Arsenic, Antimony and Selenium Removal
from Mine Water by Anaerobic Bioreactors at Laboratory Scale

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EXECUTIVE SUMMARY

Passive water treatment technologies are increasingly being considered for mine site closure in the Yukon and efforts are currently underway to test, compare and contrast passive treatment technologies with conventional technologies. This study aims to provide additional information about the effectiveness of passive treatment technologies for mine water treatment in cold climates. To test the hypothesis that bioreactors can effectively treat mine-impacted water at low temperatures, four bench-scale, continuous flow bioreactors were assessed for their potential to remove As, Se and Sb from mine effluent. The experiment was conducted as part of the work undertaken by the Yukon Mine Research Consortium; an industrial research body which conducts research on remediation and reclamation of Yukon mine sites to further enhance environmental stewardship in the territory.

More specifically, the objectives of this study were to 1) assess the efficiency of removal of As, Sb and Se, three metalloids, from a highly contaminated synthetic drainage in cold conditions as well as from actual leachate collected at the Eagle Gold site, 2) evaluate the impact of using wood chips as part of the composition of the bioreactor and 3) assess the impact of freeze/thaw on the bioreactors' performance. Four bioreactors in columns were built in the Yukon Research Centre lab and operated for 5 months to treat both synthetic influent and leachate collected at Eagle Gold during summer 2014. Operation was phased as follows: Phase 1) the bioreactors were operated in an environment with uncontrolled temperature in the fall until the bioreactors froze solid; Phase 2) the bioreactors were thawed in a fridge at a stable temperature of 6°C; Phase 3) the bioreactors were operated and monitored at 6°C.

Results show that all bioreactors significantly decreased As, Sb and Se concentrations even when the influent concentration was high (mimicking the "worst case scenario"). However, even though As reduction was efficient, it was not quite enough to bring the concentrations below the discharge limit threshold of 0.15 ug/L. Using drainage produced on site, 38%, 90% and 95% of As, Se and Sb was removed. Using highly contaminated drainage with an average of 5 mg/L As, 0.5 mg/L Se and 0.03 mg/L Sb, the removal efficiencies were recorded at >85% for Sb, >87% for As, and >99% for Se. This study is one of very few studies reported in the literature which demonstrates antimony removal from water by an anaerobic bioreactor.

In addition to the metal removal performance assessment, the results indicate that addition of 20% spruce chips in the composition of the bioreactor substrate improved As removal in the first phase of the study and helped mitigate the impact of freeze/thaw on As, Sb and Se

removal. It is thought that the solid substrate provides both an adequate support to either protect and/or favor biofilm growth as well as to provide a surface onto which As can adsorb. Overall, this study demonstrates the potential application of passive anaerobic bioreactors as a technique to remove As, Sb and Se from mine water effluent. It also suggests that the addition of wood chips to bioreactors may be a suitable amendment in bioreactors built in the Yukon where cold temperatures and freeze/thaw conditions occur.

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1. BACKGROUND

The use of passive anaerobic bioreactors for treatment of mine drainage is quickly emerging as an efficient, long-term, and cost-effective alternative to active water treatment for mine closure (USEPA 2014; INAP 2010; 2001; MEND 1996), and they are now being proposed in the closure planning of operating and proposed Quartz mining projects in the Yukon. Passive anaerobic bioreactors function based on the ability of Sulfate-Reducing Bacteria (SRB) to produce sulfide, which in turn reacts with dissolved metals to produce an insoluble sulfide mineral. Several examples of bioreactors operating in cold climates have been reported and compiled in a review released recently (Ness et al 2014) but the capacity of passive anaerobic bioreactors to perform in cold climates is not yet a proven technology. In collaboration with the Yukon Mine Research Consortium, Yukon College and the NSERC Industrial Research Chair in Mine Life Cycle have joined efforts to address this issue and to conduct research on the impact of cold climate on anaerobic bioreactors. In 2013/2014, four bench-scale bioreactors treated As, Cd, Cu, Se and Zn contaminated water for over one year at room temperature, then at 6°C, and finally at 3°C. Several publications were issued form this research, including Janin and Harrington (2013), Janin and Harrington (2014) and Janin (2014). Building on the findings from the previous experiment, the research presented in this report is focused specifically on metalloids: As, Sb and Se. The objectives of this study were to 1) assess the efficiency of removal of the three metalloids by anaerobic bioreactors in cold conditions, 2) evaluate the impact of using wood chips as part of the composition of the bioreactor and 3) assess the impact of freeze/thaw on the bioreactors performance.

The addition of wood chips was found to be beneficial for As removal in the previous lab-scale bioreactors studied at Yukon College (Janin 2014) therefore this study was also designed to evaluate the impact of using wood chips in bioreactors. At the Wood-Cadillac mine site, in northwestern Quebec, a 50m x 57m x 1m thick bioreactor made exclusively of wood products (barks and wood chips) was commissioned in 1999. Its operation between May 2000 and October 2002 was summarized by Germain and Cyr (2003) and Tasse et al (2003). In general, this reactor performed well, with reported As concentrations in the effluent generally maintained under 57 ug/L; however a decrease in the performance of the bioreactor after a few years was observed and attributed to the degradation of the wood products and subsequent compaction of the filling. Hence, while the wood products were capable of promoting sulfate reduction and As removal, the bioreactor comprised of 100% of wood as the substrate was less effective. Thus, this study was designed to use only 20% by volume (v/v) wood chips made from local black spruce trees.

