the dissolution of As and Fe from sediments; however, Mn reduction was unaffected. Total and Fe(II)

concentrations were predominantly less than 0.5 mg/L, and much less than at the reference site. Total As concentrations at BF-V-2 were similar to those measured at the reference site (BF-F), with a slight increase with depth. The TDS concentration was high (9.5 mg/L) above the sediment-water interface but was generally below 3 mg/L in the pore waters farther below the interface. The Mn concentrations at BF-V-2 were similar than concentrations measured at the reference site from the sediment-water interface to 30 cm depth, below which Mn dissolution occurred (Mn concentrations greater than 6000 mg/L were measured). Despite relatively low dissolved element concentrations in pore water at this site, there were significant ($p < 0.05$) positive correlations between Fe and Mn concentrations, and between As and Mn concentrations in the pore waters (results not shown).

Dissolved element concentrations at the Wasta reference site along the Cheyenne River (CR-W, Fig. 2d) were less than those measured at the Fruitdale reference site along the Belle Fourche River (BF-F; Fig. 2a), indicating that the lower Cheyenne River above the Belle Fourche River confluence is not a substantial source of As. Reducing conditions were measured below 6-cm depth at site CR-W, with Fe and As pore water concentrations being consistent with depth (Fig. 2, Table S2). The Mn concentration profile at CR-W differed compared to that at BF-F where dissolution occurred near the sediment-water interface. There were significant ($p < 0.05$) positive correlations between As, Fe, and Mn concentrations measured in pore water samples at BF-F, indicating similar relations to redox conditions.

At the Cheyenne River Bridger sampling locations, CR-B-1 and CR-B-2 (Fig. 2e, f), which were ~25 km downstream from the Belle Fourche-Cheyenne River confluence and potentially containing mine tailings, elevated Fe and As concentrations were measured in sediment pore waters relative to reference concentrations. Suboxic conditions were measured at both sites below about 20 cm depth, which were likely to induce Fe, As, and Mn dissolution (Fig. 2, Table S2). At sampling locations CR-B-1 and CR-B-2, which were in backwater channels on the floodplain, similar peak As concentrations of 352 and 307 μg/L, respectively, were measured with those peak concentrations occurring in the most reductive zone (Fig. 2, Table S2). The As (III)/(V) ratio measured in pore water at this site was less than 0.6 when total As was greater than the EPA drinking water standard of 10 μg/L (EPA 2016), except under highly reducing conditions in which As(III) was the predominant form of As. Similar to the Belle Fourche River sites, Mn and Fe concentrations were greatest under reducing conditions at this site, with significant positive correlations ($p < 0.05$ that correlation equal zero) between Fe, As, and Mn concentrations.

3.2 Sediments

3.2.1 Elemental Analyses

Elemental analyses of sediment [S, Fe, As, Mn, total C, and organic C (reported as LOI)] for each sampling location are summarized in Fig. 3, with data listed in Table S3. The BF-V-1 analyte profiles (Fig. 3b) were generally consistent and similar to concentrations measured at the reference site (BF-F; Fig. 3a), with the exception of As concentration, which was as much as 27 times greater (160 to 270 ppm) than the concentration of 10 ppm measured at the reference site. Average concentration of Fe in sediments at the BF-V-1 site was 42,700 ppm (Table S3), with the average Fe concentration at the reference site being 27,500 ppm, with little depth variability. The Mn concentrations in sediments at this site were similar to those measured at the reference site, with S concentration varying between 2000 and 3000 ppm, approximately 500 ppm greater than background was measured at the reference site (Fig. 3, Table S3). No significant correlations were indicated between As, Mn, S, and Fe concentrations in these sediments. Organic carbon concentration (LOI) averaged approximately 0.31% and total carbon decreased from about 20,000 ppm at 3 cm depth to about 12,000 in sediments at depths below 21 cm at the BF-V-1 sampling location (Fig. 3, Table S3).

