ARSENIC SPECIATION IN SEDIMENT AND PORE WATERS OF THE HISTORICAL MINING-IMPACTED BELLE FOURCH AND CHEYENNE RIVER FLOODPLAINS[1]

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Abstract: Mineral extraction and waste disposal in the Lead area of South Dakota directly discharged spent mine tailings into Whitewood Creek from 1876 until 1977. Sulfide-bearing minerals including arsenopyrite composed 7 to 8 percent of the primary ore body. Physical and chemical processes have resulted in substantial transport and deposition of arsenic-enriched materials within Whitewood Creek, the Belle Fourche and Cheyenne Rivers, and Lake Oahe (post 1958). Previous research has shown that historical sediment arsenic concentrations within the impacted floodplains range from greater than 10,000 micrograms per gram (µg/g) near the mouth of Whitewood Creek to greater than 400 µg/g in the Cheyenne River arm of Lake Oahe. Geochemical arsenic (As) interactions within sediment and pore waters were investigated to determine physical, chemical, and biological processes that may influence As transport from active floodplain sediments. Sediment pore-water dialysis chambers (peepers) were deployed over a 2-week sampling period and their contents analyzed for select trace element concentration via Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine temporal and seasonal influences associated with sediment redox geochemistry. The sediments cores were analyzed to assess the microbial activities under anaerobic and aerobic conditions. Correlating the microbial analyses with metals concentrations as well as other physical and chemical parameters within the pore water, supports conclusions made about the geochemical stability and fate of As within this system. The release of metals into the pore water appears to be controlled by seasonal variations in oxidation reduction potential with reducing conditions promoting the release of the metals. Biochemical interactions within the subsurface are also believed to affect the mobilization of these metals. This report will summarize the key research findings from on-going field work and laboratory analyses along the mining-impacted Belle Fourche and Cheyenne alluvial systems.

Additional Key Words: microbial activity, redox geochemistry

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[1] Paper was presented at the 2011 National Meeting of the American Society of Mining and Reclamation, Bismarck, ND ***Reclamation: Sciences Leading to Success*** June 11 - 16, 2011. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

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Proceedings America Society of Mining and Reclamation, 2011 pp 539-551
DOI: 10.21000/JASMR11010539
`http://dx.doi.org/10.21000JASMR/1101050539`

Introduction

The Belle Fourche and Cheyenne Rivers have been impacted by mining activities which took place in the northern Black Hills of South Dakota during the previous 120 years. Between 1876 and 1977, spent mine tailings from these mining activities were directly discharged into Gold Run Creek near the headwaters of Whitewood Creek, Belle Fourche, and Cheyenne Rivers watershed. It has been estimated that nearly 120 million tons of tailings containing heavy metals and arsenic have been deposited along the Belle Fourche and Cheyenne Rivers (Marron, 1992). Sediments within this fluvial system are continually being reworked and transported via fluvial processes as they migrate towards Lake Oahe of the Missouri River reservoir system located in central South Dakota (Fig. 1).

