PASSIVE TREATMENT OF MINING INFLUENCED WASTEWATER WITH BIOCHEMICAL REACTOR TREATMENT AT THE STANDARD MINE SUPERFUND SITE, CRESTED BUTTE, COLORADO[1]

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Abstract. A pilot biochemical reactor (BCR) with a design flowrate of 3.8 l/m (1 gpm) has been operating at the Standard Mine Superfund Site for over four years, since August, 2007. The pilot system is entirely passive, using solar energy to power sampling equipment and pumping requirements. BCR treatment relies on biological and chemical reactions within an anaerobic reactor comprised of organic and inorganic materials including woodchips, straw, limestone and bacterial inoculum. The BCR pilot has been treating mining influenced wastewater (MIW) since construction was completed in the summer of 2007. Polishing and aeration of BCR effluent is accomplished in an aerobic polishing cell (APC) containing wetland plants in two of the three cells. The Standard Mine BCR is constructed at an elevation of 3,353 meters (11,000 ft) above MSL with an average annual snowfall of 10.2 m (400 in). Limited BCR treatment data from reactors operating under harsh alpine conditions was available before this system was constructed. Operation and monitoring of the BCR has been year round since 2007. Due to the inaccessibility of the site during winter months, an automated sampling system was designed incorporating Teledyne ISCO™ (ISCO) samplers, Hydrolab™ sondes, and a satellite transmission system reporting site operational parameters on a daily basis. In addition to automated sampling, grab samples were taken monthly throughout the 2010/2011 winter using backcountry skiing equipment to access the site.

Contaminants of concern (COCs) in the MIW include Cd, Cu, Pb, Mn, and Zn. High metals removal has been observed in BCR effluent since the beginning of operation. In 2009, 2010, and 2011 the average percent removal efficiency for cadmium, Cu, Pb, and Zn exceeded 98%. The pilot study is notable for a long operating period and low analytical laboratory detection limits for metals. BCR treatment of cadmium, Cu, and Pb to less than 5 µg/L has been demonstrated indicating that BCR is capable of approaching or meeting stringent aquatic life water quality standards when operated under harsh high alpine conditions. Both metals and nutrient removal are discussed in relation to receiving stream water quality standards. BCR performance is discussed with additional discussion of performance of BCR effluent polishing by aerobic lagoon.

Additional Key Words: Anaerobic, BCR, passive treatment, acid rock drainage (ARD), acid mine drainage (AMD), sulfate reducing bacteria, aerobic polishing

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Introduction

The Standard Mine pilot biochemical reactor (BCR) was constructed in 2007 to treat mine influenced wastewater (MIW) from the Standard Mine Superfund site. The site is located within the Ruby Mining District, approximately four miles west of Crested Butte, Colorado at an elevation of near 3,353 m (11,000 ft) above sea level. Mining activity began around 1874, with significant operations for extraction of Pb, Zn, Ag, and Au between 1931 and 1966 when mining operations were abandoned. The approximately 4.0 ha (10 acre) site consists of six separate levels of mine workings. The pilot is located at the foot of the adit level one workings (Adit) and accepts discharge from interconnected adit levels one through three (DRMS, 2007). Adit discharge currently enters Elk Creek, which feeds into Coal Creek, Crested Butte's water supply. In addition, the first 60-90 m (200-300 ft) above the Elk Creek confluence is capable of supporting a brook trout fishery (USEPA, 2011). Therefore, elevated concentrations of metals from Adit discharge are a concern for human and animal health.

Remoteness and climatic conditions of the site have proven a challenge in operation and monitoring of the pilot BCR. However, low laboratory detection limits have provided unmatched insight into BCR performance at high elevation alpine environments. Snow cover exists on site typically from late November until as late as mid-July with typical annual snowfall ranging between 10.2 and 17.8 m (400 and 700 in). NRCS weather station No. CO07K115 located near the site at comparable elevation of 3,262 m (10,700 ft) provides an average winter temperature near -9°C (15°F) December through February and average summer temperature near 10°C (50°F) June through August.

The Standard Mine pilot BCR consists of a mixture of limestone-buffered organic substrate which typically includes organics such as hay, woodchips, sawdust, and a source of inoculum to encourage growth of sulfate reducing (and other) bacteria. Full scale BCR's are typically designed with the intent to operate for up to twenty years with minimal operations and maintenance "O and M". A volunteer passive treatment system outside of an abandoned Pb-Zn mine in County Wicklow, Ireland has been operating for more than a century, removing an estimated 95 percent of the discharged Zn (Beining and Otte, 1997).

The Standard Mine pilot BCR was originally designed as a short term scientific study, with an expected operational study period of one year to examine BCR treatment in high alpine conditions. However, because of the value of data produced in the study, the pilot BCR study was extended and has been in operation for more than four years, and is expected to continue for an additional two and one half years per request of the Colorado Department of Public Health and Environment (CDPHE). Because of this significant extension of operational life past the intended pilot study design life, additional "O and M" efforts have been required and several intermittent stoppages in flow have occurred, mainly due to the atypical use of a solar powered pump to feed the pilot reactor. It is important to note that these stoppages have provided data showing minimal impact on treatment performance upon restart of the BCR, even after extended stoppages.

In September 2007, the pilot BCR began treating approximately 3.8 liters per minute (l/m) (one gallon per minute (gpm)) of adit discharge and has operated with intermittent stoppages in flow since. The adit discharge (BCR influent) is net acidic, containing elevated loadings of Cd, Cu, Fe, Pb, Mn, and Zn (Auer, 2009; PWT, 2009). With the exception of Fe, these metals are surface water Contaminants of Potential Concern (COPCs) for discharge into Elk Creek (SRC, 2007). Concentrations of these metals exceed CDPHE standards for Elk Creek (Detailed system design and background can be found within a previously produced paper (Reisman et al., 2008).

