Pilot Bioreactors Commission and Operation at Minto Mine

2014 Preliminary Results

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EXECUTIVE SUMMARY

Four (4) pilot anaerobic bioreactors were commissioned at the Minto mine site, in the summer of 2014 by Amelie Janin, NSERC industrial Research Chair at Yukon College, and Capstone staff (Figure 1). Installation was completed on August 7th, 2014 and operation started on August 20th 2014. Bioreactor substrate composition varied amongst the bioreactors and included mixtures of creek sediments, low-grade or river gravel, wood chips or biochar (a coal made out of wood). Monitoring of the bioreactors stopped on September 23rd 2014 when the bioreactors were dismantled and stored for the winter.

Preliminary results obtained during the one month of operation after commissioning suggested that:

- Bioreactors were able to reduce selenium below Minto Mine's effluent discharge limits, as regulated under its water use licence (QZ96-006 Amendment #8);
- Copper concentrations were reduced by the bioreactors to a lesser extent than selenium concentrations;
- Two out of the four bioreactors affected the pH of the effluent so that the effluent did not meet the mine effluent discharge limits;
- Chipped wood seemed to release organic acid in the effluent (lower pH, higher Total Organic Content) in the first month of operation; and
- No exceedance of the mine effluent discharge limits were observed for NO_3, NO_2 and NH_3, although high PO4 (not regulated) was observed in the effluent of the biochar amended reactor.

Figure 1 Pilot-scale bioreactors at Minto Mine (Picture taken in August 2014)

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1. BACKGROUND

Minto Mine (Minto) is an open pit and underground copper mine that has been in commercial production since 2007. The mine is operated by Minto Explorations Ltd., a wholly-owned subsidiary of Capstone Mining Corp. Anaerobic bioreactors have been suggested as a semi-passive solution for long term water treatment of copper (Cu) and selenium (Se) at the Minto mine. Building on Capstone Mining Corp's partnership with Yukon College through the Industrial Research Chair program, this project focussed on the commissioning and short-term operation of four anaerobic bioreactors at the Minto site. The objectives of this project were to start testing and to assess the potential of passive anaerobic bioreactors on-site at a small-scale for Cu and Se treatment. More specifically, the treatment targets were based on Minto's existing water Use Licence QZ96-006 Amendment #8 (WUL) and were defined as 50 ug/L for Cu and 3 ug/L for Se.

1.1. ANAEROBIC BIOREACTORS FOR METAL REMOVAL

(Extracts from "Performances of lab-scale anaerobic bioreactors at low temperature using Yukon native microorganisms" by A. Janin and J. Harrington in the Proceedings submitted for the Mine Water Solution in Extreme Environments, April 2015, Vancouver, BC).

Water management in the mining industry has become a priority focus at all stages of the mine life cycle. Passive water treatment approaches are seen as a solution where long-term treatment of water impacted by old mine workings, waste rocks, tailings facility or other mine components are required after closure. Past research efforts led to the development of anaerobic bioreactors targeting the removal of metal contaminants from mine-impacted water using sulfate-reducing bacteria, SRB (USEPA 2014; MEND 1996) and numerous passive anaerobic bioreactors have been successfully implemented at large scale (Alexco 2012; Gusek et al 2000, Gusek et al 2011, Kuyucak et al 2006, Sobolewski 2010, Dar et al. 2007; Wilmoth 2002; Germain and Cyr 2003; Ettner 2007, Nordwick et al 2006, Bless et al 2008). Under anaerobic conditions, sulfate (SO_4^{2-}) is reduced into sulfide (HS^-/S^{2-}) by sulfate-reducing bacteria using electrons from organic matter (represented as ethanol in equation (Eq.) 1 adapted from Nagpal et al 2000). Sulfides then react with metals to precipitate as metal sulfide salts which are generally very insoluble (Eq. 2 where a metal cation is represented as Me^{2+}, Jong and Parry 2004; Neculita et al 2010).

Eq. 1 $$2\,C_2H_5OH(aq) + {SO_4}^{2-} \xrightarrow{microbially\ mediated} HS^- + 2CH_3COO^- + H^+ + H_2O$$

Eq. 2 $$H_2S + Me^{2+} \rightarrow MeS + 2H^+$$

1.2. ANAEROBIC BIOREACTORS IN YUKON'S COLD CLIMATE

As passive bioreactors are proposed for mine closure in Yukon Territory, common concerns include the performance of biological water treatment in cold climates as low temperatures typically affect microbial growth rate. In order to improve efficiencies, various authors have looked at the addition of organic carbon to the reactor to help microorganisms sustain activities at cold temperature. It has been shown that the addition of readily metabolizable carbon such as ethanol (as used in this study), methanol, lactate, or ethylene glycol, improves the performances of anaerobic reactors (Gould et al 2012, Alexco 2012, Sobolewski 2010, Tsukamoto 1999). In addition, a new approach for cold-climate bioreactors is to include a reactive substrate within the bioreactor that will provide opportunities for retention of the metal contaminants by chemical sorption (Janin and Harrington 2013, Conca and Wright 2006). Chemical sorption is less temperature-dependent than microbial processes, thus it might prove useful under transitions to cold temperatures where microbial activity may be at least temporarily slowed. Biochar, which is defined as a carbon-rich material produced by thermal decomposition of organic material under limited supply of oxygen (Lehmann and Joseph 2009) has been used in this study. Biochar is known to have adsorption capacity for transition metals (Regmi et al. 2012; Kolodynska et al. 2012; Tong et al. 2011; Chen et al. 2011; Li et al. 2013).

Although several anaerobic bioreactors have displayed high efficiencies in cold climates (Ness et al 2014), the performance of anaerobic bioreactors still need to be broadly proven and supported by comprehensive scientific knowledge before it can be classified as best practice in northern environments. This study falls within the Chair's broader objective to generate and gather scientific evidences of the potential of passive treatment systems in Yukon.

2. METHODOLOGY

2.1. EXPERIMENTAL DESIGN

The influent water selected for the project was sourced from a mine water collection sump (water quality station W37) at the mine. Water that is collected at W37 includes mine site impacted runoff water, runoff from the drystack tailings storage facility and some localized surface and groundwater. Water from the W37 sump was pumped weekly and stored into a "feed tank" (1,000 L) where ethanol was added to further support microbial growth in the bioreactors. The water was then pumped into the four individual drums using a peristaltic pump with a multi-head channel setup at 9 ml/min (Figure 2). Water was pumped into the bottom of the bioreactors and flowed in the upward direction. The theoretical hydraulic retention time was set at 15 days, meaning that ~100 L of effluent was being treated each week by every reactor. Although the hydraulic residence time was chosen based on common values in the literature, the retention time will have to be optimized in future studies. Liquid ethanol (99.5%) was added weekly into the feed tank at 1.5 mmol/L of effluent, which was based on the average sulfate concentration of 0.9691 mmol/L (or 82.5 mg/L) measured at W37 sump between June 4th and July 13th in 2014. The ethanol requirements were calculated by taking into account that each sulfate molecule requires 8 electrons to be reduced and ethanol provides 12. Twice the stoichiometric amount was applied in this study, i.e. 1.5 mmol ethanol/L of effluent ethanol molecules required to reduce one sulfate molecule).