2. MATERIAL AND METHODS

2.1. BIOREACTOR COMPOSITION

Four bioreactors were setup during the fall of 2014 in the YRC. Each bioreactor was comprised of a black ABS plastic cylinder 53 cm tall and 12 cm in diameter, filled with variable reactor substrate. Three of the bioreactors (C9-C11) were filled with 20% by volume (or “20% v/v”) inoculum, 20% (v/v) weathered spruce chips, 20% (v/v) sand (Canadian Tire play sand) and 40% (v/v) washed pea gravel (GE Cement plant, Whitehorse). The last bioreactor, C12, was used as a control (no wood) with 20% (v/v) inoculum, 40% (v/v) sand and 40% (v/v) gravel. C9 was fed using influent collected on site while C10, C11 and C12 were fed with synthetic influent produced in the lab. C10 and C11 were fed with the same influent and are thus duplicates (Figure 1).

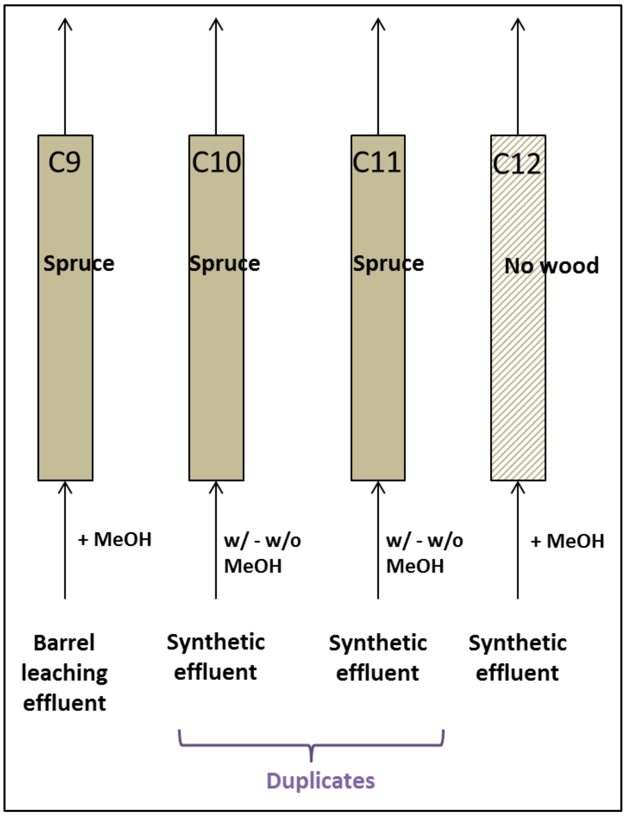

Figure 1. Experimental setup for bioreactors C9 to C12

2.2. MICROBIAL INOCULUM COLLECTION

The bioreactors required an initial inoculum of microbes to populate the reactors with sulfate reducers and hence initiate the sulfate reducing process. To best represent site conditions, sediments were collected on July 21, 2014 from two locations within the Eagle Creek drainage at the Eagle Gold project site (Figure 2, Figure 3 and Table 1). Sediment from the two locations was combined in equal parts, thoroughly mixed and used as the inoculum for the bioreactors.

Table 1. Site description where inoculum was collected

	Site Description	GPS Waypoint	Notes
Site 1	Snow patch above slow moving water, ~500 m up the road from site 2, collected just upstream of culvert	21-Jul-2014 08 W 0459700 UTM 7101160 ELEV. 881 m	Smelled strongly of organic material, ferric iron suspended in small ponds around area (Figure 4), neutral pH
Site 2	In sediment pond site	21-Jul-2014 08 W 0459089 UTM 7100954 ELEV. 838 m	No obvious scent of sulfur but dark organic material. Faster moving water.

Figure 2. Site 1 inoculum collection picture

Figure 3. Site 2 inoculum collection iron puddle

Figure 4. Site 1, showing iron hydroxide precipitate

2.3. CONDITIONS OF OPERATION

The bioreactors were initially filled up with barrel leachate (C9) or synthetic effluent (C10 to C12) from the bottom up using a Masterflex peristaltic pump at 10 rpm. The pump was stopped once the four reactors were saturated and effluent started to flow out of the reactors. On August 29th, 2014, the reactors were then allowed to sit with no influent feed to facilitate incubation of the microorganisms contained in the creek sediment. Upward flow was restarted on September 29th, 2014 with the pump setup at 4.7 rpm with Masterflex L/S13 tubing and with a calculated flow rate of 0.25 mL/min. The reactors were monitored over a five month period until early March 2015. Over the first two months (Phase 1), the bioreactors were operated in an insulated but not heated building called “cold storage”. The temperature in the building fluctuated, ultimately causing the temperature of the effluent to slowly decrease until the end of November. The columns were then allowed to freeze solid and the pump was stopped (Phase 2). On Dec 18th 2014, the columns were brought inside to thaw and set up in a refrigerator where the temperature was set at 6°C ± 0.4°C for a one month period (Phase 2 continued, Figure 5). In January 2015 (Phase 3), after thawing, the pump was restarted at 4.7 rpm and flow was reestablished. The conditions of operation are detailed in Table 2.