). CDPHE standards are used as a reference for comparison purposes and are not intended to represent potential discharge standards which have not yet been determined (CDPHE, 2007). Detailed system design and background can be found within a previously produced paper (Reisman et al., 2008).

Table 1. CDPHE Water Quality Standards for Elk Creek

Parameter	**Acute Standard[1/]**	**Chronic Standard[1/]**	**Adit Discharge[2/]**	**MDL Range**
Cd, dissolved (mg/L)	0.0012	0.00031	0.13	0.0003 - 0.025
Cu, dissolved (mg/L)	0.009	0.0062	0.21	0.0002 - 0.058
Fe, total (mg/L) (water supply)	NL	0.3	9.1	0.021 - 0.1
Fe, total (mg/L)	NL	1.0 (TREC)[3/]	9.1	
Pb, dissolved (mg/L)	0.04	0.0016	0.31	0.00025 - 0.023
Mn, dissolved (mg/L)	2.59	1.43	10.9	0.0005 - 0.2
Zn, dissolved (mg/L)	0.099	0.086	24.7	0.005 - 0.045

Notes:

1/ Acute and chronic standards based on hardness value of 65 mg/L

2/ Adit discharge calculated as the average BCR influent between August 2007 and October 2011

3/ TREC refers to a total recoverable metals standard
NL refers to a not listed water quality standard

Fundamental BCR biological and chemical treatment processes are summarized as (Thomas, 2002):

- Biological reduction of sulfate to sulfide resulting in subsequent precipitation of metal sulfides;
- Elevation of alkalinity resulting from reduction of sulfate and dissolution of substrate limestone;
- Metal hydroxide precipitation; and
- Trace metal sorption by metal hydroxides and organic media.

In addition to the above listed processes, some biological reduction of other elements such as Se will occur within the BCR, resulting in precipitation once reaching their elemental form.

Previous studies involving post treatment polishing of the Standard Mine pilot BCR effluent have examined a chitin reactor for polishing of Mn (Reisman et al., 2009), a four cell aerobic polishing cell (APC) for polishing of Fe, Mn, organics, and nutrients, and a mixing study exploring blending BCR effluent and untreated adit discharge to examine residual treatment capacity of BCR effluent. The mixing study evaluated reducing the metals and acidity load associated with the MIW, reducing the biochemical oxygen demand (BOD) and sulfide concentrations of the BCR effluent, and ultimately reducing the footprint requirements for a passive treatment system utilizing BCRs (Smart et al., 2010).

Materials and Methods

The Standard Mine pilot BCR was fed approximately one gpm net acidic drainage from the Standard Mine Adit level 1 discharge over the study period. The BCR influent water was characterized as having an average pH of 6.2 standard units (su), positive oxidation reduction potential (ORP), and containing elevated sulfate, dissolved metals, and an average alkalinity of 20.6 mg/L.

Adit discharge was delivered through two four inch PVC pipes to a surge anticipation tank and was fed to the reactor by a small intermittently operating solar powered pump. Hydraulic residence time within the reactor is approximately 31 hours (Reisman et al., 2009). BCR influent flow was measured by a flume and ISCO 730 bubbler Module™. BCR influent and effluent ORP, temperature, and pH were measured in 15 minute intervals using two Hach Hydrolab MS5™ sondes located in the influent surge anticipation tank and effluent discharge standpipe respectively. Temperature, pH, and flow were transmitted daily by satellite to a website for remote monitoring of pilot performance. The most recent satellite transmission system has been successfully transmitting daily monitoring data since it's installation in September 2009.

Typically bi-monthly to bi-weekly BCR influent and effluent grab samples have been taken at the site since operation of the BCR began. APC effluent grab samples were collected when the APC was accessible, during summer months in 2009 and 2010. In 2011 the first cell of the APC, constructed to operate for one season, was compromised and the APC was ruled inoperable.

BCR grab samples were collected using the peristaltic pump on two ISCO™ samplers from the BCR influent surge anticipation tank and BCR effluent discharge standpipe respectively. The ISCO samplers were used for weekly sampling during winter months through the 2010/2011 winter. Operational issues with auto-sampling during freezing winter months brought about decommissioning of automated sampling during the winter of 2011/2012.

BCR influent and effluent sampling points are accessible inside of a shed (Shed) located onsite for winter access and protection against weather. A 12-volt solar system was installed in the Shed for power to operate the autosamplers, pump, and satellite transmission equipment. During winter months, the Shed has been covered by as much as fifteen feet of snow and was uncovered for access to sampling equipment.

Since September 2008, approximately 54 sets of BCR influent and effluent grab sample have been collected. Regularly sampled parameters measured include Cd, Cu Fe, Pb, Mn, Zn, Ca, sulfate, sulfide, nitrate-nitrite, and ammonia. BCR and APC effluent BOD was measured during the summer months of 2009 and 2010.

Metals removal data sampled between September 4, 2008 and October 20, 2011 are presented. Field (pH, temperature, ORP, DO) and general parameter data (nitrogen and sulfur species, and BOD) presented were sampled within dates as discussed. Temperature and pH were measured by sondes, all other parameters were measured from field grab samples. The BCR was delivered approximately 1 gpm during the period which data is presented, with a number of slight variations in flow and intermittent stoppages. Non-detect results with a MDL higher than the acute stream standards were removed from consideration for data comparison purposes.

Remaining non-detect results were incorporated in data as one half the MDL. MDL values were not included in removal percentage calculations.

Results and Discussion

Field Parameters

Reactor pH, temperature, ORP and DO are presented in Figure **1** and 2 and Tables 2 through 4. Influent pH data available between September, 2008 and January 2012 are presented in Figure **1**. As shown, there was a substantial decrease of influent pH noticeable during spring months, and an increase of effluent pH noticeable throughout late summer and fall months. Table **1** presents average pH of the data set and selected data for spring months.