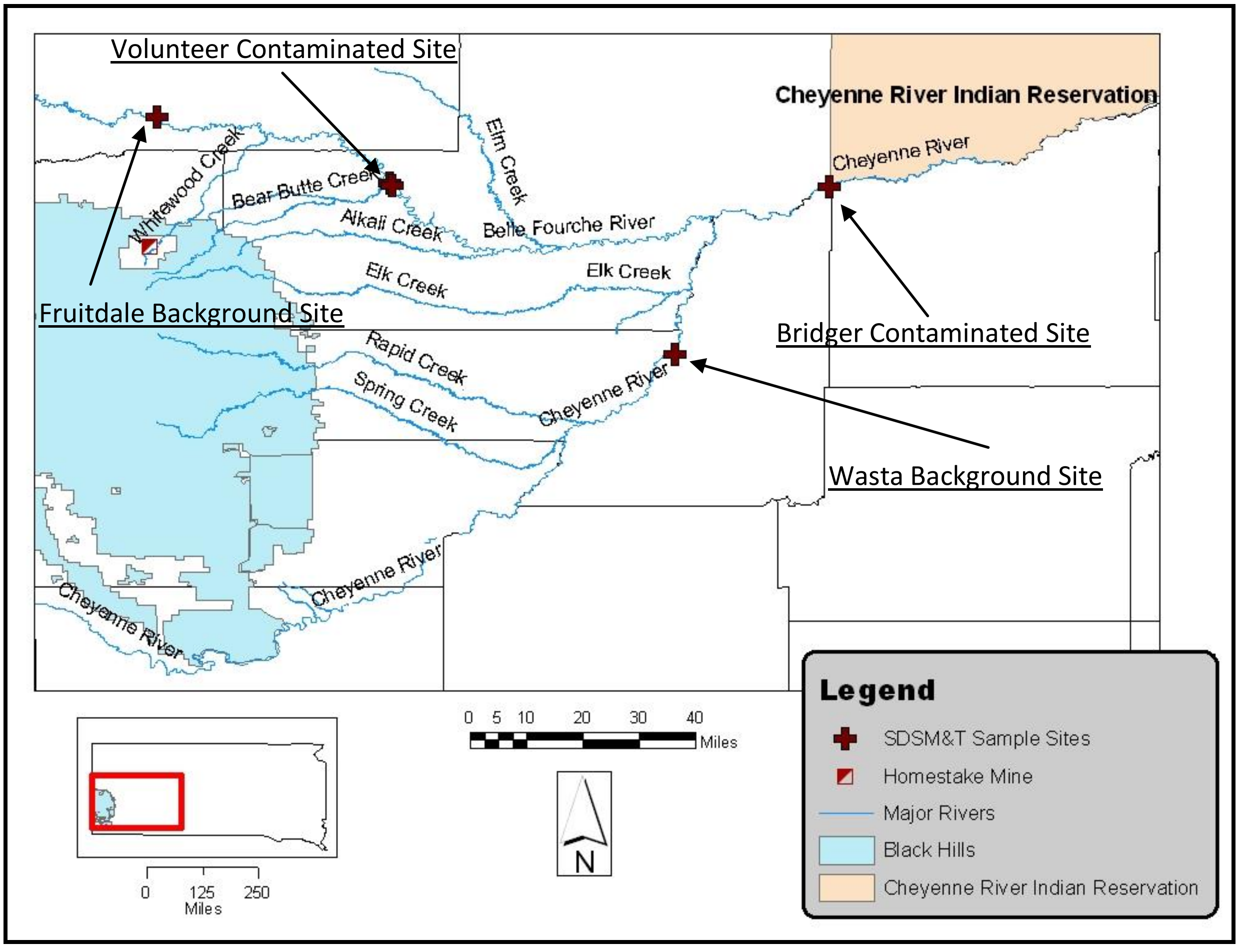

Figure 1. South Dakota outline of sampling site locations for the study area encompassing the Belle Fourche and Cheyenne River fluvial systems of western South Dakota.

The focus of this report is on the fate and transport mechanisms of As within the mining-impacted fluvial systems in the Belle Fourche and Cheyenne Rivers. Sediments along

Whitewood Creek have historically had the highest concentrations of As, exceeding 10,000 µg/g at several locations (Goddard, 1989). The upper reaches of Whitewood Creek were listed on the National Priority List by the U.S. Environmental Protection Agency (US EPA) in the late 1970s, but have since been remediated and declassified, although long term monitoring continues to this day (US EPA, 1990). Further downstream, Goddard (1989) reported elevated sediment As existed within the Belle Fourche (> 3500 µg/g) and the Cheyenne River (>530 µg/g), far exceeding the regionally established 10 µg/g background concentration.

The dynamic fate and transport mechanisms of As within the mining-impacted fluvial system were studied by assessing interactions between the alluvial sediments and pore water. The sampling sites consisted of two mining-influenced locations along the Belle Fourche and Cheyenne River, and at two background sites located upstream from the confluence of their respected contaminant loading streams (Fig. 1). This report will describe the sampling and analytical methods used, and will present preliminary results related to the pore water biogeochemistry controlling As transport at these study sites.