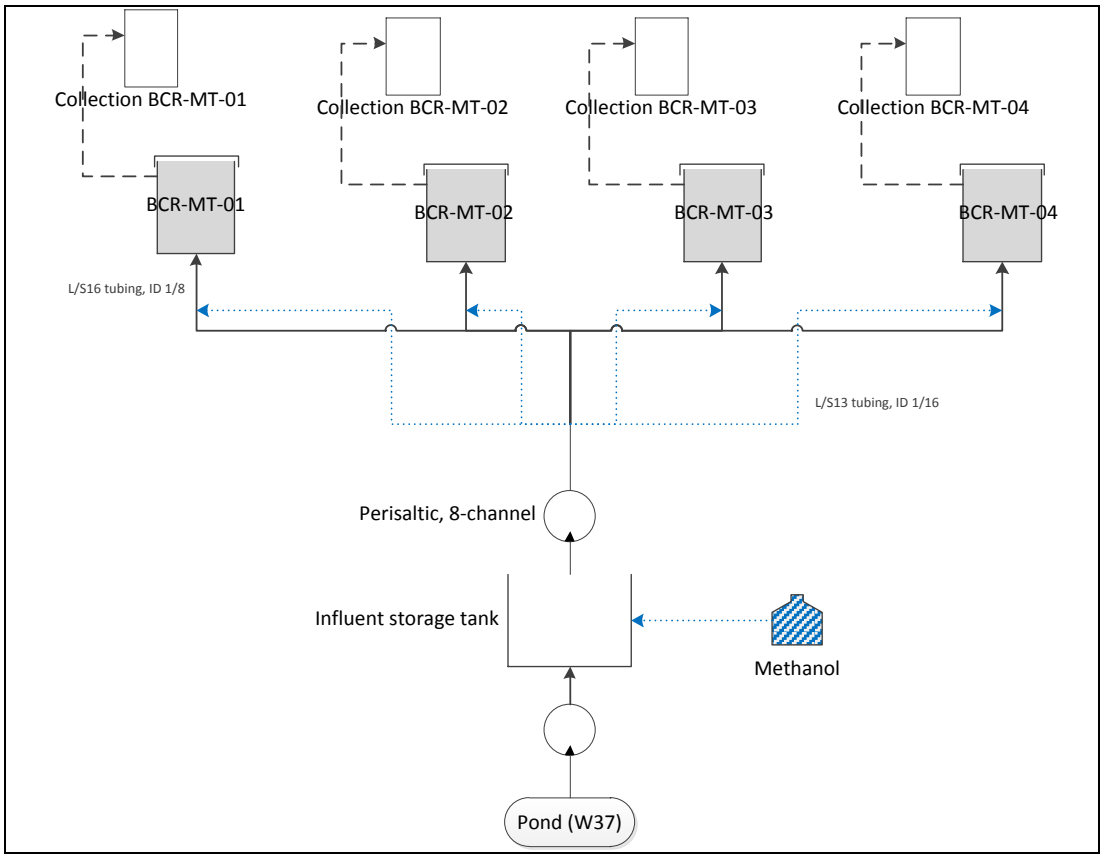

Figure 2 Bioreactors influent feed setup

2.2. BIOREACTORS COMPOSITION

The bioreactors were composed of fluvial gravel collected from a gravel borrow source on the Minto access road, crushed gravel from low grade run-of-mine waste rock, wood chips (50% (v/v) dry spruce and 50% (v/v) dry poplar) from Yukon College and biochar from Titan Clean Energy Projects based out of Saskatoon, SK. In addition, all the bioreactors contained “creek sediments” which provided microbial inoculum. This inoculum was collected on site, at W32. BCR-MT-01 was considered a “control” Bioreactor, filled with only fluvial gravel and creek sediment. BCR-MT-02 and 03 were similar, including 37% (v/v) wood chips, but using either river gravel or low-grade gravel. Finally, BCR-MT-04 was filled with low-grade gravel and wood biochar from Titan Clean Energy Projects (Figure 3). Composition of each bioreactor is provided in Table 1. The bioreactors mixtures were prepared independently and homogeneously mixed by hand in a wheelbarrow (Figure 4).

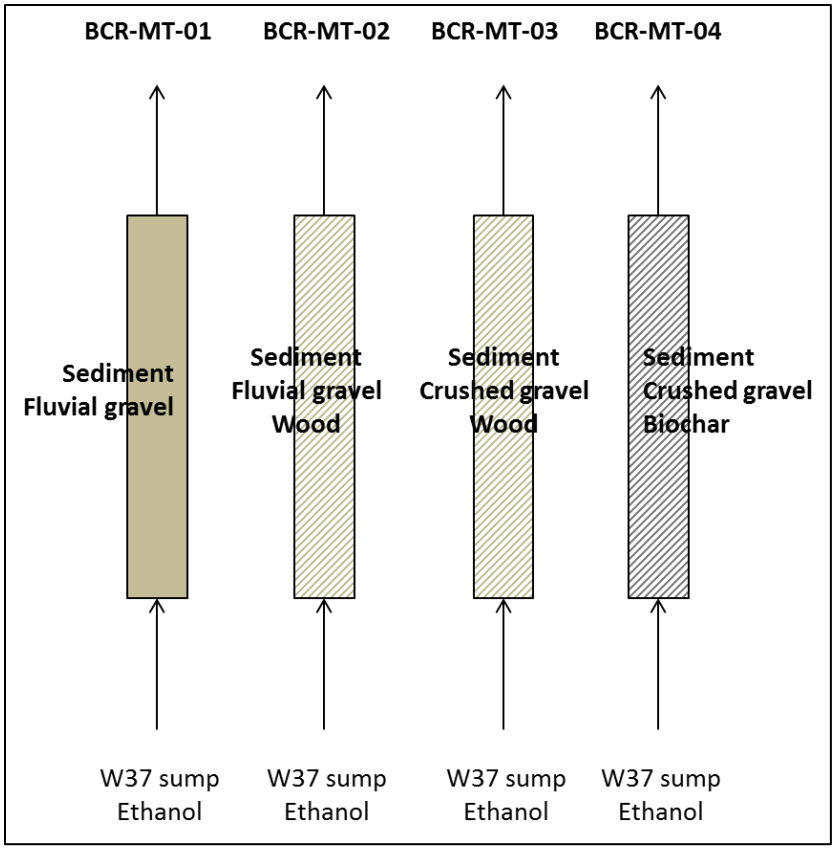

Figure 3 Substrate composition overview

Table 1 Composition of the pilot bioreactors setup at W37

	Measured density (kg/L)	Measured weight (kg)	Calculated volume (L)	Proportions by weight (%)	Proportions by volume (%)
BCR-MT-01					
Creek sediment	1.49	44.68	29.99	13.1%	14.2%
Fluvial gravel	1.64	296.2	180.6	86.9%	85.8%
Total		340.9	210.6		
BCR-MT-02					
Creek sediment	1.49	44.82	30.08	18.2%	14.3%
Fluvial gravel	1.64	165.0	100.6	66.9%	47.7%
Wood	0.46	36.80	80.00	14.9%	38.0%
Total		246.6	210.7		
BCR-MT-03					
Creek sediment	1.49	44.70	30.00	20.5%	14.0%
Crushed gravel	1.31	136.5	104.2	62.6%	48.6%
Wood	0.46	36.80	80.00	16.9%	37.3%
Total		218.0	214.2		
BCR-MT-04					
Creek sediment	1.49	44.70	30.00	17.9%	14.7%
Crushed gravel	1.31	175.1	133.7	70.3%	65.6%
Biochar	0.73	29.32	40.16	11.8%	19.7%
Total		249.1	203.8		

Figure 4 Bioreactors substrate mixture preparation

2.3. BIOREACTORS CONSTRUCTION

Bioreactors were built August 6-7th, 2014 by Amelie Janin and Sabrina Clarke (summer student at YRC) and by Rick Martin (Minto), and Aaron McGinty, (Selkirk First Nation summer student) at the Minto mine.