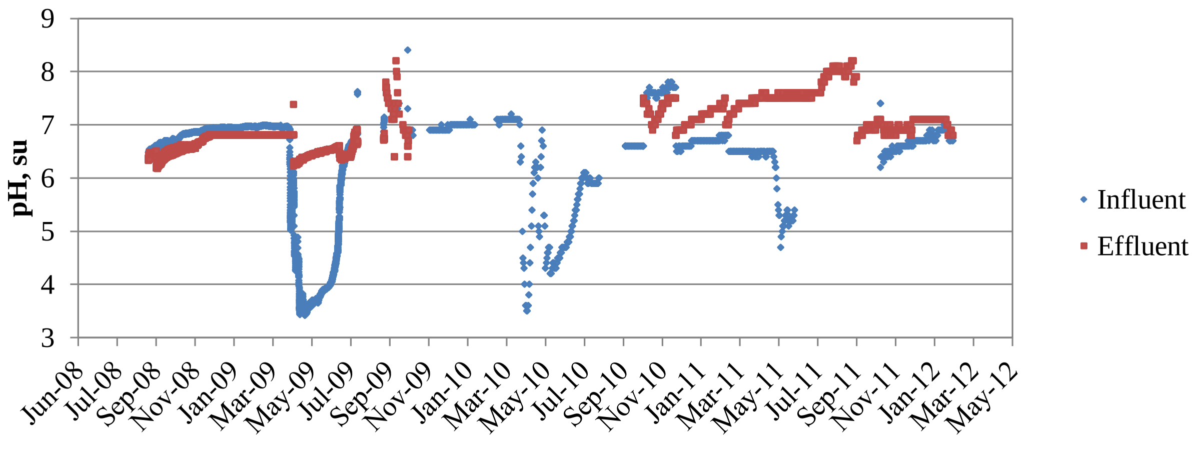

Figure 1. pH of BCR Influent and Effluent

In 2010, flow from the Adit peaked near 51 m^3/hr (225 gpm) in early June and was elevated between mid-May and through early July due to spring snowmelt runoff (Manning et al., 2011). The decrease in BCR influent pH coincides with this peak in flow and can be contributed to the flush of the water storage within the mine workings during this period, resulting in a flush of acidity due to lower winter flow rates from the adit. This acidity flush is buffered by limestone within the reactor. The BCR effluent pH increase during the warmer summer and early fall months was attributed to an increase in biological activity, resulting in an increased sulfur reduction and removal of H ions (see Fig. 9 and 10, to be shown later in the paper).

Table 1. Average pH of BCR Influent and Effluent

pH (su)	All Data	April - June
BCR Influent	6.2	3.9

BCR Effluent	6.7	-

Average effluent pH is somewhat above average influent throughout the year. This is expected and can be attributed to removal of hydrogen ions during anaerobic respiration and buffering by reactor limestone via the addition of alkalinity.

BCR influent and effluent temperature data available between September, 2008 and January 2012 are presented in Figure **1**. In general, the rate of biological treatment is positively correlated with temperature. Influent temperature ranged between 0.2 and 5.3 °C (32.4 and 41.5°F). Effluent temperature ranged between 0.8 and 7.8 °C (33.4 and 46.0°F) (Figure 2). As expected at a cold site, the temperature data revealed significant seasonal variation in both the influent and effluent BCR water temperature.

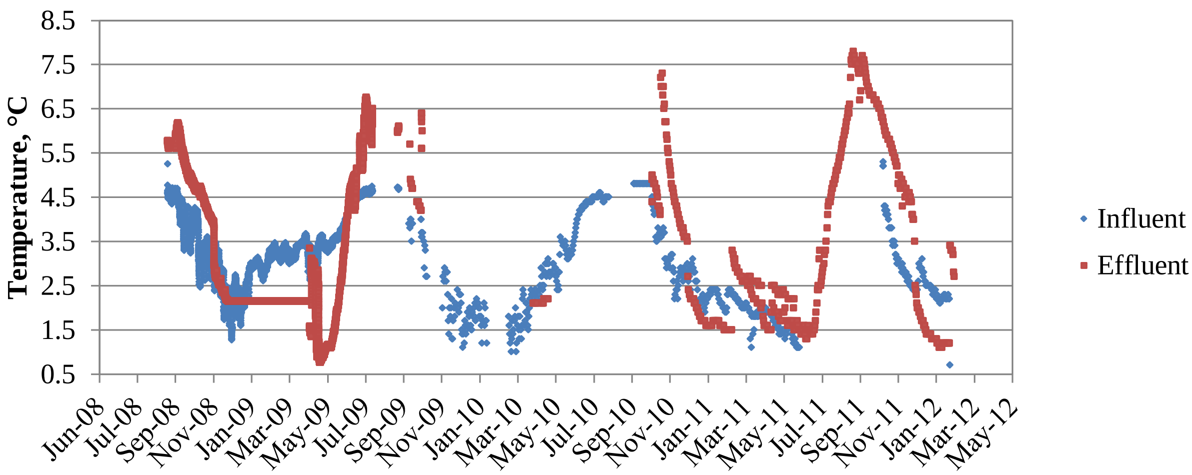

Figure 2. Temperature of BCR Influent and Effluent

Table 2. Average Temperature of BCR Influent and Effluent

Temperature °C (°F)	All Data	Summer [1/]	Winter [2/]
BCR Influent	3.4 (38.1)	4.0 (39.2)	2.9 (37.2)
BCR Effluent	3.2 (37.8)	4.0 (39.2)	2.6 (36.7)

NOTES: 1/ Summer data is May through October

2/ Winter data is November through April

BCR effluent ORP values ranged between -131 and -328 mV, and averaged -252 mV during the study period (Table 4). Influent ORP field measurements ranged between 8 to 220 mV and averaged 117 mV (Table 4). Data indicated that the BCR effluent was consistently anaerobic, a primary operational goal conducive to sulfate reduction.