Previous Studies

The Whitewood Creek area, and the impacts associated with long-term direct discharge of tailings into Gold Run Creek (an upper tributary of Whitewood Creek), has been the focus of numerous studies. The principal previous investigations are those by Goddard (1989), Cherry et al. (1986a, b, c), Horowitz et al. (1988), Marron (1988, 1989, 1989a, 1992) and the U.S. Environmental Protection Agency (1971). These studies provide an excellent overview of localized historical mining-impacts within the Whitewood Creek region and also the Belle Fourche and Cheyenne Rivers. The summary provided below highlights several key findings regarding the source material (tailings), physical and chemical conditions found in the depositional sediments, and interactions between surface and groundwater within the Whitewood Creek floodplains.

Source Materials

The predominant source of As and other heavy metal contaminants within the study site is from historical gold mining activities in the Lead, South Dakota area. The Precambrian aged rock formations mined for their gold typically contained in excess of 0.8% arsenopyrite (Noble, 1950). Almost a billion tons of ore was mined from this area (U.S. EPA, 1990) with an estimated 120 million tons still being held within the Belle Fourche and Cheyenne Rivers alluvial systems. In 1971 it was reported by US EPA that of a daily load of 2,735 tons of suspended solids directly discharged into Whitewood Creek, 9.5 tons was As (Goddard, 1989). Before 1920, the ore was crushed to sand or smaller sized particles by stamp mills, whereas after 1920, ball-and-rod crushers produced finer grained material. The finer grained material, known as "slimes", consisted of 85% of its particles < 0.045 mm, with the remaining ranging between 0.075 and 0.045 mm size fractions. The material became sorted as it was transported downstream with a large variability in percentages of sand to silt sized partials as one travels downstream (Goddard, 1989).

Contaminated Sediments.

Studies by Goddard (1989) reported mean concentrations of sediment As along Whitewood Creek were 1,920 µg/g, with peaks reported as high as 11,000 µg/g. Sediment As within the Belle Fourche River generally decreased from the confluence with Whitewood to the Cheyenne River, ranging between 400 to 1,300 µg/g, with localized peaks exceeding 3,500 µg/g. The Cheyenne River was reported to contain the lowest mean sediment As (70 µg/g), with peaks as high as 530 µg/g. The U.S. EPA (1971, 1973a) reported As concentrations within the impacted hydrologic system generally exceeded regional background (~10 µg/g) by 200x or greater.

Contaminated Waters.

Studies by Cherry et al. (1986a, b, c) described the existence of a seasonal metals flux within subsurface fluvial pore waters during spring and early summer flooding. Once the floodplain materials were saturated and the water recession began, dissolved metal concentrations within the porewaters were thought to be redistributed within the alluvial aquifer, or flushed into surrounding surface waters. It was believed As was adsorbed onto iron and aluminum oxides, with geochemical modeling efforts reporting that the release of As into the pore waters increased with an increased sulfate concentrations present within the sediments (Cherry et al., 1986a, b, c).

Sampling Methods

Pore Water Sampling.

Pore water sampling can be difficult without disturbing in situ subsurface conditions. For this study, pore water dialysis chambers (commonly referred to as "peepers") constructed based upon studies by Hesslien (1976) and Urban et al. (1997) were used. The primary design criterion of the peeper chamber is to obtain a sufficient volume of pore water to meet specific analytical requirements. The peepers were 76.2 cm x 45.7 cm x 2.5 cm and were constructed using plexiglass (Fig. 2). The 2.54 cm thickness was designed to minimize the impact on the bed sediments while thin enough to allow for simple deployment without excavation. Plexiglass covers were placed on both sides of the base plate to affix the 0.45 µm dialysis membrane. Circular 1.5 cm diameter cells were drilled through the plexiglass and filled with de-ionized and deoxygenated water prior to deployment. There were 18 cells contained within each of the 32 rows, with each row providing approximately 40 mL of sample. Nylon bolts were used to affix the outer plates connected to the base plate, and were tightened to ensure minimal interaction between cell chambers occurred.

The peepers were submerged in a deionized distilled water bath bubbled with N_2 gas for 24 hours prior to deployment. During transport, the peepers remained covered and submerged within the water until immediately before deployment in the field. The peepers were driven into the saturated soils vertically, perpendicular to an existing surface or ground water flow direction. The samplers remained in the field for two weeks to ensure equilibrium between the sampler chamber and the sediments was established. After two weeks, the peeper was removed and the contents from within the individual pore water chambers sampled within 1hr of extraction using a 10mL syringe (Fig. 2). The contents of two rows were combined into one sample for analysis.