The figures that follow present photos of the procedure used to fill up the bioreactors; BCR-MT-01 is represented in this sequence. Figure 5 shows the inlet T-tubing with sand underneath, which distributed the influent at the bottom of the drum. A first layer of river gravel was added around the distribution tubing to limit the risk of clogging (Figure 6) then fibreglass was inserted above the distribution system to protect it (Figures 7 and 8). The pre-prepared mixture of substrate was then added in the drum up the outlet height (Figures 9 and 10).

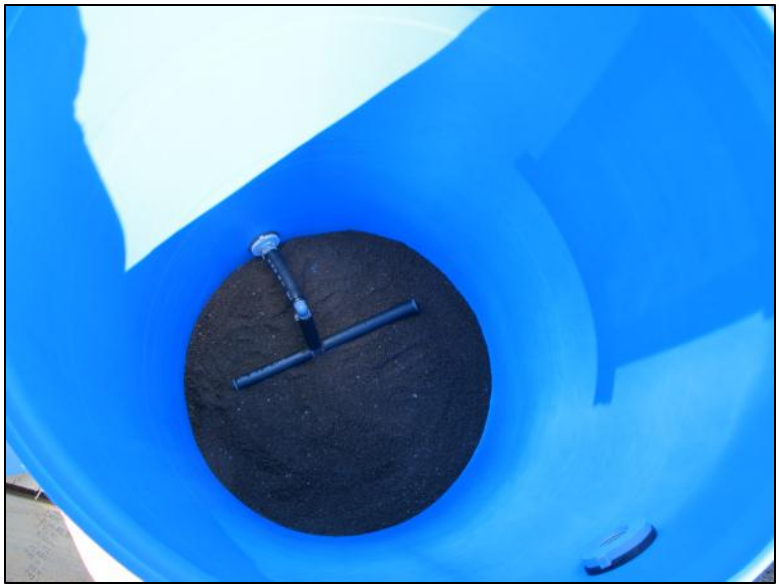

Figure 5 Distribution tubing at the bottom of a bioreactor

Figure 6 Addition of river gravel around the distribution tubing

Figure 7 Addition of fibre glass above the distribution tubing

Figure 8 Bottom of the bioreactor, before filling up with substrate

Figure 9 Beginning of the bioreactor filling with substrate

Figure 10 Filled bioreactor

In addition to the outlet, a monitoring port was installed inside the reactors, using a perforated PVC pipe (24'' long) installed in the top cap (Figure 11). This allowed for temperature monitoring inside the bioreactors using temperature probes.

Figure 11 Monitoring port

2.4. BIOREACTORS MONITORING

Influent and effluent of the reactors was sampled weekly by Minto staff along with pH, conductivity and temperature measurements. Samples were filtered in the field using 0.45um syringe filters for dissolved metals analysis. Samples that were collected on the first sampling event on September 4th were sent to Maxaam Analytics lab for analysis, while the subsequent samples collected on September 13th, 18th and 23rd were sent to Yukon College for total and dissolved copper and selenium (CuT, CuD, SeT, SeD), and Total Organic Carbon (TOC) analysis at the YRC lab. Samples for NH_3, NO_2, NO_3 and PO_4 were sent to and analyzed at Minto's on-site lab.

Water was pumped into the reactors from August 20th to September 23rd, for a total of 34 days, and then the bioreactors were decommissioned for the winter and stored on site (Table 2). Samples were collected at weekly intervals on September 4th, 13th, 18th and 23rd.

Table 2 Bioreactors operation timeline

	From	To	Comments
Bioreactor prep	31-Jul-14	1-Aug-14	
Initial fill-up	1-Aug-14	7-Aug-14	Pump at 80 rpm
Incubation	7-Aug-14	20-Aug-14	Pump stopped
Normal operation	20-Aug-14	23-Sep-14	Pump at 19.2 rpm
Winter storage	23-Sep-14		

2.5. SAMPLE ANALYSIS

Samples collected on September 13th, 18th and 23rd were analyzed for total and dissolved Cu and Se using a Perkin Elmer PinAAcle Graphite Furnace Atomic Absorption (GFAA) analyzer (Perkin Elmer, Waltham, MA). The Quantification Limits (QL) used in this work have been defined as the 10-σ over 10 blanks and were 0.6 ug Cu/L and 0.7 ug Se/L. Calibrations were conducted on a daily basis using single element standard (SCP Science, Baie D'Urfé, QC) and blanks and mixed verification standards (Perkin Elmer, Waltham, MA) were analyzed every 15 samples. Standards were made from commercial standards purchased from SCP Science.
Analyses of nutrients were conducted by Minto Exploration staff in the internal lab. Using internal standard operation procedures, the detections limits are 0.01 mg/L for NH_3, 0.1 mg/L for NO_3 and 0.01 mg/L for NO_2.

3. PRELIMINARY RESULTS

3.1. FIELD OBSERVATIONS

The four bioreactors, BCR-MT-01, 02, 03 and 04 were incubated from August 7th to 20th, then operated with flowing water for approximately a month. Field observations are presented in Table 3. Based on the volume measured every week, approximately 300 L of water was circulated through each of the 200 L bioreactors during the monitoring period corresponding to one and a half turn-over. Effluents were often described as having low clarity or high turbidity. This is expected in the early stage of bioreactor operation, when small particles from the substrate materials are initially flushed out in the first few turn-overs. This includes biochar particles, which colored the effluent from BCR-MT-04 black. In addition, the smell of sulfur was observed, which might indicate the presence of hydrogen sulfide. Hydrogen sulfide is also a product of sulfate reduction, which may indicate that sulfate-reducing bacteria successfully established.

Table 3 Field observations at sampling events

Date	Bioreactor	Effluent volume (L)	Clarity	Effluent temp-erature (°C)	Time of day	Comments
4-Sep-14	BCR-MT-01	120	<25 cm	4.7	2:25 PM	Light brown.
	BCR-MT-02	120	<25 cm	8.5	2:30 PM	Light brown.
	BCR-MT-03	120	<25 cm	6	2:35 PM	Light brown.
	BCR-MT-04	120	<25 cm	9	2:40 PM	Light brown.
13-Sep-14	BCR-MT-01	100	60 cm	7.9	9:45 AM	
	BCR-MT-02	102	12 cm	8.2	9:50 AM	Smelly
	BCR-MT-03	104	20 cm	7.9	9:55 AM	Smelly
	BCR-MT-04	100	20 cm	8.2	10:00 AM	
18-Sep-14	BCR-MT-01	55	55 to 30L	4.3	10:30 AM	Light sheen, no odor
	BCR-MT-02	55	55 to 50L	5.5	10:25 AM	Full sheen on surface, strong odor
	BCR-MT-03	55	55 to 40L	5.1	10:05 AM	Light sheen on surface, strong odor
	BCR-MT-04	55	55 to 50L	5.7	10:15 AM	Light sheen on surface, less odor than MT03
23-Sep-14	BCR-MT-01	37	37 to 0L	2.7	2:20 PM	Full visibility
	BCR-MT-02	37	37 to 0L	7.1	2:10 PM	Odor of sulphur
	BCR-MT-03	37	37 to 33L	3.8	2:00 PM	Sheen on surface, frothy on surface, no odor, required lot of filters
	BCR-MT-04	37	37 to 20L	7	1:45 PM	Water color black, no odor

Note: Clarity was observed in the field either as the depth (in cm) until which someone could not see through or as the volume graduations (in L) one could read from the surface. Observations can be compared from one bioreactor to another but not from one week to another.