Figure 5. Operation of the C9 to C12 bioreactors in the laboratory fridge at 6°C

Table 2. Conditions of operation for reactors C9 to C12 (P1: Phase 1; P2: Phase 2; P3: Phase 3)

Time period	Operating conditions	Period referred to as:
Aug 29 – Sept 29, 2014	Incubation period (flow stopped)	
Sept. 29, 2014	Start continuous feed with influents	
Oct. 2, 2014 – Nov. 25, 2014	Operation in cold storage at ambient temperature (5.4 rpm, temperature decreasing from 15°C to freezing)	P1 - “Ambient temperature”
Nov. 25 2014 – Dec 18, 2015	Columns freezing (pump stopped)	P2 - “Freeze/thaw”
Dec. 18, 2014 - Jan. 5, 2015	Thawing in fridge at 6°C (pump stopped)	P2 - “Freeze/thaw”
Jan. 5 - March 3, 2015	Continuous feed in fridge at 6°C (5.4 rpm)	P3 - “6°C operation”

* HRT hydraulic retention time

2.4. INFLUENT COLLECTION AND PREPARATION

2.4.1. Barrel leachate

Victoria Gold has been operating a geochemical field barrel monitoring program since 2012 for which eight open top barrels were filled with crushed rock representative of overburden, ore or waste rock (fresh/oxidized or altered graniodorite, or meta sediments, Figure 6, Lorax 2014). The barrel leachate is representative of the water chemistry which might be encountered at closure. Rain water (or snowmelt) falling on the open top of the barrels is allowed to percolate through the crushed rock. The leachate is then collected in buckets located under each barrel. Leachate samples from the buckets were collected on June 19th and July 22nd, 2014. The leachate from the eight barrels has variable composition and volumes which were mixed together to produce the influent called “Comp. June” and “Comp. July” as described later in section 2.5.1. Before being used to feed the C9 reactor, 1% ethanol (Fisher Scientific, Alcohol denatured) was added to the influent on Sept 29th and Oct 31st, 2014 and on Jan 5th and Feb 19th, 2015 to support microbial activities in the cold temperatures. Addition of liquid carbon sources, such as ethanol, has been shown to support the microbial community and maintain its activity and population throughout the winter months (Tsukamoto et al, 2004; EPA, 2005; Gould et al, 2012; Sobolewski, 2010).

Figure 6. Field barrel experimental setup on site

2.4.2. Synthetic influent

The C10-12 reactors were fed with synthetic influent prepared in the laboratory with DI water and sulfate salts (As_2O_5, $FeSO_4$, SeO_2, Sb_2S_3 and $NaSO_4$) at pH 8. These synthetic influents were made with relatively high As, Se and Sb target concentrations (Table 3), which are representative of the potential worst case scenario predictions for water quality as presented in Lorax (2014). To make the synthetic influent, a concentrate solution was made in August 2014 with a concentration one hundred times higher than the target and at pH 2 to help keep metal salts under a soluble form. The C10-12 influent contains approximately 5 mg/L of As and 0.5 mg/L of Se and Sb. This concentrate was then used to make the synthetic influent called VGC1, VGC2, VGC3 and VGC4. The pH of the synthetic solution was adjusted to 8 using an NaOH solution at a concentration of 40g/L and 1% ethanol was added to feed the microbial population in the C10-C12 reactors.

Table 3. Synthetic influent target concentrations

Element	Target concentration	Source
pH	8	NaOH
As	3 mg/L	As(V)2O5
Sb	0.5 mg/L	Sb(III)2S3
Se	0.5 mg/L	SeO2
Fe	5 mg/L	FeSO4
SO4	900 mg/L	NaSO4
Ethanol	1%	Alcohol Denatured

2.5. INFLUENT CHARACTERISTICS

2.5.1. Barrel leachate

The composite influent was sampled on a regular basis and analyzed for pH, As, Se, Sb, Total Organic Carbon (TOC) and SO_4. The influent contains approximately 0.1 mg/L of As, 0.01 mg/L of Se and 0.1 mg/L of Sb, although there is some variability in the concentration of metals in the batch collected in June versus the one collected in July (Table 3).

Table 4. Characteristics of the C9 Influent (N/A: Not Available)

Batch Number	Date sampled	Metal concentrations (µg/L)			SO_4	TOC	pH
		As	Sb	Se	(mg/L)	(mg/L)	
Comp. June 2014	29-Sep-14	45.3	117.9	0.7	369.4	N/A	N/A
	2-Oct-14	46.4	113.1	16.6	410.9	2416.7	7.55
	10-Oct-14	48.6	126.3	15.8	403.1	2298.7	7.78
	17-Oct-14	46.6	115.9	16.4	445.8	2545.1	8.00
	24-Oct-14	46.6*	115.9*	16.4*	445.8*	2545.1*	8.00*
Comp. July 2014	31-Oct-14	101.9	94.8	9.6	282.0	2250.4	7.95
	10-Nov-14	106.8	87.8	9.4	175.1	2203.4	7.67
	17-Nov-14	102.3	89.1	8.5	195.4	2155.2	7.38
	25-Nov-14	101.0	87.3	8.6	176.8	2446.2	7.68
	12-Jan-15	120.7	92.6	11.5	211.2	1989.6	7.85
	21-Jan-15	91.4	96.2	10.9	175.6	1229.5	7.76
	2-Feb-15	22.6	99.5	11.7	199.0	1743.9	7.52
	12-Feb-15	145.6	108.3	13.3	224.8	698.8	7.76
Comp. June 2014	19-Feb-15	146.4	117.9	13.7	109.1	131.0	7.70
	25-Feb-15	114.4	97.0	12.1	233.3	2350.3	7.63
	3-Mar-15	96.8	87.5	TBA	178.82	1974.3	7.40
Average		**88.6**	**103.1**	**11.3**	**258.0**	**1881.5**	**7.7**
Standard Deviation		**39.7**	**13.1**	**4.1**	**106.1**	**745.7**	**0.2**

*Volume of influent was too low to be sampled; therefore concentrations and pH are assumed to be the same as the week before.