Sediment in cores collected at BF-V-2 exhibited the greatest concentration of mine-tailing contaminants compared to all other sites (Fig. 3c). Analytes measured within the top 15 cm of core were similar to analyte concentrations measured at the reference site except for As concentration (Fig. 3, Table S3). Concentrations of S, Fe, As, and Mn all substantially increased below 21-cm depth, peaking at 6600, 69,500, 1010, and 1860 ppm (all at 27.4 cm), respectively. Concentrations of S, Fe, and Mn in sediments sampled at this site were about twice as much as concentrations in sediments at the reference site. The As concentration at this sampling location was about 50 times the As concentration at

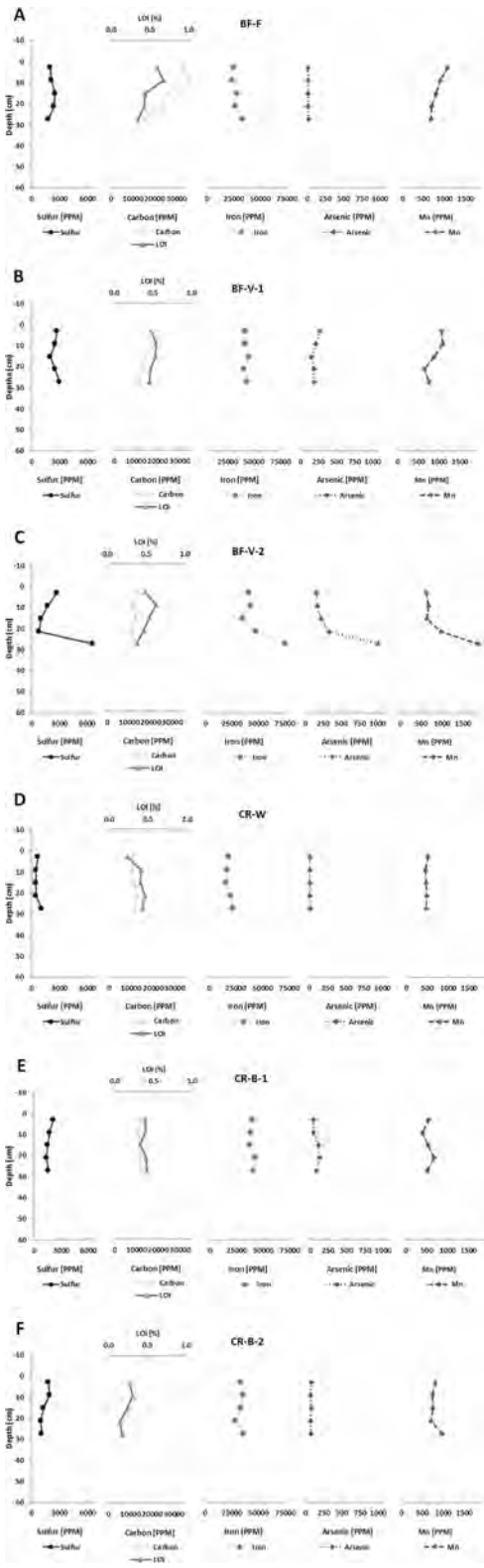


Fig. 3 Selected sediment results for the Belle Fourche River (BF) and Cheyenne River (CR) sampling locations with horizontal line indicating the sediment-surface water interface [**a** Fruitdale reference site, sampling location BF-F; **b** Volunteer site, sampling location BF-V-1; **c** Volunteer site, sampling location BF-V-2; **d** Wasta reference site, sampling location CR-W; **e** Bridger site, sampling location CR-B-1; and **f** Bridger site, sampling location CR-B-2]. Each data point shown represents one analytical result from a sample collected at the specified depth

the reference site, and the greatest concentration measured of the sampling locations (Fig. 3, Table S3).