3.2. FLOW – HYDRAULICS

Flow rates are presented in Table 4 and are calculated using equation 3 and based on the observed volume on each of the outlet tanks. It should be noted that the volume markings on the outlet tank were made manually and may not be accurate and in addition, the outlet tanks had a 120 L capacity. Therefore, the tanks had likely outflowed before the first sampling event on September 4th, and the volume reading of 120 L was likely an underestimate.

Eq. 3 $$Effluent\ flow\ rate = \frac{Volume\ of\ collected\ effluent}{Duration\ of\ effluent\ collection}$$

Importantly, flow measurements indicate that the bioreactors received equivalent flow rates and were operated in the same conditions, which allows for easier comparison between the four bioreactors. The target flow rate was 9 ml/min and the measured rates were 7.8, 7.6 and 8.6 ml/min on average.

Table 4 Bioreactors flow characteristics from Aug-20-2014 to Sept 21-2014

Date	Bioreactor	Volume outlet (L)	Duration (days)	Flow (mL/min)	Comments
20-Aug-14	N/A	N/A	0	N/A	
4-Sep-14	BCR-MT-01	120	15	5.6	Likely overflowed, underestimated
4-Sep-14	BCR-MT-02	120	15	5.6	Likely overflowed, underestimated
4-Sep-14	BCR-MT-03	120	15	5.6	Likely overflowed, underestimated
4-Sep-14	BCR-MT-04	120	15	5.6	Likely overflowed, underestimated
13-Sep-14	BCR-MT-01	100	24	7.7	
13-Sep-14	BCR-MT-02	102	24	7.9	
13-Sep-14	BCR-MT-03	104	24	8.0	
13-Sep-14	BCR-MT-04	100	24	7.7	
18-Sep-14	BCR-MT-01	55	29	7.6	
18-Sep-14	BCR-MT-02	55	29	7.6	
18-Sep-14	BCR-MT-03	55	29	7.6	
18-Sep-14	BCR-MT-04	55	29	7.6	
21-Sep-14	BCR-MT-01	37	32	8.6	
21-Sep-14	BCR-MT-02	37	32	8.6	
21-Sep-14	BCR-MT-03	37	32	8.6	
21-Sep-14	BCR-MT-04	37	32	8.6	

3.3. INFLUENT WATER QUALITY

Water was pumped from the W37 pond into a 1000 L feed tank. Although water chemistry was not expected to change significantly, samples for total metals and dissolved metals were collected at each sampling event. On September 4th, these samples were sent to a Maxxam Analytics lab (Maxxam) and were analyzed for a full suite of dissolved and total metals. Data are presented in Table 5. Effluent discharge limits for metals set by Minto's WUL are included for comparison.

Selenium is the only metal which exceeded the prescribed limit in the WUL. Total and dissolved selenium were measured at 6.9 ug/L and 6.4 ug/L respectively on September 4th. In the following sampling events, total selenium was measured at 5.3, 5.4 and 5.8 ug/L on September 13th, 18th and 23rd, respectively. Dissolved selenium represented the majority of the total selenium (Data presented in Appendix 1).

Copper did not exceed the WUL limit of 50 ug/L. Total Cu was measured at 48.9 ug/L on Sept 4th by Maxxam and at 42.5, 43.7 and 43.2 ug/L by the YRC lab in the following sampling events (Appendix 1). Unlike selenium, dissolved copper was significantly lower than total copper, indicating that, on average, 27% of Cu was in the particulate form (>0.45 um particle size).

Table 5 Total and Dissolved metals measured in the "BCR-Tank" influent samples collected on Sept 4th 2014

Parameter	Unit	Total	Dissolved	WUL Discharge limit (Total)
Hardness (CaCO3)	mg/L	477	464	
Sulfate	mg/L	N/A	128	
Organic Carbon (C)	mg/L	43	N/A	
Aluminum (Al)	µg/L	23.9	11.8	
Antimony (Sb)	µg/L	<0.50	<0.50	
Arsenic (As)	µg/L	0.38	0.4	
Barium (Ba)	µg/L	126	134	
Beryllium (Be)	µg/L	<0.10	<0.10	
Bismuth (Bi)	µg/L	<1.0	<1.0	
Boron (B)	µg/L	<50	<50	
Cadmium (Cd)	µg/L	0.041	0.044	0.15
Calcium (Ca)	mg/L	129	127	
Chromium (Cr)	µg/L	<1.0	<1.0	
Cobalt (Co)	µg/L	<0.50	<0.50	
Copper (Cu)	µg/L	48.9	46.9	50
Iron (Fe)	µg/L	119	50	
Lead (Pb)	µg/L	<0.20	<0.20	
Lithium (Li)	µg/L	<5.0	<5.0	
Magnesium (Mg)	mg/L	37.8	35.6	
Manganese (Mn)	µg/L	214	204	
Mercury (Hg)	µg/L	<0.010	<0.010	
Molybdenum (Mo)	µg/L	8.2	8.1	
Nickel (Ni)	µg/L	1	1.1	
Phosphorus (P)	µg/L	26	23	
Potassium (K)	mg/L	4.81	4.89	

Table 5 (Continued) Total and Dissolved metals measured in the "BCR-Tank" influent samples collected on Sept 4th 2014

Parameter	Unit	Total	Dissolved	WUL Discharge limit (Total)
Selenium (Se)	µg/L	6.89	6.4	3
Silicon (Si)	µg/L	8040	7970	
Silver (Ag)	µg/L	<0.020	<0.020	
Sodium (Na)	mg/L	22.2	21.7	
Strontium (Sr)	µg/L	1310	1340	
Sulphur (S)	mg/L	50	51.9	
Thallium (Tl)	µg/L	<0.050	<0.050	
Tin (Sn)	µg/L	<5.0	<5.0	
Titanium (Ti)	µg/L	<5.0	<5.0	
Uranium (U)	µg/L	3.16	3.14	
Vanadium (V)	µg/L	<5.0	<5.0	
Zinc (Zn)	µg/L	57.8	55.8	150
Zirconium (Zr)	µg/L	<0.50	<0.50	

3.4. SELENIUM REMOVAL

Selenium was one of two targeted metals for treatment and the objective was to reduce it to less than the WUL effluent discharge limit of 3 ug/L. Figure 12 presents the selenium concentration before and after the treatment by each of the four bioreactors. Reduction of the selenium concentration was observed in the four reactors in the first month of operation, with values below discharge limits (3 ug/L). It should be noted that results were often below the detection limit of 0.7 ug/L when analyzed at the YRC lab. The reduction of selenium follows a similar trend to results observed from bench-scale bioreactors at Yukon College treating either a synthetic mine drainage (Janin 2014a) or dewatering water from the Wolverine mine (Janin 2014b). Prior to decommissioning, on Sept 23rd, selenium removal efficiencies of >86% were measured.