BCR influent and effluent DO averaged 9.2 and 2.0 mg/L respectively and APC effluent DO averaged 6.1 mg/L (Table 4).

Table 3. Average ORP and DO of BCR Influent, BCR Effluent, and APC Effluent

	BCR Influent	**BCR Effluent**	**APC Effluent**
Average ORP (mV)	117	-252	17.7
No. Samples	11	12	12
Average DO (mg/L)	9.2	2.0	6.1
No. Samples	17	18	12

NOTES: BCR Influent and Effluent sampled 7/17/2009-10/20/2011
APC Effluent sampled 7/17/2009-9/22/2010

Metals Removal

Cadmium – BCR influent dissolved Cd concentrations ranged between 0.06 and 0.20 mg/L (Fig. 3). BCR effluent dissolved Cd concentrations ranged from below the lowest detection limit of 0.000125 mg/L to a maximum detected value of 0.00043 mg/L. The average percent removal for dissolved Cd in the BCR was 99.8 percent. BCR effluent Cd averaged 0.00019 mg/L, less than the chronic water quality standard of 0.00031 mg/L (Table 1). Dissolved Cd increased slightly in the APC to an average of 0.00063 mg/L likely due to the presence of Cd in soils used to plant the vegetation, the disturbance of sediment that had precipitated in the APC earlier in system operation, or influence from surrounding rock formations.

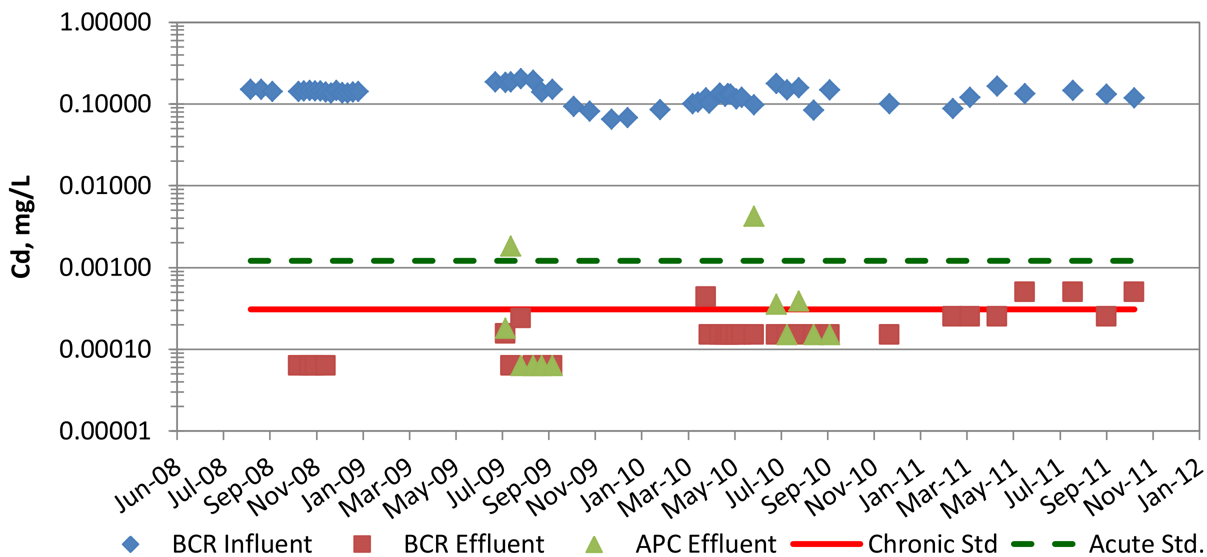

Figure 3. Dissolved cadmium in BCR Influent, BCR, Effluent, and APC Effluent

Copper – BCR influent dissolved Cu ranged between 0.003 and 0.99 mg/L (Fig. 4). BCR effluent dissolved Cu ranged between below the lowest detection limit of 0.0002 mg/L and a maximum detected value of 0.0094 mg/L. The average removal percentage for dissolved Cu in the BCR was 98.6 percent. BCR effluent dissolved Cu averaged 0.0014 mg/L and APC effluent averaged 0.0028 mg/L, below the chronic water quality standard of 0.0062 mg/L.