Sediment Sampling.

Sediment samples were collected adjacent to the peeper location to provide comparisons between the solution (porewater) and mineral phase interactions. The sediment samples were collected after the peepers had been removed from the sediment. The sediment samples were collected using a sleeved, stainless steel, 30.5 cm in length, 5 cm diameter AMS Inc split core sampler. The split coring unit was assembled according to the AMS Spit Core instructions and driven into the sediment using an AMS slide hammer. After the coring process, the sleeve containing the sediment was removed, capped and sealed with wax to preserve the in situ conditions. The core was preserved on ice during transport to the lab, at roughly 4°C until analysis in the lab.

Figure 2. Schematic of pore water dialysis chamber (peeper) construction (left) and sampling procedures using a 10mL syringe after peeper extraction from the field (right). 1 represents the cover sheet; 2 the filter membrane; and 3. the sampling chamber.

Pore Water Analyses.

The peepers porewaters were analyzed using both field and laboratory methods. Each composited sample (2 rows) resulted in ~ 80 mL of sample, stored within a 1000 mL beaker under shading (to minimize UV oxidation of As). Field measurements included: temperature, total dissolved solids (TDS), specific conductivity, oxidation/reduction potential (ORP), pH, and aqueous Fe(II). The measurements for TDS, and pH were completing using a calibrated EXTECH® ExStik® II pH / Conductivity meter field multiprobe, while ORP was determined using OAKTON® Waterproof ORPTestr® 10 probe. Between 25 and 100 µL of the composited sample was assayed for Fe(II) following methods by Stookey (1970). Approximately 40 mL was filtered passed through an ion exchange As speciation cartridge containing an aluminosilicate medium, which removes As(V) from the passing solution, following procedures by Meng (1997). The filtrate was stored in a separate 250 mL polyurethane sample bottle and analyzed for total As concentration [assumed to represent As(III)]. The remaining composited sample (~ 35 mL) was placed in a sample bottle and utilized for total metals analysis. As(V) was determined by subtracting the speciated As(III) sample from the un-speciated total As. All samples were preserved using 2 mL of concentrated HNO_3. All pore water samples were analyzed for: Al, As, Cd, Ca, Cd, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se and Na, by the USGS-National Water Quality Lab (NWQL) in Denver, CO using an Agilent 7500ce ICP-MS instrument with an octopole reaction system. The octopole reaction system (ORC) was used to minimize known interference of As with ArCl, TiAl, and CuC common for ICP-MS analysis.

Sediment Analyses.

A total of four cores were collected at each sampling site. One sediment core from each site was preserved at -5°C for an assay of the microbial community profile using a Biolog EcoPlate microbial analysis (Biolog, 2010). Sediment cores were sliced into 5 equal length sections while frozen, and assayed following methods by Biolog. Each 3 to 6g sample was vortexed with deionized water and centrifuged at 3000 rpm. 25mL of centrate was pipetted into each Biolog EcoPlate cell and incubated either aerobically or anaerobically at 25°C for 7 days. Ecoplate substrate utilization was determined every 24 hr using the Biolog plate reader. Substrate utilization was indicative of color change within the individual wellplates.

Results and Discussion

Many of the results from this study are pending at the date of this paper submission. For this paper, discussion will only include microbial community assay results for the sampling site sediments, and pore water quality and As speciation results for the peepers. Table 1 is a complete list of pore water analyses at each sampling site.

At the Belle Fourche - Fruitdale site (background), the Biolog assays indicated that moderate anaerobic microbial activity existed throughout the sediment column depth. For aerobic incubations, minimal microbial activity existed near the sediment surface, while no aerobic microbial activity was determined at depths greater than 15 cm. For sediment porewaters, TDS concentrations were 2.26-1.61 g/L while Fe(II) ranged between 0.23-135 mg/L below the sediment surface. As reducing conditions prevailed beginning at 2 cm depth, As(III) concentrations increased to ~37 µg/L, while As(III)/(V) ratios ranged from 1.92 to 0.1. The presumably high As porewater concentrations observed at this background site were tentatively attributed to trace As commonly found within Pierre Shale, the predominant geologic formation for this region. We speculate that trace concentrations of As become bound to iron oxides found within geologic medium near redox boundaries, and are released during reductive dissolution of the iron oxides.