For sediment cores collected at the Cheyenne River sampling locations, greater As and Fe concentrations (as high as 130 and 38,300 ppm, respectively) were measured at sampling location CR-B-1 (within the river channel) than at CR-B-2 (Fig. 3, Table S3, backwater site). The As concentrations at both sampling locations exceeded the As concentration measured at the reference site (CR-W; 10 ppm; Fig. 3, Table S3). At sampling locations CR-B-1 and CR-B-2, the As, Fe, and Mn concentrations in sediments generally peaked above the 21-cm depth, and decreased below that depth, similar to that observed the reference site (Fig. 3, Table S3). There were no significant correlations between As, Fe, and Mn concentrations in sediments at these two sampling locations. Organic C concentrations (LOI) at the CR-B-1 and CR-B-2 sampling locations were greater than three times those measured at the reference site, with S concentrations at these sampling locations being more than two times those measured at the reference site (Fig. 3, Table S3). Total S concentrations also decreased with depth from approximately 2000 to 1400 ppm in sediments at these sampling locations, corresponding to the depth at which reducing conditions prevail and porewater concentrations of elements increased (Fig. 3, Table S3).

3.2.2 Sequential Extractions

Sequential extraction results from sieved sediment samples are provided in Fig. S5. Arsenic concentrations from both the Belle Fourche and Cheyenne River cores at sampling locations with mine tailings (BF-V-1, BF-V-2, CR-B-1, and CR-B-2) were primarily associated with strongly adsorbed (extraction 1), amorphous and poorly crystalline Fe oxyhydroxides (extraction 2), and highly crystalline/residual Fe-As (extraction 5) phases (Fig. S5). The CR-B-2 core was an exception to that pattern, in that

15–20% less As was associated with the strongly adsorbed phase (Fig. S5). Typically, 5–10% of As was in the form of ionic or acid volatile sulfide (AVS) bound in each core, although recently deposited sediments (samples from the top of the core) had higher ionic-bound fractions. The AVS-bound As concentration was generally low (less than 10% of total extracted As) for all cores. For the BF-V-1, BF-V-2, and CR-B-1 sampling locations, 40 to 60% of the total As was strongly adsorbed or associated with amorphous/poorly crystalline Fe (Fig. S5). The As concentration was most variable in the inert/highly crystalline phases between cores and varied at redox transition zones (Fig. S5). The extraction results further signify the strong association of As to various Fe phases in the matrices of these sediments. Highly crystalline Fe typically composed 55–60% of total extractable Fe, and amorphous/poorly crystalline Fe composed 20–30% of the total extractable Fe (Fig. S5). The amorphous and poorly crystalline phase-associated Fe is thought to be a substantial source of As during redox-controlled dissolution because As, which has been incorporated into Fe crystal structure, is less mobile (Ford 2002; Pedersen et al. 2006).

3.2.3 Microbial Analysis

Following the microbial logistic growth model approach of Salomo et al. (Salomo et al. 2009), microbial AWCD behavior of the sediments at the Belle Fourche and Cheyenne River sampling locations differed from microbial behavior at the reference sites, and from each other (Table S4; Figs. S6 and S7). All Cheyenne River sampling locations (CR-W, CR-B-1, CR-B-2) exhibited a rapid degree of substrate utilization [i.e., greater microbial activity indicative of greater exponential rate of AWCD change (p) values for both aerobic and anaerobic and incubations]. In contrast, sediment samples collected at the Belle Fourche sampling locations (BF-F, BF-V-1, BF-V-2) exhibited either slower, delayed, or no microbial activity below 12-cm depths (Fig. S5, Table S4). Substrate utilization was lowest in the sediment sample collected at BF-V-2 (which contained the highest sediment As concentration), principal component analysis (PCA) results (Fig. 4a) confirm the uniqueness of the Belle Fourche anaerobic microbial communities. The grouping of the Cheyenne River sampling locations and BF-F and BF-V-1 sites along the first principal component axis (F1 axis, Fig. 4a) indicates similarities in anaerobic guild utilizations. The results also indicate greater guild utilization in the Cheyenne River system compared to the Belle Fourche River system. A notable result along the aerobic first principal-component axis (F1, Fig. 4b) is the grouping of the Belle Fourche River sampling locations (including the reference site), and CR-B-1 and CR-B-2 (but not the associated reference site CR-W). This result shows the effect of the Belle Fourche sediment (affected by mine tailings) to reduce aerobic respiration of guild substrates, effectively reducing the aerobic microbial community functional capacity.