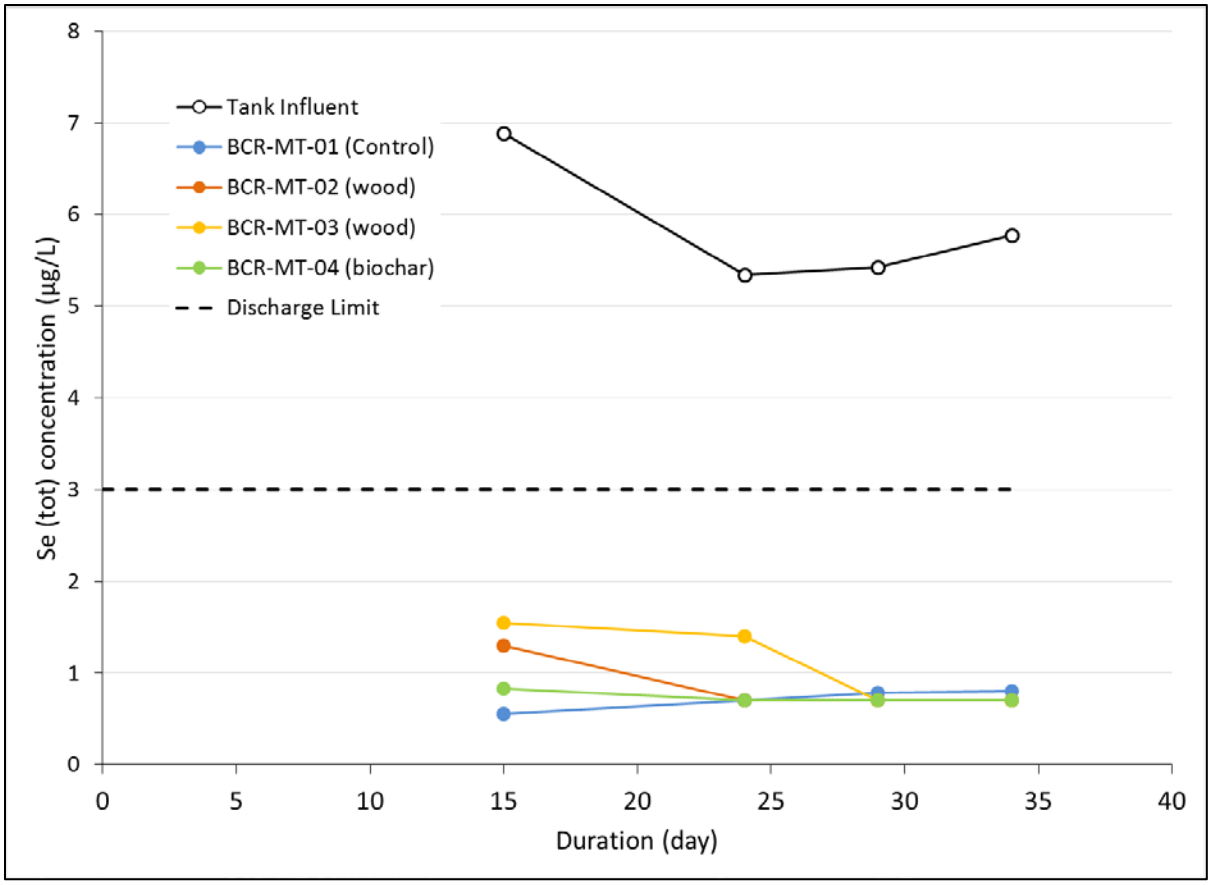

Figure 12 Selenium concentration in influent and effluent of the four bioreactors (BCR-MT-01 to -04) between August 20th to September 23rd 2014 (Discharge Limit of 0.003 mg/L)

3.5. COPPER REMOVAL

Copper was the second targeted metal for treatment by the bioreactors. Figure 13 presents the total copper concentrations before and after treatment. The first sample collected on September 4th in the outlet on the biochar amended reactor (BCR-MT-04) was measured at 128 ug/L by Maxxam, above the WUL effluent discharge limit of 50 ug/L. It is unclear if this high copper concentration was a result of the flush of the bioreactor after incubation or if this is an outlier. The following measurement taken on September 13th, when the 200 L bioreactor was still being flushed (220L passed through on Sept 13th), was much lower, at 23.9 ug/L, therefore it seems more likely that the 128 ug/L measured is an outlier. Cu concentrations in the influent were close to the discharge limit of 50 ug/L, and a decrease in Cu concentration was observed after treatment by all four bioreactors in one month of operation. On September 23rd, at 30 days, Cu removal efficiencies were measured at 57% for the control reactor, BCR-MT-01; 43 and

48% respectively for the wood amended reactors, BCR-MT-02 and BCR-MT-03; and 13% for the biochar amended reactor, BCR-MT-04. These results are promising and are expected to improve when the community of microorganisms better establish in warmer summer temperatures in future operating periods. In a previous study of lab-scale bioreactors conducted at YRC, Cu concentrations below 10 ug/L were consistently observed at 20 degrees Celsius with peaks up to 35-65 ug/L when the temperature was decreased to 6 or 3 degrees Celsius. However, after about 30 days in cold temperatures, SRB acclimatized and Cu concentrations returned to less than or near the 10 ug/L level (Janin and Harrington 2014). Further monitoring of the bioreactors in the spring-summer-fall season will provide interesting information related to copper removal potential by the anaerobic bioreactors.