Table 1. Pore water analysis results.

Sampling Site	Depth from sediment Surface [cm]	ORP [mV +,-]	TDS [g/L]	Fe(II) [mg/L]	As Total [µg/L]	As III [µg/L]	As V [µg/L]	Mn [µg/L]	As III/V Ratio
BF-F-1-P	-10	169	2.26	0.23	3.80	2.50	1.30	32	1.92
	-2	160	0.87	0.14	1.90	0.84	1.06	66	0.79
	0	133	0.89	0.23	3.60	0.90	2.70	850	0.33
	2	-46	0.92	10.92	36.60	3.40	33.20	4090	0.10
	6	-83	0.96	30.55	90.10	10.60	79.50	5980	0.13
	10	-79	1.15	43.59	135.00	17.80	117.20	5970	0.15
	14	-91	1.23	47.72	99.70	27.80	71.90	5730	0.39
	18	-81	1.41	45.51	88.70	32.90	55.80	6400	0.59
	22	-84	1.45	48.27	80.10	37.90	42.20	6720	0.90
	26	-86	1.47	43.68	68.70	29.00	39.70	6950	0.73
	30	-66	1.46	36.61	50.80	23.30	27.50	7080	0.85
	34	-64	1.47	31.01	47.60	18.50	29.10	6950	0.64
	38	-73	1.52	31.01	39.80	14.80	25.00	6420	0.59
	42	-70	1.61	28.53	38.60	12.30	26.30	5960	0.47
	46	-87	1.61	24.77	40.60	15.80	24.80	5380	0.64
BF-V-1-P	-6	185	2.38	0.10	36.00	10.00	26.00	18	0.38
	-2	169	2.73	0.67	29.80	7.90	21.90	23	0.36
	0	177	2.63	0.24	31.40	6.90	24.50	119	0.28
	2	187	2.23	0.14	56.10	12.30	43.80	307	0.28
	6	161	2.15	0.24	100.00	15.80	84.20	495	0.19
	10	105	1.75	0.63	186.00	16.30	169.70	1240	0.10
	14	-28	2.12	6.69	385.00	141.00	244.00	5460	0.58
	18	-71	2.19	46.13	1940.00	1380.00	560.00	9230	2.46
	22	-67	2.04	51.43	1960.00	1490.00	470.00	9330	3.17
	26	-68	2.16	45.46	1360.00	1060.00	300.00	9350	3.53
	30	-72	2.63	45.17	1390.00	1050.00	340.00	10400	3.09
	34	-72	2.4	49.60	1990.00	1610.00	380.00	7930	4.24
	38	-87	3.11	51.72	2570.00	1890.00	680.00	6930	2.78
	42	-72	3.22	47.29	1780.00	1280.00	500.00	9150	2.56
	46	-72	4.18	47.67	1770.00	1300.00	470.00	10000	2.77
BF-V-2-P	-6	245	9.5	0.48	32.50	16.30	16.20	188	1.01
	-2	245	3.7	0.19	23.10	13.00	10.10	147	1.29
	0	250	3.68	0.43	47.00	10.80	36.20	126	0.30
	2	243	3.76	0.05	43.80	7.90	35.90	366	0.22
	6	243	2.86	0.00	50.80	3.20	47.60	23	0.07
	10	233	2.96	0.10	37.00	5.20	31.80	20	0.16
	14	227	2.77	-0.29	32.00	5.40	26.60	35	0.20
	18	222	2.66	0.19	30.90	3.60	27.30	243	0.13
	22	199	2.61	0.10	46.10	3.00	43.10	2020	0.07
	26	68	2.37	2.65	110.00	28.30	81.70	4210	0.35
	30	34	2.15	4.14	12.90	44.40	-31.50	6650	-1.41
	34	29	2.35	5.87	121.00	33.60	87.40	7140	0.38

Table 1. Continued.