3.2.4 X-Ray Diffraction and SEM

The mineralogy of both the Belle Fourche and Cheyenne Rivers cores was predominantly quartz (~ 70% weight average) (Table S5). Calcite and/or dolomite were present throughout all sediment cores, with the exception of the deepest core section at BF-V-2. The presence of carbonate is a likely source of pH buffering of pore waters. Minerals with high cation exchange capacities (e.g., muscovite, kaolinite, and montmorillonite) were greater by more than two times at sites downstream from mining areas, compared to their corresponding reference sites, although cation exchange capacity is not relevant for binding of oxyanions like As(V) and As(III). For XRD analysis, sulfide-related minerology did not constitute a notable fraction of the core minerology analyzed from the sites even though mine tailings were known to contain 7–8% sulfide minerals. The sulfide minerals measured in the tailings (7–8%) are thought to be oxidized to secondary minerals in the fluvial system, although some unoxidized lenses of tailings have been reported in this area (Cherry et al. 1986; Fuller and Davis 2003; Goddard 1989). Potential iron-oxide rinds known to exist within mineral surfaces likely did not impede analyses of potential iron sulfide mineral concentrations in these sediment samples due to pulverization techniques used in sample preparation. Because total S concentrations were likely below detection limits for XRD analysis (based on personal communication with XRD instrumentation operator), the concentrations may instead reflect dilution of the tailing and/or oxidation of sulfide minerals and loss of oxidized sulfur species prior to deposition.

Iron-rich sediments bound with localized As were identified for sampling location BF-V-2 using SEM (Fig. 5). EDS confirmed that 1.12% of total As was in