2.5.2. Synthetic influent

The synthetic influent was also sampled on a regular basis and analyzed for pH, As, Se, Sb, TOC and SO4. The As, Se and Sb concentrations measured (Table 5) differed from the target concentrations (Table 3).

Average As and SO_4 are higher than their target concentrations (5093 ug/L vs. 3000ug/L and 1661 mg/L vs. 900mg/L, respectively). Antimony, on the other hand, is lower than the target concentration (31 ug/L versus 500 mg/L). The low antimony concentration is due to the low solubility of the black Sb_2S_3 salt used to make the synthetic water. Black grains of non-dissolved antimony were seen in the bottle of concentrate. The high sulfate content is partly due to the addition of H_2SO_4 which was added to help Sb salt dissolution.

Table 5. Characteristics of C10-12 Influent

Batch Number	Date sampled	Metal concentrations (µg/L)			SO_4	TOC	pH
		As	Sb	Se	(mg/L)	(mg/L)	
VGC1	29-Sep-14	5865.2	32.4	524.1	1566.3	N/A	N/A
	2-Oct-14	4772.6	4.3	492.3	2681.3	2615.7	7.97
VGC2	10-Oct-14	4442.7	25.3	502.1	2899.2	2546.1	7.76
	17-Oct-14	4176.7	25.8	463.3	2778.0	2352.0	7.73
	24-Oct-14	6730.7	57.5	586.7	2062.1	2225.2	6.69
VGC3	31-Oct-14	5325.4	40.1	568.8	2633.0	2464.6	8.45
	10-Nov-14	4453.3	26.2	555.2	880.4	2541.3	8.20
	17-Nov-14	4351.2	26.8	547.0	1236.3	2523.4	7.59
	25-Nov-14	4351.2*	26.8*	547.0*	1236.3*	2523.4*	7.59*
	12-Jan-15	737.9	26.0	493.2	1380.2	2161.0	8.94
	21-Jan-15	5091.0	25.6	526.9	967.1	1283.7	8.15
VGC 4	2-Feb-15	8227.1	56.2	725.9	704.2	820.6	7.76
	12-Feb-15	5644.7	33.2	626.4	655.4	499.2	7.72
	19-Feb-15	5644.7*	33.2*	626.4*	655.4*	499.2*	8.04*
	25-Feb-15	6392.7	25.9	558.6	1148.6	2647.8	6.45
	3-Mar-15	5691.1	41.76	662.1	177.12	2175.2	7.39
Average		**5093.2**	**31.2**	**551.6**	**1660.9**	**2056.7**	**7.8**
Standard Deviation		**1742.6**	**13.9**	**68.4**	**840.4**	**750.7**	**0.7**

*Volume of influent was too low to be analyzed; therefore concentrations and pH are assumed to be the same as the week before.

2.6. FLOW RATES

The volume of effluent produced by the bioreactors was monitored weekly and presented in Table 6 below. The flow rates for C9-C12 reactors were calculated from the weekly volume measured (flow rate = volume of effluent collected / duration over which the effluent was collected) while the residence time was calculated using the total volume of the reactor (including the volume of solid material + the volume of voids) divided by the flow rate.

Average flow rates were 0.13, 0.14, 0.13 and 0.10 mL/min, respectively, for C9, C10, C11 and C12. Average residence times for C9, C10, C11 and C12 were 21, 22, 28 and 31 days, respectively. Average residence times are calculated based on flow rates, thus the variability of residence times from week to week can be attributed to occasional plugging of the tubes that feed the reactors which affects the volume of effluent collected each week.

Table 6. Volumes of effluent collected from C9-C12 during Phases 1-3, with calculated flow rates and hydraulic residence times.

Bioreactors	C9		C10		C11		C12	
	V_{eff}	Flow rate	V_{eff}	Flow rate	V_{eff}	Flow rate	V_{eff}	Flow rate
Sampling date	(mL)	(mL/min)	(mL)	(mL/min)	(mL)	(mL/min)	(mL)	(mL/min)
2-Oct-14	785	0.182	775	0.179	735	0.170	275	0.064
10-Oct-14	1880	0.163	1880	0.163	1880	0.163	1365	0.118
17-Oct-14	1380	0.137	1350	0.134	1255	0.125	955	0.095
24-Oct-14	2200	0.218	2200	0.218	2200	0.218	1550	0.154
31-Oct-14	40	0.004	1150	0.114	1080	0.107	530	0.053
10-Nov-14	1880	0.131	1810	0.126	1785	0.124	900	0.063
17-Nov-14	1875	0.186	1830	0.182	1770	0.176	1225	0.122
25-Nov-10	1855	0.161	1255	0.109	1395	0.121	760	0.066
12-Jan-15	n/a	n/a	n/a	n/a	1715	0.025	1595	0.023
21-Jan-15	985	0.076	1005	0.078	1055	0.081	965	0.074
2-Feb-15	2580	0.149	1410	0.082	2145	0.124	2100	0.122
12-Feb-15	1820	0.126	n/a	n/a	2670	0.185	2730	0.190
19-Feb-15	1540	0.153	n/a	n/a	1540	0.153	1080	0.110
25-Feb-15	720	0.083	1920	0.222	800	0.093	1880	0.218
Total (L)	**19.54**		**16.59**		**22.03**		**17.91**	
Min (mL/min)		**0.004**		**0.078**		**0.025**		**0.023**
Max (mL/min)		**0.218**		**0.222**		**0.218**		**0.218**
Average (mL/min)		**0.136**		**0.146**		**0.133**		**0.105**
Average residence time (days)		**21***		**22**		**28**		**31***