Sampling Site	Depth from sediment Surface [cm]	ORP [mV +,-]	TDS [g/L]	Fe(II) [mg/L]	As Total [µg/L]	As III [µg/L]	As V [µg/L]	Mn [µg/L]	As III/V Ratio
CR-W-1-P	0	153	3.21	0.37	4.40	1.10	3.30	4030	0.33
	2	20	2.83	2.89	9.80	2.10	7.70	6540	0.27
	6	-36	2.67	7.98	12.80	5.00	7.80	5410	0.64
	10	-52	2.59	9.72	19.70	11.00	8.70	4340	1.26
	14	-71	2.56	12.20	20.60	14.70	5.90	3510	2.49
	18	-71	2.54	11.47	22.50	16.10	6.40	3330	2.52
	22	-87	2.64	11.56	23.50	15.80	7.70	3270	2.05
	26	-61	2.61	12.93	23.40	18.40	5.00	2820	3.68
	30	-58	2.59	11.28	22.50	15.00	7.50	3000	2.00
	34	-57	2.63	12.38	22.30	19.60	2.70	2920	7.26
	38	-56	2.58	12.29	24.10	19.30	4.80	2650	4.02
	42	-63	2.54	10.18	25.80	22.00	3.80	2590	5.79
	46	-51	2.65	11.28	23.90	20.00	3.90	2420	5.13
	50	-59	2.63	9.36	23.10	19.50	3.60	2080	5.42
	54	-59	2.68	11.37	20.60	16.60	4.00	1940	4.15
	58	-49	2.75	14.68	20.90	16.50	4.40	1980	3.75
CR-B-1-P	-2	257	13.04	0.05	12.50	8.80	3.70	33	2.38
	0	262	8.94	0.18	6.00	4.50	1.50	23	3.00
	2	257	6.67	0.14	3.90	2.40	1.50	27	1.60
	6	261	4.25	0.32	6.30	2.50	3.80	216	0.66
	10	253	3.48	0.41	12.40	1.70	10.70	2020	0.16
	14	167	3.29	1.51	41.40	3.60	37.80	3320	0.10
	18	5	3.29	10.77	107.00	5.20	101.80	2800	0.05
	22	-41	3.19	18.12	173.00	31.20	141.80	2950	0.22
	26	-57	3.22	22.36	210.00	52.10	157.90	3100	0.33
	30	-62	3.27	25.56	339.00	159.00	180.00	3930	0.88
	34	-49	3.09	23.37	352.00	194.00	158.00	4020	1.23
	38	-41	3.08	25.42	287.00	124.00	163.00	3660	0.76
	42	-33	2.99	19.72	252.00	85.70	166.30	3750	0.52
	46	-10	2.96	19.40	193.00	59.40	133.60	3970	0.44
	50	-12	3.04	9.31	192.00	37.00	155.00	4010	0.24
	54	0	3.13	17.11	165.00	22.30	142.70	3410	0.16
CR-B-2-P	-10	253	7.09	0.14	11.70	7.60	4.10	53	1.85
	-6	262	7.26	0.41	10.80	3.70	7.10	65	0.52
	-2	276	3.5	0.82	12.50	2.10	10.40	414	0.20
	0	275	2.63	0.36	24.60	2.70	21.90	1980	0.12
	2	256	2.92	0.32	22.10	3.10	19.00	1250	0.16
	6	252	2.89	0.32	27.20	4.00	23.20	2190	0.17
	10	220	2.77	0.41	42.90	3.90	39.00	5180	0.10
	14	19	2.45	3.28	103.00	37.50	65.50	7320	0.57
	18	-18	2.86	8.67	12.20	82.30	-70.10	7670	-1.17
	22	-49	2.85	16.43	307.00	189.00	118.00	6930	1.60
	26	-34	2.86	15.20	221.00	135.00	86.00	8740	1.57
	30	-41	2.87	13.55	195.00	124.00	71.00	10800	1.75
	34	-17	2.75	12.59	170.00	102.00	68.00	8970	1.50
	38	-7	2.35	10.72	146.00	66.70	79.30	9230	0.84
	42	1	2.6	6.11	110.00	49.10	60.90	6290	0.81