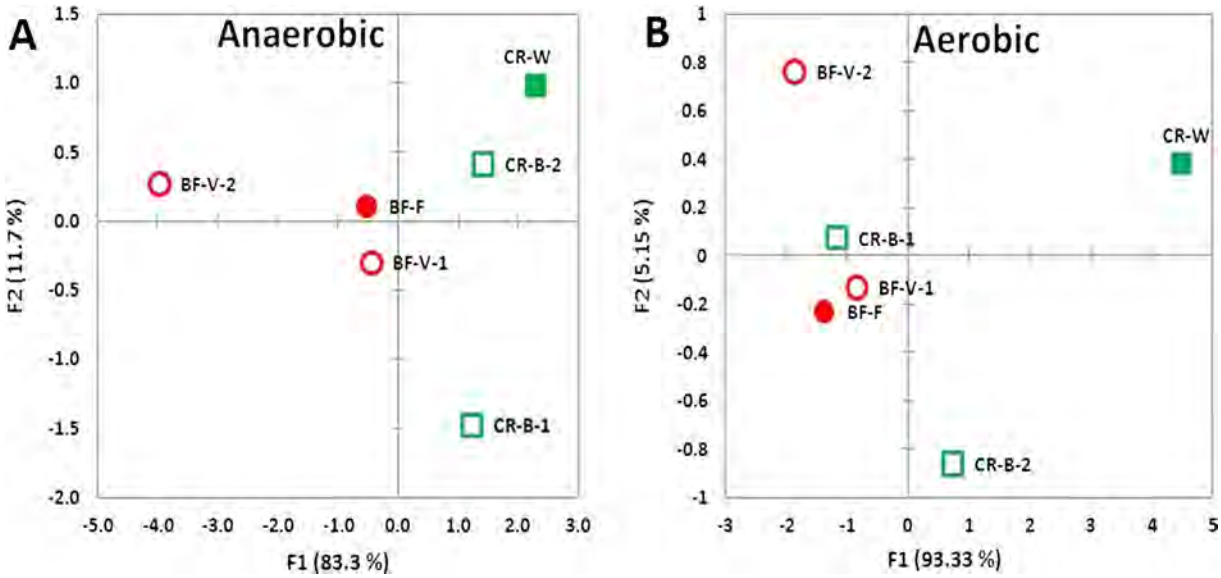
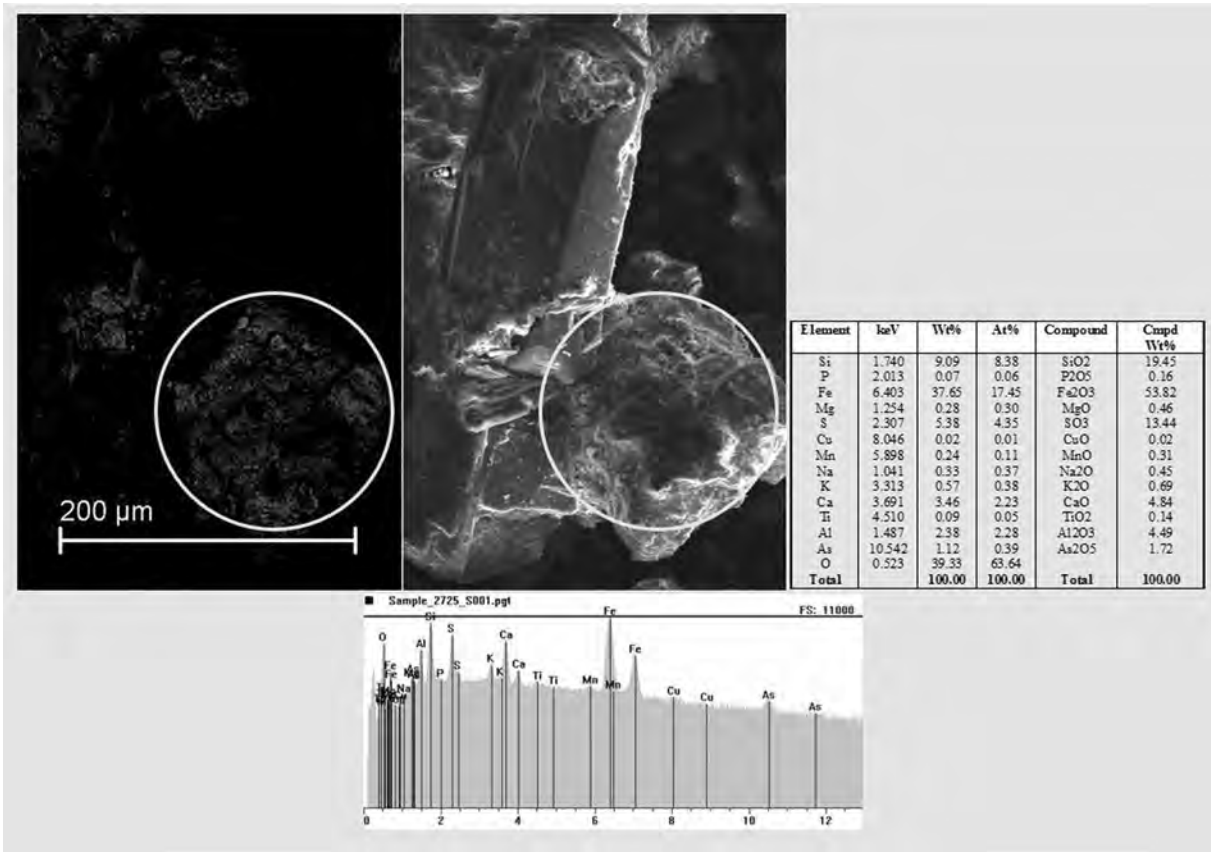