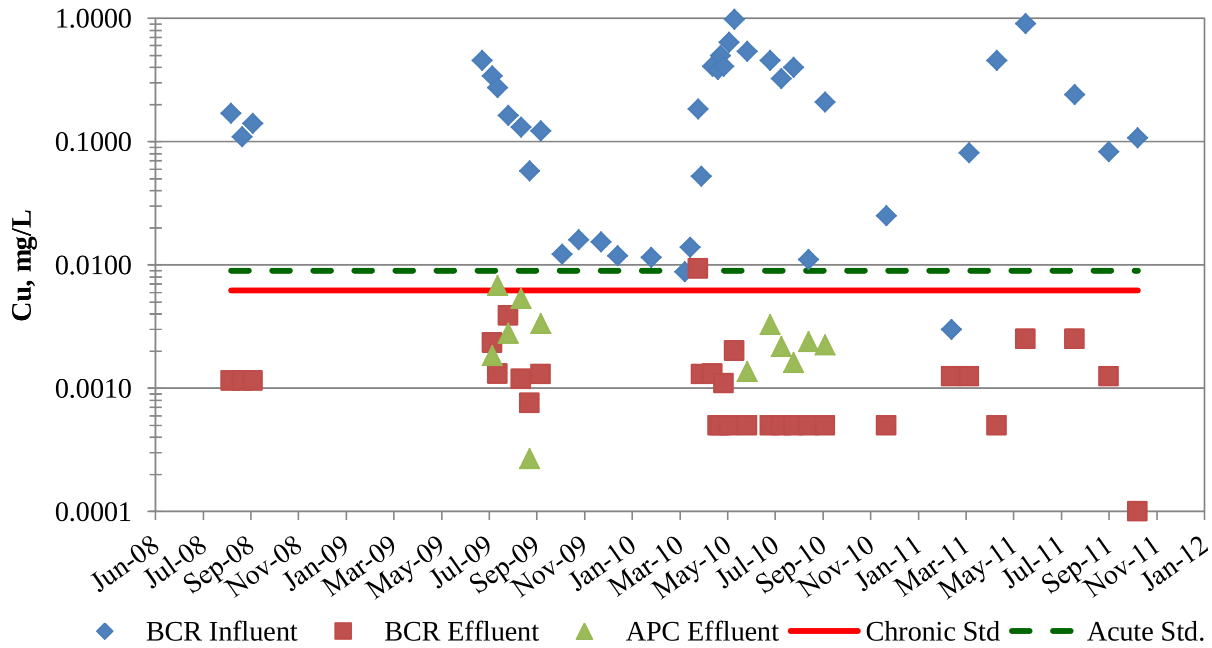

Figure 4. Dissolved copper in BCR Influent, BCR, Effluent, and APC Effluent

Iron – BCR influent total Fe ranged between 0.89 and 89.8 mg/L (Fig. 5). BCR effluent total Fe ranged between 0.02 and 11.7 mg/L. The average removal percentage for total Fe in the BCR was 95.0 percent. BCR effluent total Fe averaged 0.56 mg/L and APC effluent averaged 0.54 mg/L, below the chronic water quality standard of 1.0 mg/L. If Elk Creek is subject to a water supply water quality standard of 0.3 mg/L, the BCR effluent average would be slightly higher than the standard. It is expected that operation of the APC could be optimized in a full scale system to increase Fe removal and meet that discharge standard.

Pb – BCR influent dissolved Pb ranged between 0.0082 and 2.07 mg/L (Fig. 6). BCR effluent dissolved Pb ranged between 0.00025 mg/L and a maximum detected value of 0.0038 mg/L. The average removal percentage for dissolved Pb in the BCR was 98.4 percent. BCR effluent dissolved Pb averaged 0.00215 mg/L and APC effluent averaged 0.0038 mg/L, above the chronic water quality standard of 0.0016 mg/L. If data inputted as half of the MDL is removed from analysis, the average BCR effluent dissolved Pb is below the chronic standard at 0.0013 mg/L.