Two separate sampling locations were sampled along the Belle Fourche River (BF-V-1 and BF-V-2). BF-V-1 was located in a low energy depositional region along the bank of the river. Both sites exhibited a significant decrease in microbial activity under both aerobic and anaerobic conditions. These reduced microbial populations appear to be attributed to either differing substrate utilization capacities that were not supported by the Ecoplate incubation trays, or by metal-microbe induced inhibition due to the presence of mine tailings that existed at the sampling sites. TDS concentrations for both sites were similar to the background Fruitdale site (~2.5 g/L), with the highest values (9.5 µg/L) reported near the sediment-water interface. For the first site, Fe(II) profiles were similar to the background site, however As concentrations far exceeded background, with the elevated concentrations ranging between 100 to 2570 µg/L. The site was predominately reduced, promoting As(III) throughout depth and a As(III/V) ratio averaging 3.07. Manganese concentrations were also elevated to ~10,000 µg/L. For the second sampling site (BF-V-2), oxidizing conditions prevailed to 34 cm depth, with As(V) being the predominate As species averaging 40.4 µg/L with an average As(III/V) ratio of 0.2 which was similar to the background site.

The Cheyenne River - Wasta background site exhibited significant aerobic and anaerobic microbial activities microbial activities throughout the soil depth. TDS concentrations were typically 2.5-3 g/L, while Fe(II) concentrations were consistently ~ 10 mg/L. Total As was much lower than other sites (<25 µg/L) while manganese was ~ 5,000 µg/L near the sediment-water interface, and declined to ~ 2,000 µg/L at depth.

Two separate sampling locations were sampled along the Cheyenne River (CR-B-1 and CR-B-2). Both of these sites were located within an abandoned meander which experiences seasonal flooding. Microbial activities were significantly different compared to observations from the Wasta background site. For the first site, elevated anaerobic microbial activities existed near the sediment surface, and decreased at depth, while aerobic activities were low for the entire core profile. For the second sampling site, anaerobic activities were similar to those observed for the background site, while aerobic activities were slightly decreased near 10cm depth and were consistent with the background site elsewhere. TDS values were elevated to greater than 9 g/L for both sampling sites above the sediment-water interface, and reduced to ~3 g/L below 10 cm. Fe(II) exceeded 20 mg/L under reducing conditions, which is more than double the Fe(II) concentrations observed for the background site. For the first site, total As concentrations exceeded 350 µg/L, with roughly equal presence of As(III) to As(V) (0.79) at depths with elevated concentrations, while manganese concentrations remained consistent at ~ 4,000 µg/L under reducing conditions. For the second site, Fe(II) concentrations were similar to the background site except for a brief increase to 20 mg/L near the redox boundary. Total As also increased to 300 µg/L near the redox boundary, and then decreased to ~100 µg/L at depth. Arsenic (III/V) ratios averaged 0.71 and reducing conditions also promoted the presence of manganese to a maximum of ~10,000 µg/L.

Conclusion

Both the Belle Fourche and Cheyenne River fluvial systems have been heavily impacted by historical mining activities which has resulted in elevated heavy metal concentrations within the alluvial sediments and associated pore waters. Arsenic, Fe and Mn concentrations observed at the Belle Fourche and Cheyenne River sites tend to vary depending on specific biogeochemical equilibrium conditions that existed during sampling, while preliminary interpretation of the microbial profile results suggest that As mobility appears biotically-influenced. In general, the most contaminated site on the Belle Fourche River contained more than 19x more pore water As compared to its background site, while the Cheyenne River contained 7x pore water As compared to its background site. All metals concentrations in the pore water increased significantly as conditions became reducing at the redox boundary, suggesting seasonal movement of this boundary may be one of the driving mechanisms for metals release from the sediments. Microbial activity generally decreased from the background to the contaminated sites along the Belle Fourche River while microbial activity along the Cheyenne River remained relatively active and unchanged. A lack of microbial activity in the most contaminated sediments may be due to an adaptation of the microbes to utilize energy sources other than what was represented in the Biolog analysis (carbohydrates). A sulfur based energy source may be being utilized by these microbes or the toxic environment may prevent microbe activity completely but further research is needed to make a definitive conclusion. On-going studies will provide further insight towards controlling biogeochemical mechanisms that may influence As fate and transport within these mining-impacted fluvial systems.

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