Fig. 4 Principal component analysis of the anaerobic (**a**) and aerobic (**b**) Biolog Ecoplate incubations showing differences in average substrate guild utilization of sediment microbial communities at selected sampling locations in the Belle Fourche and Cheyenne River Basins [Fruitdale reference site, sampling location BF-F; Volunteer site, sampling location BF-V-1; Volunteer site, sampling location BF-V-2; Wasta reference site, sampling location CR-W; Bridger site, sampling location CR-B-1; and Bridger site, sampling location CR-B-2]. The closer the data points are to each other, the more similar their substrate utilization rates are. The F1 and F2 axes of the anaerobic incubation describe 83.3 and 11.7% of the sample variation, respectively, whereas the F1 and F2 axes of the aerobic incubation describe 93.3 and 5.15% of the sample variation, respectively

the form of elemental As, whereas 1.72% of As was in the form of arsenic pentoxide (As_2O_5). However, because As and Fe were undetected in crystalline form, it could be assumed both were finely disseminated and bound within amorphous or nanocrystalline phases. An abundance of gypsum crystals were identified via SEM and XRD at sampling location BF-V-2 (Fig. 5 and Table S5), and the crystals appear to be the product of the sulfate-sulfide equilibrium coupled with acid buffering by carbonate minerals as predicted by Cherry et al. (Cherry et al. 1986).

4 Discussion

Alluvial sediment and associated pore waters along the Belle Fourche River were affected by deposition of mine tailings discharged during historical mining operations. Both the spatial variability of tailings deposition, as visually observed between sampling locations, and the fluctuations of sediment and pore water redox boundaries appear to influence As (re)mobilization. Redox-caused dissolution of As and other trace elements in pore water was apparent at sampling location BF-V-1 where significant positive correlations ($p < 0.05$) existed between Fe, Mn, and As concentrations (Fig. 2b). Arsenic-manganese sediment complexes did not appear to be a primary control for As dissolution in transitional redox zones. Instead, As-Fe concentrations in pore water indicate active dissolution and release of As under reducing conditions. Concentrations of reduced Fe in sediments were similar to those reported by Goddard (Goddard 1989) in which as much as 99% of total dissolved Fe was in the form of Fe(II). Sediment-extraction results (Fig. S5A) at sampling location BF-V-1 indicate lesser amounts of As associated with strongly adsorbed, amorphous and poorly crystalline phases below 18-cm depth in sediments at this location, with reducing conditions potentially promoting rapid As dissolution or loss of easily reducible iron over time through microbial reduction and upward transport. This relation may be associated with solid-phase Fe transformation to magnetite (Fe_3O_4), goethite [FeO(OH)], or other crystalline forms, reducing reactive surface area and promoting As dissolution during fluctuating redox conditions (Dixit and Hering 2003; Pedersen et al. 2006). Furthermore, As and other anions may be incorporated in internal mineral structures of those minerals (Fendorf et al. 2010) albeit to a lesser extent than mineral-surface complexation. The



Element	keV	Wt%	At%	Compound	Cmpd Wt%
Si	1.740	9.09	8.38	SiO2	19.45
P	2.013	0.07	0.06	P2O5	0.16
Fe	6.403	37.65	17.45	Fe2O3	53.82
Mg	1.254	0.28	0.30	MgO	0.46
S	2.307	5.38	4.35	SO3	13.44
Cu	8.046	0.02	0.01	CuO	0.02
Mn	5.898	0.24	0.11	MnO	0.31
Na	1.041	0.33	0.37	Na2O	0.45
K	3.313	0.57	0.38	K2O	0.69
Ca	3.691	3.46	2.23	CaO	4.84
Ti	4.510	0.09	0.05	TiO2	0.14
Al	1.487	2.38	2.28	Al2O3	4.49
As	10.542	1.12	0.39	As2O5	1.72
O	0.523	39.33	63.64		
Total		100.00	100.00	Total	100.00

Fig. 5 Selected results from sediment cores from sampling location BR-V-2. SEM upper left paired image with backscatter (left) and secondary (right) detection images. SEM results showing Fe-rich particles and associated As (circled particle) and energy-dispersive X-Ray spectroscopy (EDS) report and spectrum of the partical (EDS report, right, and EDS spectrum, bottom). A gypsum crystal is also identifiable by its shape (the long blade-shaped crystal) in the left side of the secondary detection image

prolonged presence of reduced Fe(II) in transitional aquifers may promote adsorption of As(V) onto Fe(III) oxides, an effective scavenger of As in abiotic systems (Fendorf et al. 2010; Kocar et al. 2010; O'Day et al. 2004; Pedersen et al. 2006).