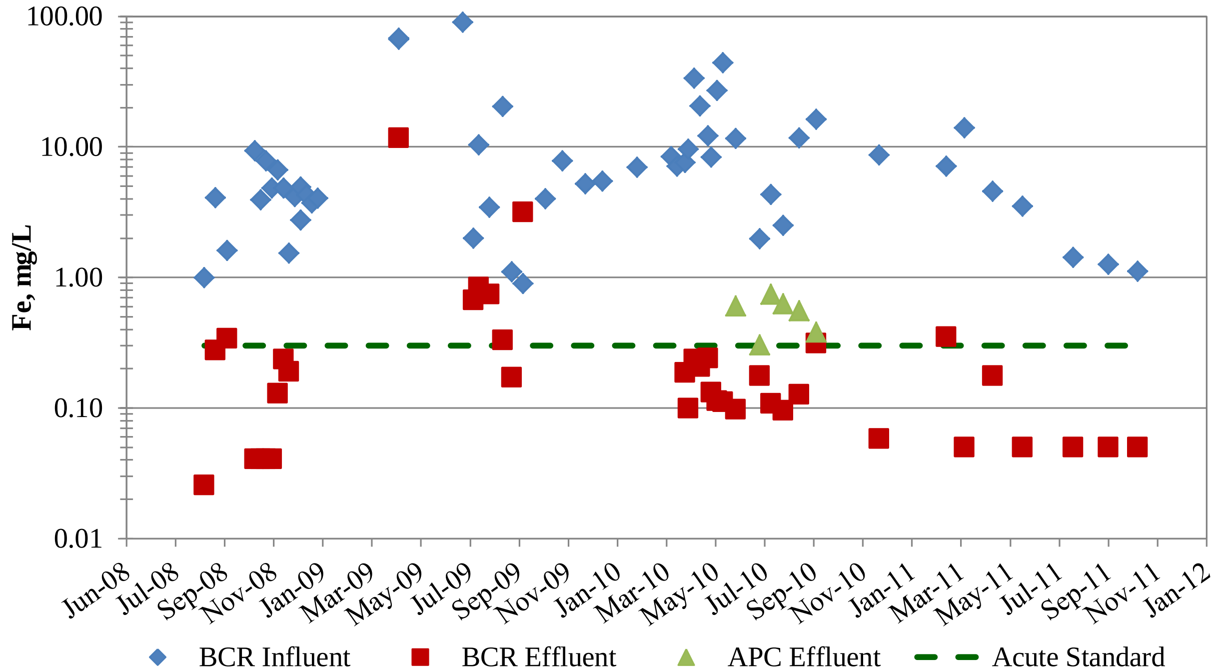

Figure 5. Total iron in BCR Influent, BCR Effluent, and APC Effluent

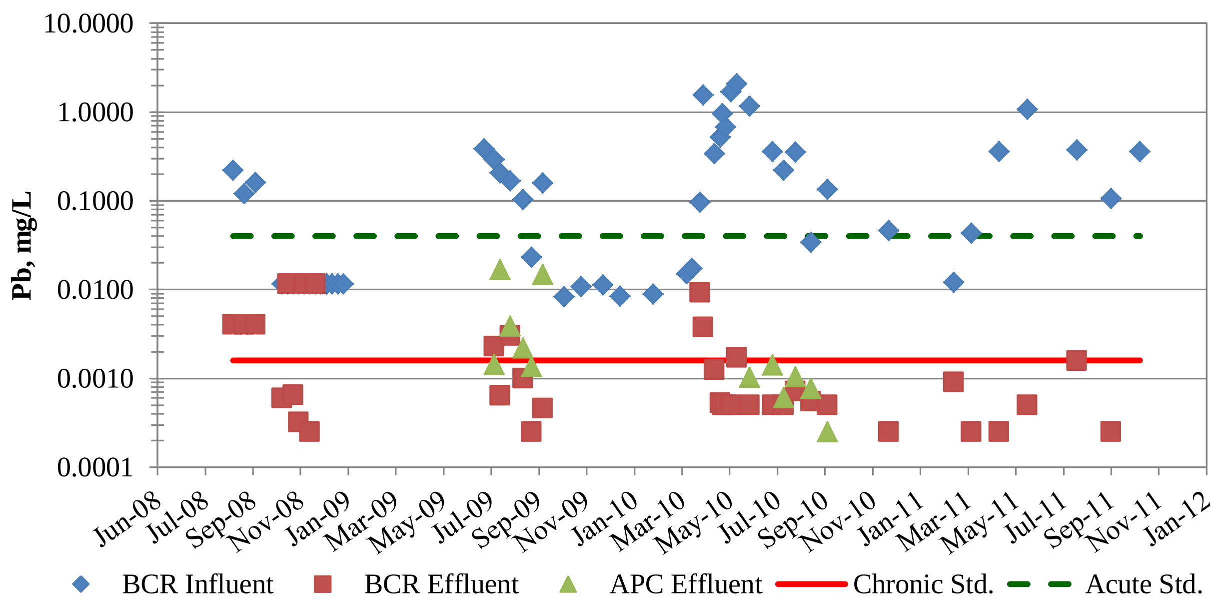

Figure 6. Dissolved Pb in BCR Influent, BCR, Effluent, and APC Effluent

<u>Manganese</u> – BCR influent dissolved Mn ranged between 5.4 and 13.2 mg/L (Fig. 7). BCR effluent dissolved Mn ranged between 3.6 mg/L and 12.7 mg/L. BCR effluent dissolved Mn was greater than influent concentrations during a two month period in the spring of 2010. BCRs are

not typically designed for the purpose of removing Mn, rather, Mn removal is expected to occur in an APC (once the APC is mature and fully vegetated (Robbins et al., 1999) in a full scale system. APC effluent averaged 4.1 mg/L, above the chronic water quality standard of 1.43 mg/L.

Removal of dissolved Mn from BCR influent after the APC averaged 42.2 percent in 2009 and 87.7 percent in 2010. The APC effluent was below the dissolved Mn chronic water quality standard during the summer of 2010 in four out of six grab samples.

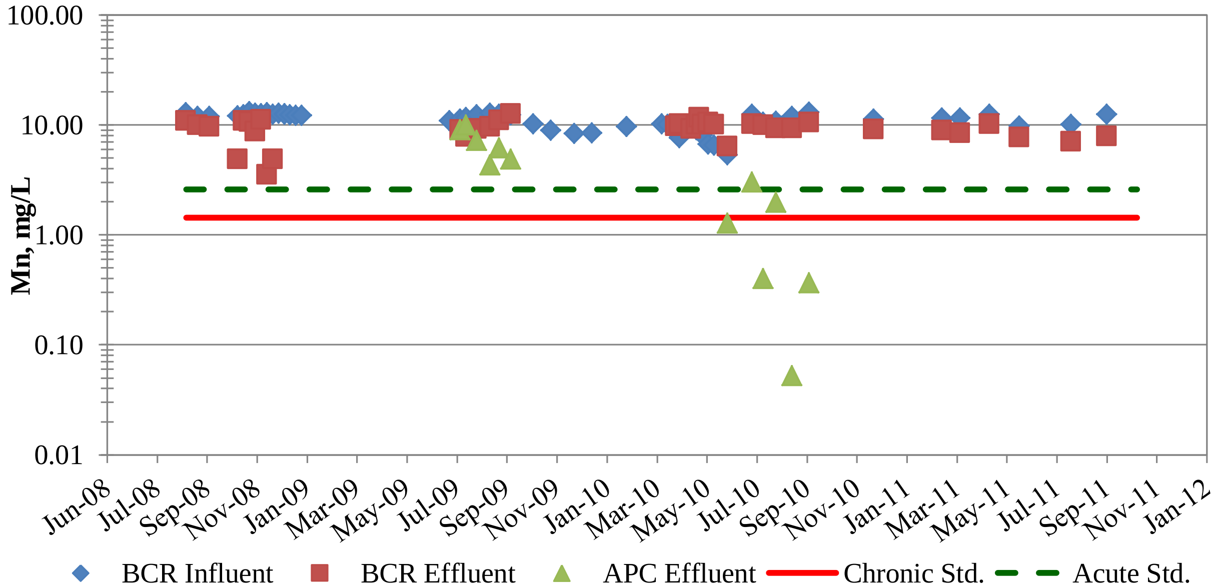

Figure 7. Dissolved manganese in BCR Influent, BCR, Effluent, and APC Effluent

<u>Zn</u> – Similar to dissolved Cd and Mn, BCR influent dissolved Zn concentrations were relatively stable during the study period. BCR influent ranged between 14.9 and 32.1 mg/L (Fig. 8). BCR effluent dissolved Zn ranged between a minimum detection limit of 0.001 mg/L and a maximum detected value of 0.45 mg/L. The average removal percentage for dissolved Zn in the BCR was 99.6 percent. BCR effluent dissolved Zn averaged 0.073 mg/L, below the chronic water quality standard of 0.086 mg/L. However, concentrations increased in APC effluent averaging 0.14 mg/L.