*Average residence times for C9 and C12 are calculated with outliers removed (718 days and 123 days, respectively).

2.7. TEMPERATURE

As discussed above, the temperature fluctuated during Phase 1 when the reactors were stored in the insulated, non-heated building where the ambient temperature dropped from 15°C to 0.2°C. Daily temperature fluctuations in this building were thought to be minor (large building, insulated). During Phase 2, between November 26th 2014 and January 5th 2015, the columns were still in the cold storage building. The temperature was not monitored weekly but was below freezing. While, this building is not heated, based on outside temperatures, temperatures in the building during this period were estimated to be between 0°C and -20°C. After January 5th, the temperature was set in the fridge at 6°C and was monitored weekly. Air temperatures are presented in Table 7.

Table 7. Air temperature monitored during operation of the C9-C12 bioreactors during Phases 1-3

Monitoring date	Duration (day)	Location	Temperature (°C)	Period referred to as
2-Oct-14	3	Cold storage	15.1	"Ambient temperature"
10-Oct-14	11	Cold storage	9.6	"Ambient temperature"
17-Oct-14	18	Cold storage	12.8	"Ambient temperature"
24-Oct-14	25	Cold storage	n/a	"Ambient temperature"
31-Oct-14	32	Cold storage	3.7	"Ambient temperature"
10-Nov-14	42	Cold storage	2.1	"Ambient temperature"
17-Nov-14	49	Cold storage	0.5	"Ambient temperature"
25-Nov-14	57	Cold storage	0.2	"Ambient temperature"
26-Nov-14 to 18-Dec-145	58 to 80	Cold storage	-20°C to 0°C	"Freeze/thaw"
18-Dec-14 to 5-Jan-15	80 to 98	Lab fridge	6.0	"Freeze/thaw"
12-Jan-15	105	Lab fridge	6.4	"6°C operation"
21-Jan-15	114	Lab fridge	6.3	"6°C operation"
2-Feb-15	126	Lab fridge	5.8	"6°C operation"
12-Feb-15	136	Lab fridge	5.6	"6°C operation"
19-Feb-15	143	Lab fridge	5.9	"6°C operation"
25-Feb-15	149	Lab fridge	5.9	"6°C operation"
3-Mar-15	154	Lab fridge	5.9	"6°C operation"

2.8. ANALYTICAL

Total metal concentrations were measured in the water samples using a Perkin Elmer PinAAcle Atomic Absorption (AA) analyzer located in the YRC laboratory. As, Se and Sb were analyzed by Graphite Furnace (GFAA). The Quantification Limits (QL) used in this work have been defined for each element using the 10-σ method (10 times the standard deviation of 10 blanks) and are 0.8 µg/L As, 0.7 µg/L Se and 4.3 µg/L Sb. Calibrations are completed on a daily basis. Duplicate samples and low and high-level standards are used to check the calibration at each 15 sample interval with an error tolerance of 20% for low level standards (low end of the calibration range) and 10% for high level standards (high end of the calibration range). Standards are made from commercial standards purchased from SCP Science. Measurements below the quantification limits are reported as "<QL", meaning that they can't be quantified although they might be detected, with measured values above detection limit (3-σ).

The pH was measured using an Oakton PCD650 meter with a double junction pH electrode.

Sulfate in water was measured using a Westco SmartChem 170 analyzer. The reference method is ASTM Method D516-90, 02. The detection limit for sulfate using this method is 4 mg/L. Calibration curves are created every day using a range of 8 standard concentrations. High, low and mid-level standards are used to check the calibration at 20 sample intervals with an error tolerance of 10%. Standards are made from commercial standards purchased from SCP Science.

Total Carbon (TC) was measured using a Skalar Formacs HT instrument. Calibrations for TC are made monthly and low-level and high level standards are used daily to check the calibration with an error tolerance of 20% for both, low and high level standards (both ends of the calibration range) and for the duplicates. Standards are made from commercial standards purchased from SCP Science. Samples have been measured for Total Carbon (TC). TC is considered here as a representation of the total organic carbon (TOC) in the samples as they are preserved with acid resulting in the conversion and loss of the total inorganic carbon (TIC) (i.e., in the equation TC=TOC+TIC if TIC=0 then TC=TOC).

3. RESULTS

Data sets for pH, metal concentrations, carbon and SO4 measured in the effluents from the reactors C9-C12 are presented in Appendix 1 for the monitoring periods between September 29th to November 25th 2014 (Phase 1) and after freeze/thaw between January 6th to February 25th 2015 (Phase 3).