On average, greater than 50% by weight of sampled sediments were finer than 125 μm (Fig. S8); however, there was no significant size fraction associations for Fe or As concentrations found within most core sections. The regional characteristics of geologic formations includes shale composed of 70% clay minerals with 60–75% of those particles less than 3.6 μm (Tourtelot 1962). The microbial reduction of Fe-clay complexes and subsequent dissolution of As in the local sediments may also be important because Fe becomes 25% less bioavailable under these conditions (Kostka et al. 2002). This phenomenon was observed at sampling locations BF-V-1 and BF-V-2 where montmorillonite and kaolinite clay content increased by about 30 and 80%, respectively, relative to contents of those minerals at reference sites. Further, lower microbial activity was observed below 12-cm depth (Fig. S6, Table S4) and appeared inhibited by the presence of mine tailings. Alternatively, the microbial community within the Belle Fourche River alluvium may have adapted to sulfur metabolism, a comparatively slower metabolic process (Fisher et al. 2007; Zhou et al. 2008).

At the BF-V-1 and BF-V-2 sampling locations, mine tailings were readily recognized, based on characteristics described by Goddard (Goddard 1989). The pore waters and sediments at this site remained oxidized throughout the sampling interval, preventing redox dissolution of Fe and As under the neutral pH conditions measured. As a result, aqueous As and Fe concentrations remained low despite elevated sediment As concentrations (160 to 1010 ppm) and Fe concentrations. Redox conditions correlated with As dissolution; however, other biogeochemical factors may provide

additional controls. Microbial carbon substrate utilization was generally lowest at both Belle Fourche River sampling locations affected by mine tailings below the 12-cm depth; however, there was no significant release of As or Fe into the pore water under the oxidizing conditions observed, further supporting evidence that microbial reduction and subsequent dissolution of metal oxides have a minor role in As mobilization in the aerobic conditions at this site. The elevated sediment As concentration at sampling location BF-V-2 may have been geochemically unaltered from its parent arsenopyrite source; however, mineralogical evidence indicates otherwise. Elevated sediment sulfur concentrations at sampling location BF-V-2 are attributed to gypsum (1.7% by weight) identified as a byproduct of Fe-sulfide oxidation (Cherry et al. 1986). Elevated gypsum content may indicate prior presence of Fe-sulfides, which could liberate bound As in adjacent sediments during oxidation.

The Cheyenne River site downstream from the Belle Fourche River confluence (Bridger sites) had As concentrations in sediment cores that were generally less than those at the Belle Fourche River sampling locations as a result of dilution of tailings. However, sediment and pore-water As concentrations were elevated compared to the upstream reference site along the Cheyenne River at the Wasta reference site (more than 8 and 6 times greater for sediment and pore water, respectively). Similar to the Belle Fourche sites, the highest concentration of As in pore waters was measured at depths with reducing conditions. However, the As (III) to As (V) ratio profiles differed. Both Cheyenne River sampling locations (CR-B-1 and CR-B-2) exhibited greater As(V) concentration relative to As(III) concentration at all but the most reducing conditions, in which As(III) concentration was slightly greater than As(V) concentration (Fig. 2e, f). Sediment As under these redox conditions likely existed as As(V) and could have been mobilized as a result of more complete oxidation of tailings downstream from source materials. Alternatively, the poor adsorption of As(V) onto lepidocrocite [γ-FeO(OH)] may have allowed rapid desorption of the As that was subsequently reduced under biotic or abiotic mechanisms (Fendorf et al. 2010; Islam et al. 2005; Pedersen et al. 2006). Extraction results confirm a high proportion of Fe existed in the highly crystalline phase, indicating that preferentially reduced Fe minerals most likely existed prior to As(V) reduction. Oxidized conditions measured in pore waters at the Cheyenne River sampling locations (CR-B-1 and CR-B-2) promoted precipitation of the redox sensitive elements (As, Fe, and Mn), effectively limiting aqueous phase concentrations of those elements (Fig. 2e, f). Further, the sampling locations with the highest concentrations of those elements in sediment cores (BF-V-1, BF-V-2, and CR-B-1) also had the greatest variability of As between the strongly adsorbed, coprecipitated with amorphous/poorly crystalline Fe, and highly crystalline Fe minerals (Fig. S5). Because less than 20% of the extractable Fe was associated with amorphous/poorly crystalline phases (~ 10% less than at sampling locations BF-V-1 and BF-V-2), sorption site availability probably was diminished, as was the potential for As incorporation into crystal lattices in sediments in the downstream direction. Total sediment S concentrations were larger in the oxidized sediments at CR-B-1 and CR-B-2, and were larger in reduced sediments than at the Belle Fourche River sites (BF-V-1, BF-V-2), potentially attributed to grain size and source variability effects.