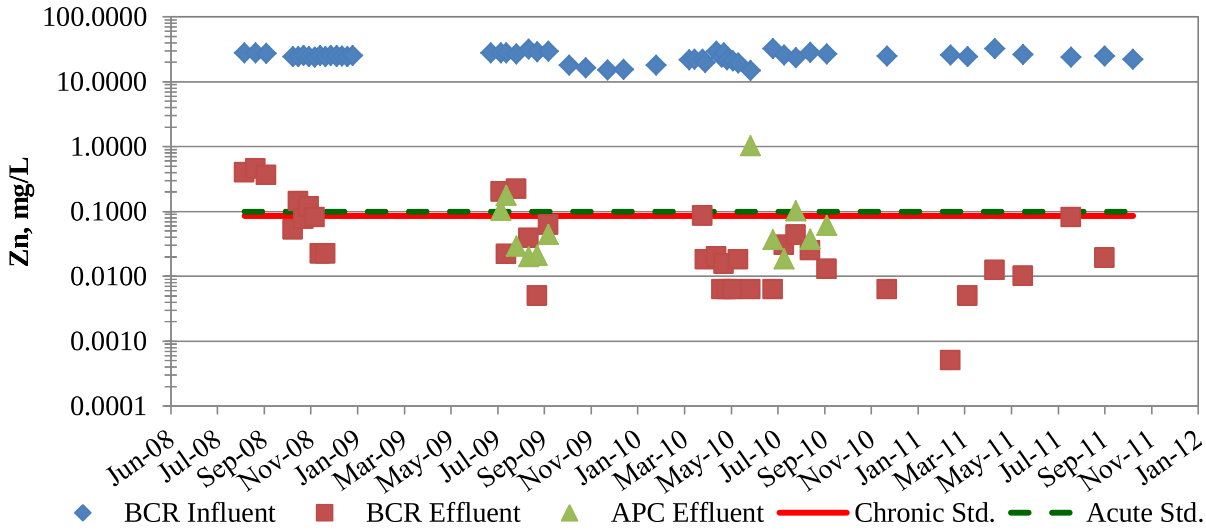

Figure 8. Dissolved Zn in BCR Influent, BCR, Effluent, and APC Effluent

Sulfate – BCR effluent sulfate concentrations were consistently less than influent sulfate concentrations (Table 5, Fig. 9) indicating that sulfate reduction was occurring in the BCR. Sulfide was not detected in the influent samples at concentrations above the laboratory detection limits as low as 0.01 mg/L as S. Effluent sulfide concentrations ranged between 2.4 to 39.0 mg/L. During 2008, the average effluent sulfide concentration was 21 mg/L as S. BCR effluent sulfide concentrations measured after May 2010 dropped averaging 5.8 mg/L as S. Influent sulfate and sulfide stayed generally the same after May 2010. However, effluent sulfate was reduced somewhat during this period indicating more efficient sulfate reduction by the BCR.

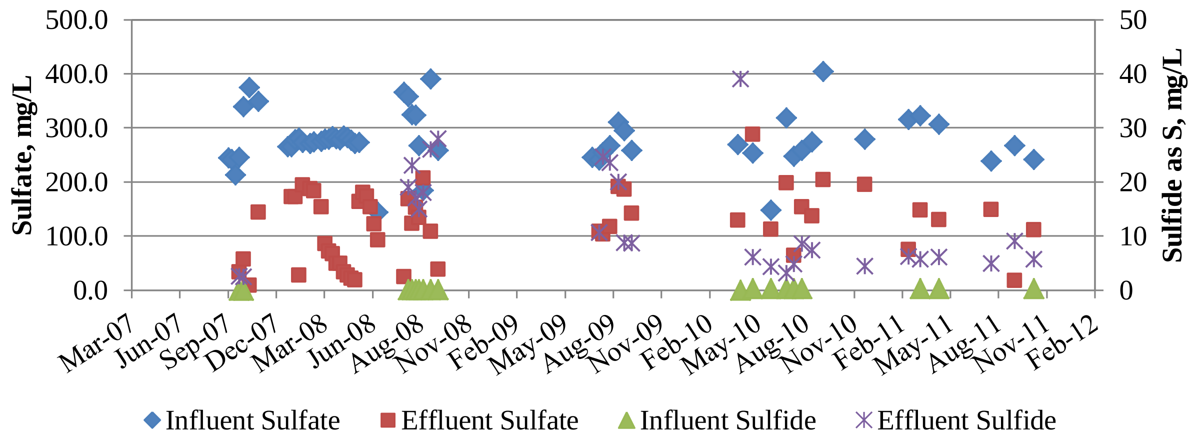

Figure 9. Sulfate and Sulfide in BCR Influent and BCR Effluent

Table 4. Average Sulfate and Sulfide in BCR Influent, BCR Effluent, and APC Effluent

	BCR Influent [1/]	BCR Effluent [1/]	Percent Removal BCR Influent to BCR Effluent	APC Effluent [2/]
Sulfate (mg/L)	281	119	57.2%	122
No. Samples	53	55	51	12
Sulfide (mg/L as S) [3/]	0.12	12.5	-	0.16
No. Samples	18	29	-	12

NOTES: 1/ BCR Influent and Effluent sampled 9/26/2007-10/20/2011
2/ APC Effluent sampled 7/30/2009-9/22/2011
3/ All influent sulfide below MDL of 0.02-0.5 mg/L

BOD – Influent BOD concentrations ranged from below the laboratory detection limit of 0.05 mg/L to 1.34 mg/L (Fig. 10). Effluent concentrations ranged from 0.05 to 143 mg/L. Major sources of BCR effluent BOD include sulfide and the organic substrate microbially degraded within the BCR cell. BCR effluent average BOD concentrations varied from 48.6 to 82.7 mg/L between the 2008 and 2011 study period (Table 6). BOD removal performance of the APC improved between 2009 and 2010 as average removal increased from 43.7 percent to 88.2 percent during this period producing an average APC effluent BOD concentration of 5.6 mg/L in 2010. BCR effluent BOD concentrations were expected to decrease as the cell aged, and 2010 effluent concentrations indicate the APC cell was reaching maturity.