3.1. VARIABILITY OF INFLUENT CONCENTRATIONS

Generally, high variability has been observed for the metal, TOC and sulfate concentrations in the synthetic influent (Table 8). As well, a significant variability has been observed for the pH of this influent, with minimum and maximum pH values measured at 6.5 and 8.9. Average pH value was 7.8 with a standard deviation of 0.8. As discussed previously, the influent was made with DI water and dissolved metal salts with the pH initially adjusted to 8 with NaOH. Along with variations in metal concentrations, it is thought that the variability in pH comes from the lack of buffering capacity of this influent, which is not representative of a drainage which would be found on a mine site.

TOC varied between 499 to 2648 mg/L over the duration of the experiment, with an average of 2057 ± 751 mg/L. This variation is due to ethanol volatilization: ethanol is added when the influent is prepared rather than weekly. As ethanol boiling point is low (78°C), some volatility is expected, which subsequently decreased TOC concentration in the influent. Also, TOC concentration in the influent decreased more quickly in Phase 3 after Day 105 when the bioreactors and the influent buckets were brought into the fridge. It is believed that air circulation in the fridge increased ethanol volatilization.

Table 8. Minimum, maximum, average and standard deviation for concentrations and pH measured weekly for the synthetic influent during Phases 1-3.

	Min	Max	Average (mg/L)	Standard Deviation (mg/L)	Coefficient of variation (%)
pH	6.4	8.9	7.8	0.8	9
As	737.9	8227	5093	1743	34
Sb	4.30	57.5	31.2	13.9	45
Se	463.3	725.9	551.6	68.39	12
SO_4	655.4	2899	1661	840.4	51
TOC	499.2	2648	2057	750.7	36

3.2. TREATMENT OF THE BARREL LEACHATE

3.2.1. Impact of treatment on pH

pH monitoring is conducted each week for the influent and effluent of the four bioreactors and the results are presented in Table 17 (Appendix 1). Small variations in pH are observed for both influent and effluent during Phases 1 and 3 (September 29th 2014 - February 25th). With an average of 7.7 and a range of 7.4-8.0, this effluent qualifies as being alkaline; however the pH of this effluent was clearly reduced by treatment through the C9 bioreactor which had an output pH of 5.9 on average.

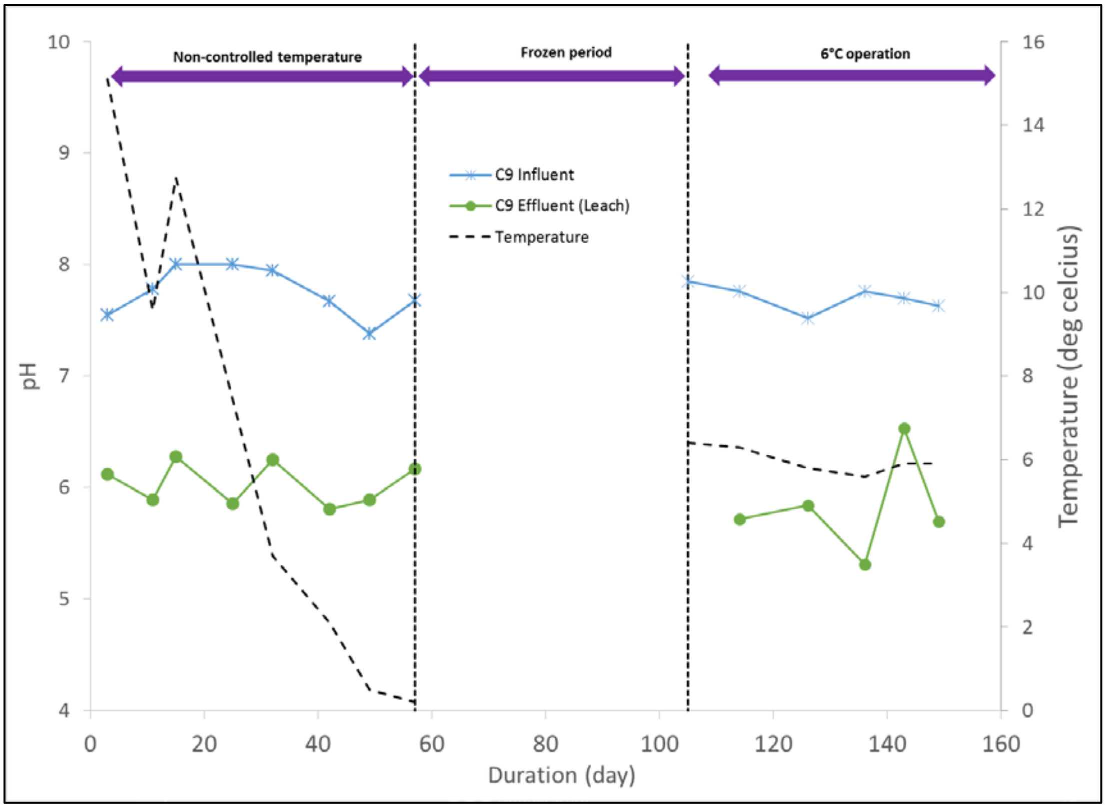

Figure 7. pH evolution for the barrel leachate from the field, before and after treatment by anaerobic bioreactor (C9) (Phases 1-3)

3.2.2. Sulfate consumption in C9 bioreactor

Sulfate concentrations in the composite barrel leachate varied between 109 and 446 mg/L and were significantly reduced (to <20mg/L) by treatment through the anaerobic bioreactor. Until February 25th 2015, a total of 0.0433 mmol of sulfate were loaded into the C9 reactor according to weekly monitoring data while 0.0013 mmol flowed out of the reactor, indicating that 97% of the sulfate was retained or reduced by the column. This indicates that sulfate reducing bacteria (SRB) are likely present and active in this bioreactor, leading to the reduction in sulfate and the possible production of sulfides.