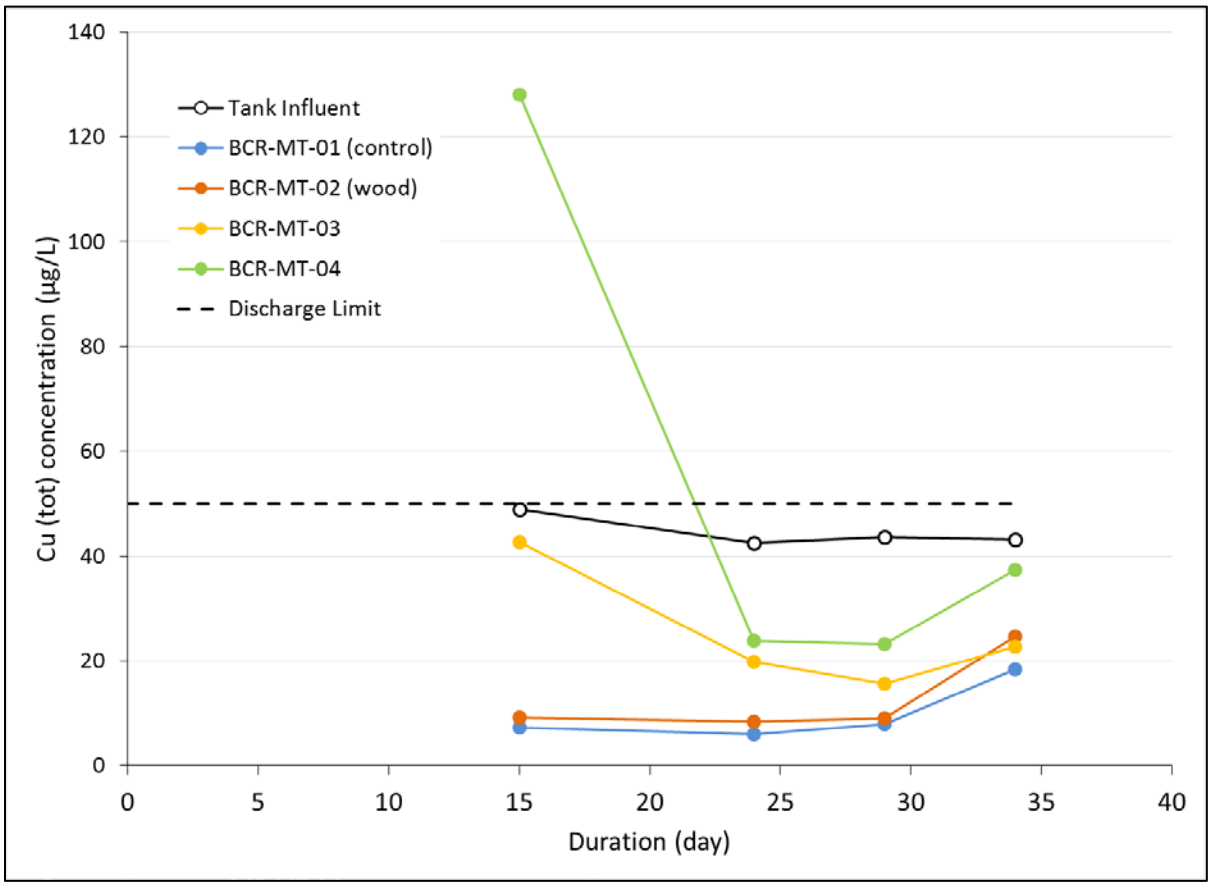

Figure 13 Copper concentrations in influent and effluent of the four bioreactors (BCR-MT-01 to -04) between August 20th to September 23rd 2014 (Discharge Limit of 0.050 mg/L)

3.6. PH

pH was measured in the field for the influent and effluent of each bioreactor. Influent pH was measured between 8.0 and 9.1 while the WUL discharge limits are 6.5 to 9. The reactors BCR-MT-01 (control) and BCR-MT-04 (biochar) did not affect the pH and exceedance of the higher limit was exceeded on Sept 18th and Sept 23rd for these two bioreactors.

The wood amended bioreactors, BCR-MT-02 and BCR-MT-03 lowered the pH by 2 to 3 pH units. Although the wood chips used to fill in the bioreactors were washed several times with tap water, the acidification is likely due to the release of organic acids by the wood chips. In this case, exceedance of the lower range of the pH limit was observed.

As many effluent samples were outside the range of pH allowed for discharge in the environment, pH should be closely monitored during the next operating period. Reduced impact to pH may potentially be observed as the microorganism community aged within the reactors in subsequent operating periods. The undesired effect on pH provides further support for the use of anaerobic bioreactors as part of a treatment series, where the effluent would flow out of the anaerobic component into an aerobic one (such as wetlands, rock filters, cascades or other).

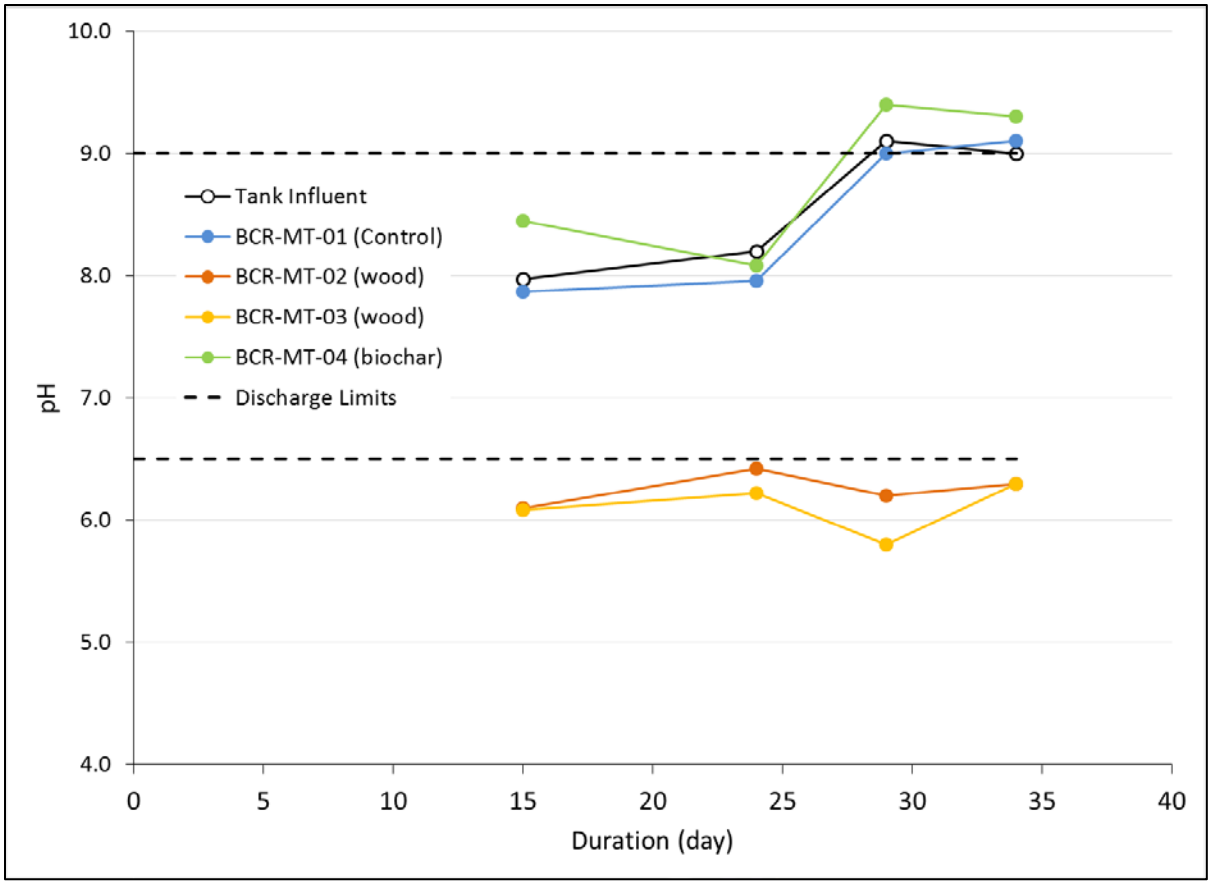

Figure 14 pH in influent and effluent of the four bioreactors (BCR-MT-01 to -04) between August 20th to September 23rd 2014 (Discharge Limit Range: 6.5 to 9)

3.7. NUTRIENTS

Ammonium, nitrate and nitrite are also regulated by Minto's WUL for discharge of effluent with limits of 0.89 mg NH_3/L, 7.65 mg NO_3/L and 0.15 mg NO_2/L. These limits were not exceeded in the bioreactors influent, nor were they exceeded in the effluents from each of the bioreactors (Table 6 to 10).

Observed trends include the reduction of nitrate concentrations by the anaerobic bioreactors, with 3.1 to 4.3 mg NO_3/L in the influent and <0.2 mg NO_3/L in the effluent in the last sampling event on September 23rd. Nitrate, an oxidized form of nitrite, was likely consumed by the reducing conditions which have established in the reactors.

Phosphate (PO_4) is not regulated and was not measured in the influent. PO_4 concentrations were significantly higher in the effluent from the biochar amended reactor, BCR-MT-04 than from the other three reactors; this is not unexpected as the willow and bone meal biochar used in this study was known to contain elevated phosphate and that the black color of the effluent reported by the field observations may indicate that some of the biochar had been flushed out of the reactor. PO_4 release is not desired and this should be monitored during future operating periods.