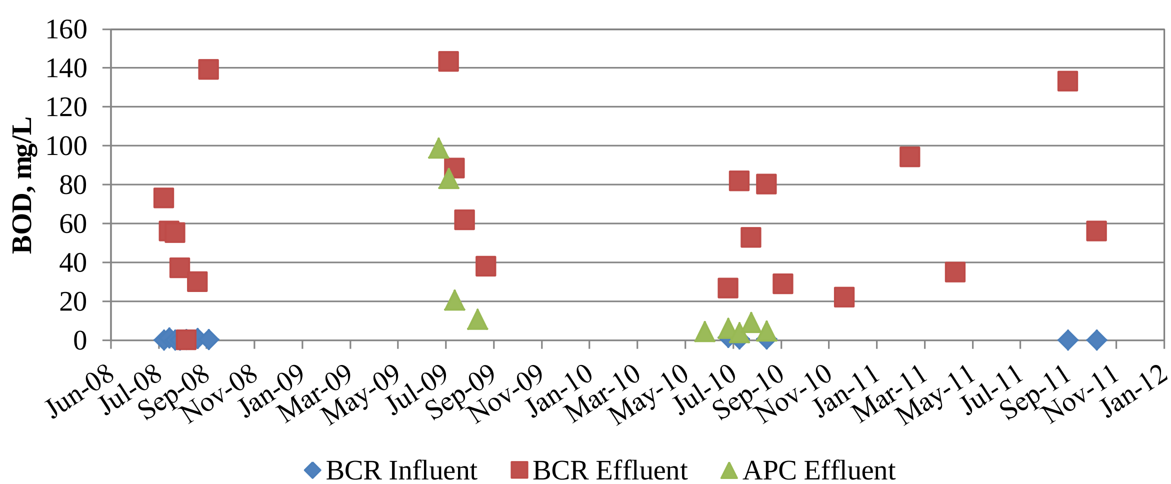

Figure 10. BOD in BCR Influent, BCR Effluent, and APC Effluent

Table 5. Average BOD in BCR Influent, BCR Effluent, and APC Effluent

Date	BCR Influent BOD (mg/L)	BCR Effluent BOD (mg/L)	APC Effluent BOD (mg/L)	Percent Removal BCR Effluent to APC Effluent
2008	0.41	55.7	-	-
2009	-	82.7	53.3	43.7%
2010	0.78	48.6	5.6	88.2%
2011	0.05	79.4	-	-
All Samples	0.44	66.7	26.8	68.4%
No. Samples	12	21	9	9

NOTES: Sampled 8/7/2008-10/20/2011

Nitrogen – The major source of nitrogen in BCR effluent is the organic substrate. This nitrogen is mobilized and partially consumed during biological treatment. Ammonia and combined nitrate and nitrite (nitrate/nitrite) analyses were performed on influent and effluent samples. Influent nitrate/nitrite ranged between 0.063 and 1.7 mg/L, with an average concentration of 0.91 mg/L (Table 7). BCR effluent concentrations ranged from below the minimum detection limit of 0.0125 to 3.5 mg/L, with an average of 0.79 mg/L.

Influent NH_3 concentrations were between 0.051 and 1.0 mg/L as NH_3-N. Effluent NH_3 concentrations ranged generally between 1.1 to 6.5 mg/L NH_3-N with a maximum hit of 20 mg/L as NH_3-N, with an average concentration of 7.2 mg/L as NH_3-N. Few NH_3 data was available prior to June 2009, however, this data averages an order of magnitude higher at 7.3 mg/L as NH_3-N suggesting maturation of the BCR cell.

Table 6. Average Nitrate-Nitrite and Ammonia in BCR Influent, BCR Effluent, and APC Effluent

	BCR Influent	BCR Effluent	APC Effluent	Percent Removal BCR Effluent to APC Effluent
Nitrate-Nitrite (mg/L)	0.91	0.79	0.031	-
No. Samples	6	14	9	-
NH_3-N (mg/L)	0.33	0.38	0.088	65.6%
No. Samples	6	22	9	9

NOTES: Sampled 7/30/2009-10/20/2011

Conclusion

Performance of two pilot-scale passive treatment technologies (BCR and APC) has been studied at the Standard Mine Superfund Site to test their ability to operate at a high-altitude, cold, remote site. The Pilot BCR has been in operation for more than four years. The APC was in operation for two summer seasons. Despite the cold climate and cold influent water temperature, the BCR is continually reducing average metals concentrations below acute stream standards for Cd, Cu, Fe, Pb, and Zn and below chronic stream standards for Cu, Pb, and Zn. The addition of an APC demonstrated effective reduction of BCR effluent BOD, nitrate-nitrite, NH_3, Mn, and sulfide.

The BCR has been shown effective for removal of metals below 5 µg/L including Cd, Cu, and Pb. Over the study period, BCR effluent concentrations of dissolved Cd, Cu, Pb (with samples below MDL removed), and Zn met chronic water quality standards on average. In addition BCR effluent total Fe met the non-water supply stream standard on average.

The BCR performance has further demonstrated that passive, biological treatment of MIW is feasible at cold, remote sites. Once the APC matured during the summer of 2010, APC effluent demonstrated Mn levels below acute and chronic stream water quality standards.

The BCR and APC technologies in full-scale application would operate passively, without energy input, and are capable of treating MIW at high altitude cold climates to concentrations below stream water quality standards without chemical addition. The typical design life of a full-scale BCR reactor would be 10 – 20 years. Due to efforts to reduce the flow coming from the adit as well as reduction in BCR substrate volume per unit of flow to the reactor due to data collected during pilot study it is likely a full-scale reactor would be substantially smaller per unit of flow volume treated. These technologies have great potential for application throughout the world for remote and non-remote sites to reduce capital, “O and M”, and overall treatment costs of conventional MIW treatment systems.

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