At sampling location CR-B-1 in the stream channel, higher concentrations of As below the 12-cm depth correlated to an increase in strongly adsorbed As under reducing conditions. There is likely a slow transition of As partitioning or coprecipitation onto Fe oxyhydroxides, which are reportedly more bioavailable than strongly adsorbed As species. Throughout the entire core from backwater sampling location CR-B-2, As was associated primarily with amorphous poorly and highly crystalline Fe, whereas the As concentration in sediment cores remained consistent at 80 ppm. Bottom core section and coarser size fractions (> 250 μm) for this sampling location contained less As and Fe associated with the poorly crystalline extraction compared to upper core section and finer size fractions. This trend indicates that As was preferentially bound to the poorly crystalline phases even though those phases represented a small portion of the total available Fe. As Fe minerals become more crystalline, As may preferentially dissolve, or if thermodynamically favored, coprecipitate with the crystalline mineral phases (O'Day et al. 2004; Smedley and Kinniburgh 2002).

5 Conclusions

The sediment and pore waters of the Belle Fourche and Cheyenne Rivers contain diverse biogeochemical

systems that appear to affect (re)mobilization of elements in stream banks affected by mine tailings. Arsenic concentration was greatest at the Volunteer site on the Belle Fourche River, although there was little evidence of As dissolution from sediment into pore water due to the combination of microbial inhibition and oxidizing conditions. Cherry et al. (Cherry et al. 1986) speculated that changes in the distribution of As and other elements in sediments and pore waters would take decades or more to occur, whereas others (Fuller and Davis 2003; Goddard 1989) indicated that seepage from the contaminated sediments and alluvium continually contribute dissolved and suspended As to adjoining waters due to the hydraulic gradients created by the seasonal fluctuations in river and alluvial water levels. Arsenic sediment movement appears to be dynamic and has unstable processes due to the physical and chemical transport of sediments, active dissolution, and gradual flushing of pore waters.

Extraction results from sediments collected along banks of the Cheyenne and Belle Fourche Rivers indicated that for sampling locations BF-V-1, BF-V-2, and CR-B-1, As in sediment cores was primarily associated with amorphous and poorly crystalline Fe oxyhydroxides and inert highly crystalline Fe minerals. However, As was mobilized into the sediment pore waters under reducing conditions via dissolution of As from poorly crystalline sorption sites. Elevated As(V) pore water concentrations were attributed to Fe reduction/dissolution processes, which reduced the adsorptive capacity of As(V) to Fe and other elements. Pore water redox gradients appeared to be the predominant mechanism of As mobilization observed in this study. The lower permeability associated with the predominance of silts and sands in the tailings-containing sediments limit the physical flushing or recharge of the pore waters; however, erosional fluvial processes have been identified as an important component in this system (Stamm et al. 2013), facilitating continued downstream transport of mine tailing deposits in this alluvial system.

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