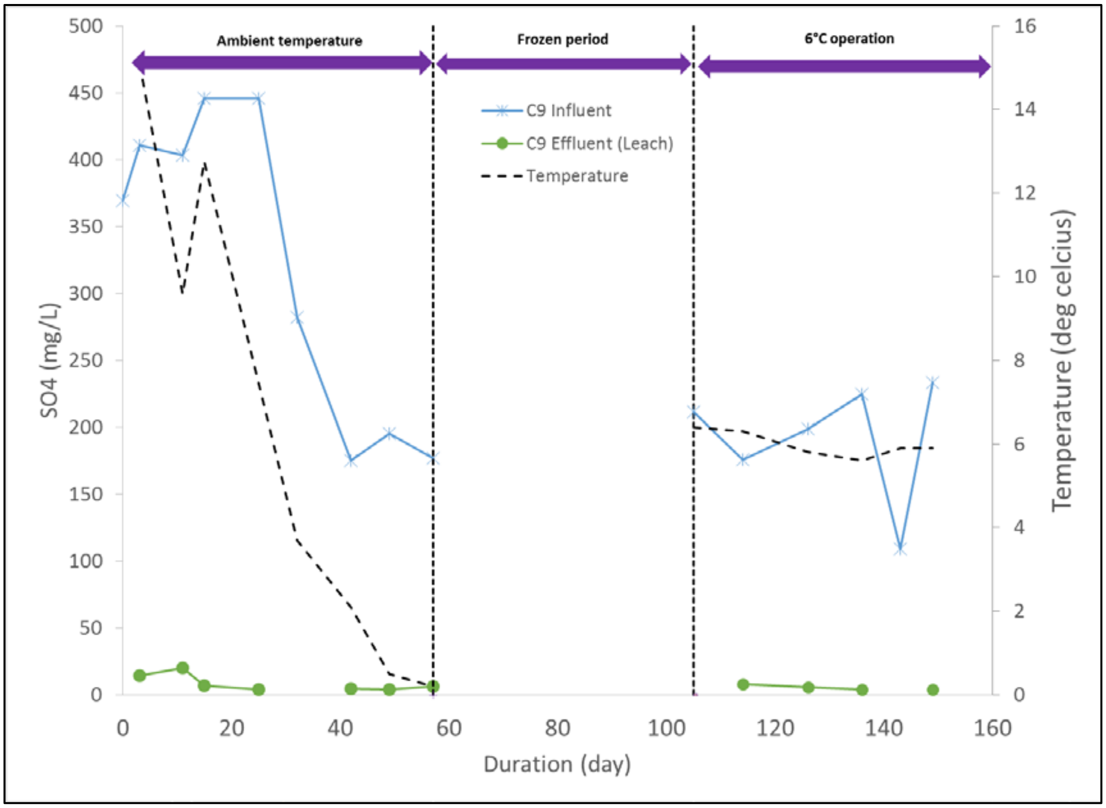

Figure 8. Sulfate concentration in C9 influent and effluent (Phases 1-3)

3.2.3. Removal of arsenic from barrel leachate

Arsenic concentrations in the composite barrel leachate used to feed the C9 reactor varied between 33.9 and 110.9 ug/L. In the first three weeks of operation when the As concentration in the influent ("Comp. June 2014") was around 50 ug/L, As was not significantly removed (Figure 9). However, once the concentration of the influent increased to above 100 ug/L after October 31st (when using "Comp. July 2014"), the As concentration was significantly lower in the effluent indicating As removal. Post-freezing, the trend is not yet clear and further monitoring may indicate how removal rates are affected.