Table 6 NH_3, NO_3, NO_2, PO_4 and conductivity data in "BCR-MT Tank" influent.

Sampling date	Duration (day)	NH_3 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)	PO_4 (mg/L)	Cond. uS/cm
4-Sep-14	15	0.04	3.4	<0.01/0.02		498.1
13-Sep-14	24	<0.01	N/A	N/A	N/A	594
18-Sep-14	29	<0.01	3.1	<0.01		934
23-Sep-14	34	0.09	4.3	0.04		940

Table 7 NH_3, NO_3, NO_2, PO_4 and conductivity data from "BCRMT-01" bioreactor.

Sampling date	Duration (day)	NH_3 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)	PO_4 (mg/L)	Cond. uS/cm
4-Sep-14	15	0.03	0.3	<0.01	0.13	492.5
13-Sep-14	24	<0.01	N/A	N/A	N/A	565
18-Sep-14	29	<0.01	<0.1	<0.01	1.14	916
23-Sep-14	34	<0.01	<0.1	<0.01	0.68	825

Table 8 **NH_3, NO_3, NO_2, PO_4 and conductivity data from "BCRMT-02" bioreactor.**

Sampling date	Duration (day)	NH_3 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)	PO_4 (mg/L)	Cond. uS/cm
4-Sep-14	15	0.11	5	<0.01	0.18	1285
13-Sep-14	24	<0.01	N/A	N/A	N/A	842
18-Sep-14	29	0.04	0.2	<0.01	0.79	1326
23-Sep-14	34	0.11	<0.1	<0.01	<0.1	1148

Table 9 **NH_3, NO_3, NO_2, PO_4 and conductivity data from "BCRMT-03" bioreactor.**

Sampling date	Duration (day)	NH_3 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)	PO_4 (mg/L)	Cond. uS/cm
4-Sep-14	15	0.11	3.4	<0.01	0.11	1053
13-Sep-14	24	<0.01	N/A	N/A	N/A	841
18-Sep-14	29	0.02	<0.1	<0.01	0.83	1318
23-Sep-14	34	0.03	<0.1	<0.01	1.1	1126

Table 10 **NH_3, NO_3, NO_2, PO_4 and conductivity data from "BCRMT-04" bioreactor.**

Sampling date	Duration (day)	NH_3 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)	PO_4 (mg/L)	Cond. uS/cm
4-Sep-14	15	0.21	0.5	0.02/0.03	2.4	1461
13-Sep-14	24	<0.01	N/A	N/A	N/A	881
18-Sep-14	29	0.5	<0.1	0.03	18.4	1309
23-Sep-14	34	0.19	0.2	0.1	25.4	1133

3.8. TOTAL ORGANIC CARBON

Total Organic Carbon (TOC) was measured and is represented graphically in Figure 15 (numerical data is provided in Appendix 1). The data clearly indicates that the wood amended bioreactors were leaching organic carbon, with 200 to 700 mg/L TOC measured. This correlates well with the observed decrease in pH and supports the hypothesis that wood chips are releasing organic acids. Generally, TOC leaching seemed to decrease over the 30 days. TOC could potentially continue to decrease in future operating periods, however is still expected to remain higher than in the effluent from the non-wood amended bioreactors. Elevated TOC could be of less importance if the anaerobic bioreactors were one component of a treatment series which included an aerobic component.

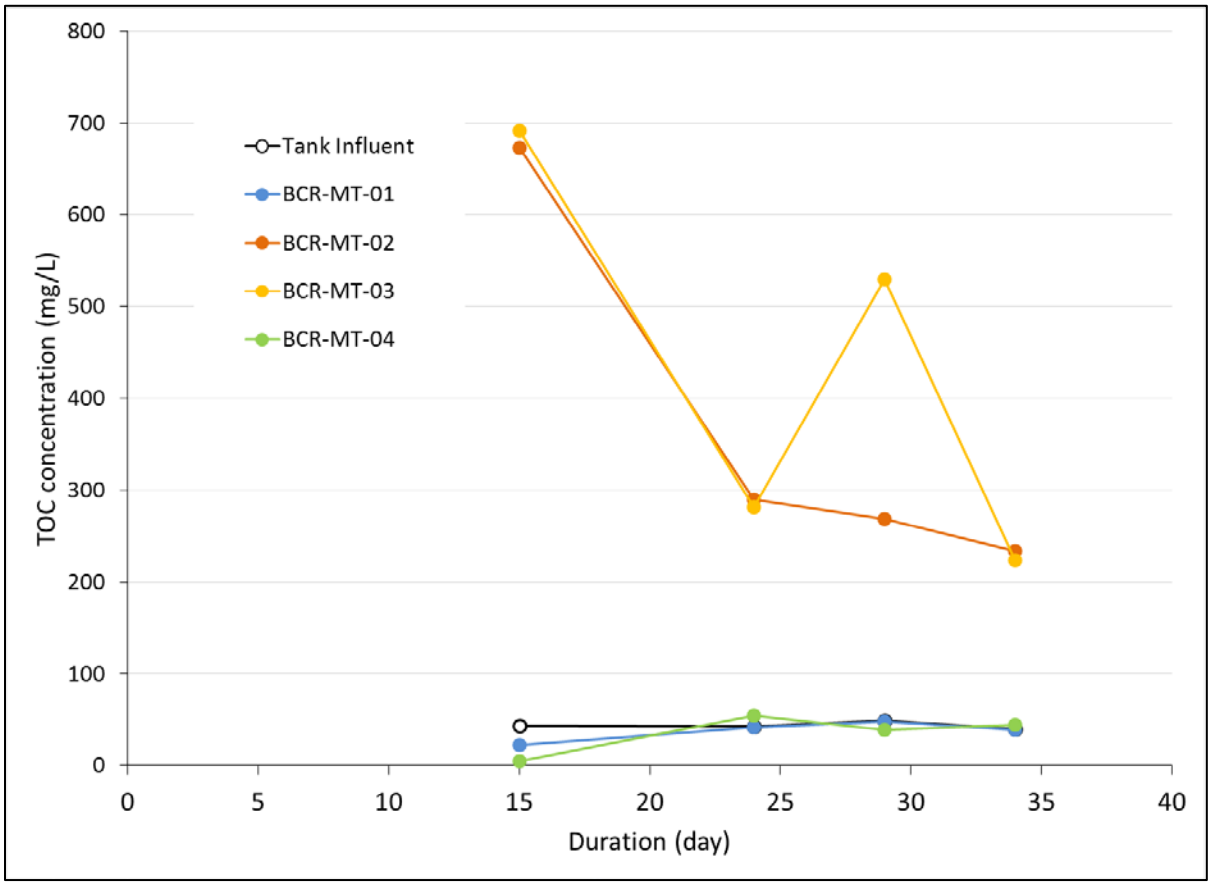

Figure 15 Total Organic Carbon in influent and effluent from the four bioreactors (BCR-MT-01 to -04) between August 20th to September 23rd 2014

3.9. BIOREACTOR PRELIMINARY COMPARISON

Preliminary results acquired over 30 days after incubation, at relatively cold fall temperatures might not allow for solid conclusions on reactor performance, however results allow for discussion on potential trends and future performance as well as experimental adjustments.

The first observation is that anaerobic conditions seemed to have established in all four reactors, as indicated by the reduction in nitrate, selenium and copper, meaning that a microbial community has established in the late summer-fall when temperatures were decreasing.

Selenium removal proved to be highly efficient in all four reactors during one month of operation. Cu removal was also efficient, but is expected to improve in subsequent operating periods. Dissolved Cu was significantly lower than total Cu in most cases and a large proportion of particulate Cu was observed in the outlet from the bioreactors (between 35 and 85% on average). Metals in particle form are considered easier to remove from water than dissolved metals as they can simply be treated by filtration such as in a sand filter. Metal particulates are also usually less likely to bio-accumulate.

The use of woodchips in anaerobic bioreactors has frequently been used to provide organic matter to the microbial community and to encourage long term reducing conditions (Neculita et al 2010; Germain and Cyr 2003, Wilmoth 2002; Bless et al 2008; etc.). In this study, bioreactors amended with wood chips (BCR-MT-02 and BCR-MT-03) performed well in terms of Cu and Se removal with concentrations below WUL discharge limits. However, it is suspected that the wood chips released organic acids, which decreased the pH below the allowable pH range for discharge. Hence, integration of wood chips in bioreactors might create issues in the short term, but further study will provide insight as to whether wood chips will support long-term reliability of the bioreactors.

Integration of wood biochar in bioreactors was tested by Amelie Janin in a previous study and led to promising results with improved performances in cold climate which was attributed to biochar's sorption capacity (Janin and Harrington 2013; Janin and Harrington 2014). This study was initially designed with wood biochar (same granulometry as wood chips) however delays in shipment of wood char to Yukon College forced us to change plans and to use willow and bone meal biochar. The granulometry of this biochar is more powder-like than wood chips, and its potassium and phosphate content is high. This change may have affected the results, explaining the release of suspended particulates (low visibility, black color of the effluent) and phosphate. Successful Se removal and relatively good removal of Cu was achieved with the pH unchanged.

At this stage, it is not possible to conclude on the potential impact of the biochar in the bioreactors, but this should be further investigated during the next operating period.

4. CONCLUSION AND RECOMMENDATIONS

The objectives of this project, which included setting up pilot bioreactors on-site and the preliminary assessment of the potential for copper and selenium treatment by anaerobic bioreactors, at the Minto mine were fulfilled. However, several recommendations for future study were suggested:

- Continued operation of the pilot bioreactors in summer 2015;
- Clarification of the Standard Operation Procedure (SOP) with the list of field parameters to be measured (water and bioreactor temperature, conductivity, water and bioreactor pH, bioreactor ORP, water level, visibility) and the list of samples to be collected (Total and dissolved Cu and Se, TOC, NO_3, NO_2, PO_4, SO_4 and TSS);
- Monthly composite sampling to be sent to a commercial lab and to Yukon College (split sample) for total and dissolved metals for laboratory comparison;
- Measurements of temperature, pH and ORP inside the bioreactors using the monitoring port (Figure 11); and
- Changing the outlet tote to use a calibrated water tank where volume measurements are more accurate.

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APPENDIX 1 – MONITORING DATA

Table a) Measured water quality parameters in bioreactor influent (BCR-Tank)

Sampling date	Duration (day)	pH	Se-T (ug/L)	Se-D (ug/L)	Cu-T (ug/L)	Cu-D (ug/L)	TOC (mg/L)	NH_3 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)	PO_4 (mg/L)	Cond. uS/cm	Temp. °C
4-Sep-14	15	7.97	6.89	6.4	48.9	16.9	43	0.04	3.4	<0.01/0.02		498.1	5.1
13-Sep-14	24	8.2	5.3	6.1	42.5	42.3	42.58	<0.01	N/A	N/A	N/A	594	8.1
18-Sep-14	29	9.1	5.4	5.7	43.7	34.2	49.12	<0.01	3.1	<0.01		934	6.8
23-Sep-14	34	9	5.8	4.9	43.2	33.4	39.77	0.09	4.3	0.04		940	7.8

Table b) Measured water quality parameters in effluent from bioreactor BCR-MT-01

Sampling date	Duration (day)	pH	Se-T (ug/L)	Se-D (ug/L)	Cu-T (ug/L)	Cu-D (ug/L)	TOC (mg/L)	NH_3 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)	PO_4 (mg/L)	Cond. uS/cm	Temp. °C
4-Sep-14	15	7.87	0.55	0.56	7.22	7.74	22.4	0.03	0.3	<0.01	0.13	492.5	4.7
13-Sep-14	24	8.0	<0.7	1.11	6.05	4.67	41.97	<0.01	N/A	N/A	N/A	565	7.9
18-Sep-14	29	9.0	0.78	0.72	7.90	4.79	48.09	<0.01	<0.1	<0.01	1.14	916	4.3
23-Sep-14	34	9.1	0.80	<0.7	18.45	4.05	38.66	<0.01	<0.1	<0.01	0.68	825	2.7

Table c) Measured water quality parameters in effluent from bioreactor BCR-MT-02

Sampling date	Duration (day)	pH	Se-T (ug/L)	Se-D (ug/L)	Cu-T (ug/L)	Cu-D (ug/L)	TOC (mg/L)	NH_3 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)	PO_4 (mg/L)	Cond. uS/cm	Temp. °C
4-Sep-14	15	6.1	1.3	0.94	9.27	1.76	673	0.11	5	<0.01	0.18	1285	8.5
13-Sep-14	24	6.4	<0.7	<0.7	8.41	2.12	289.76	<0.01	N/A	N/A	N/A	842	8.2
18-Sep-14	29	6.2	<0.7	<0.7	9.09	0.82	268.94	0.04	0.2	<0.01	0.79	1326	5.5
23-Sep-14	34	6.3	<0.7	<0.7	24.70	1.62	233.38	0.11	<0.1	<0.01	<0.1	1148	7.1

Table d) Measured water quality parameters in effluent from bioreactor BCR-MT-03

Sampling date	Duration (day)	pH	Se-T (ug/L)	Se-D (ug/L)	Cu-T (ug/L)	Cu-D (ug/L)	TOC (mg/L)	NH_3 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)	PO_4 (mg/L)	Cond. uS/cm	Temp. °C
4-Sep-14	15	6.08	1.55	1.01	42.7	11	691	0.11	3.4	<0.01	0.11	1053	6
13-Sep-14	24	6.2	1.4	<0.7	19.85	4.62	281.19	<0.01	N/A	N/A	N/A	841	7.9
18-Sep-14	29	5.8	<0.7	<0.7	15.66	1.75	529.59	0.02	<0.1	<0.01	0.83	1318	5.1
23-Sep-14	34	6.3	<0.7	<0.7	22.64	1.24	223.89	0.03	<0.1	<0.01	1.1	1126	3.8

Table e) Measured water quality parameters in effluent from bioreactor BCR-MT-04

Sampling date	Duration (day)	pH	Se-T (ug/L)	Se-D (ug/L)	Cu-T (ug/L)	Cu-D (ug/L)	TOC (mg/L)	NH_3 (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)	PO_4 (mg/L)	Cond. uS/cm	Temp. °C
4-Sep-14	15	8.45	0.83	0.94	128	90.4	<5	0.21	0.5	0.02/0.03	2.4	1461	9
13-Sep-14	24	8.1	<0.7	<0.7	23.89	22.01	54.06	<0.01	N/A	N/A	N/A	881	8.2
18-Sep-14	29	9.4	<0.7	<0.7	23.21	55.94	38.53	0.5	<0.1	0.03	18.4	1309	5.7
23-Sep-14	34	9.3	<0.7	<0.7	37.35	21.78	43.87	0.19	0.2	0.1	25.4	1133	7