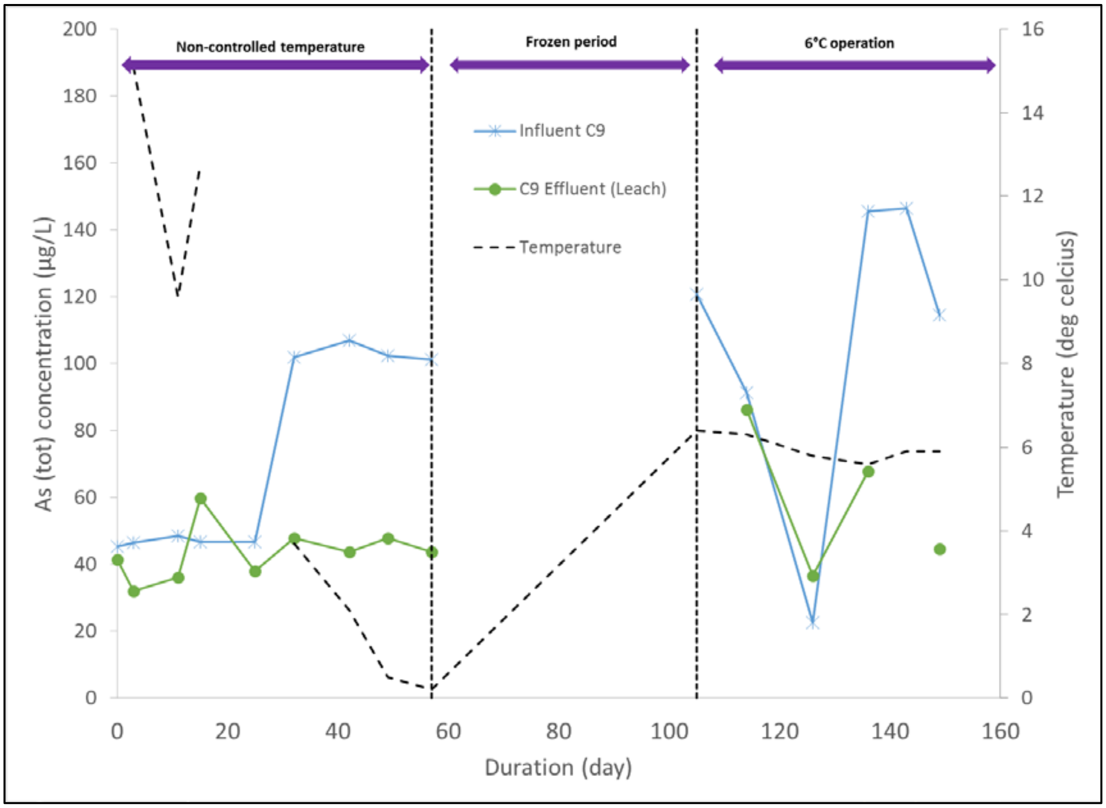

Figure 9. As concentration in influent and effluent from the C9 reactor (Phases 1-3)

3.2.4. Removal of antimony from barrel leachate

The Sb concentrations were reduced to below the quantification limits of 4.3 ug/L in all the samples analyzed except one, which was measured at 4.8 ug/L (Figure 10 and Table 20, Appendix 1). The low and/or non-existent detection of antimony in these samples cannot be attributed to analytical errors as all the analytical quality controls passed as reported in Appendix 2. Hence these results suggest that Sb was reduced from 87.3-126.3 ug/L down to below 4.8 ug/L by the anaerobic bioreactor.

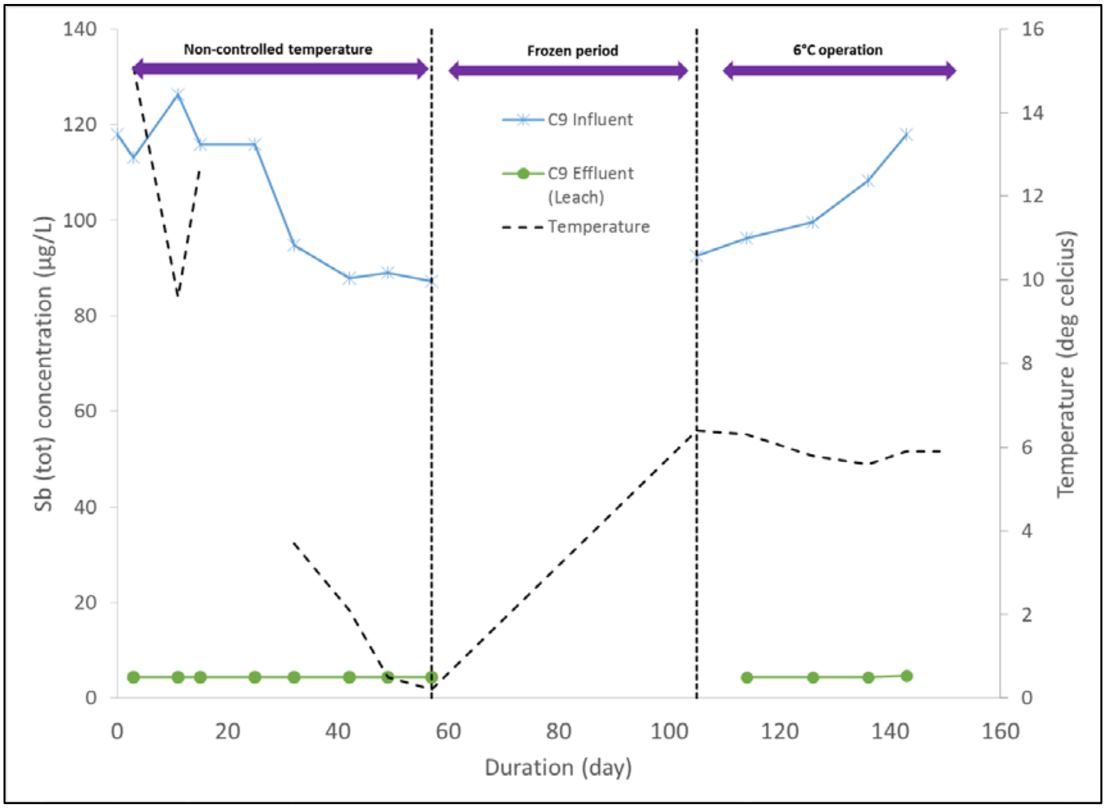

Figure 10. Sb concentrations in influent and effluents from the C9 reactor (Phases 1-3; quantification limit is 4.3 ug/L, value below the limits are reported as 4.3)

3.2.5. Removal of selenium from barrel leachate

With an average influent concentration of 11.3 ug/L, the Se concentrations in the effluent of the bioreactor C9 are measured consistently below the Quantification Limit (QL) of 0.7 ug/L between day 15 and 57 when the column started freezing (Figure 11 and Table 20 Appendix 1).

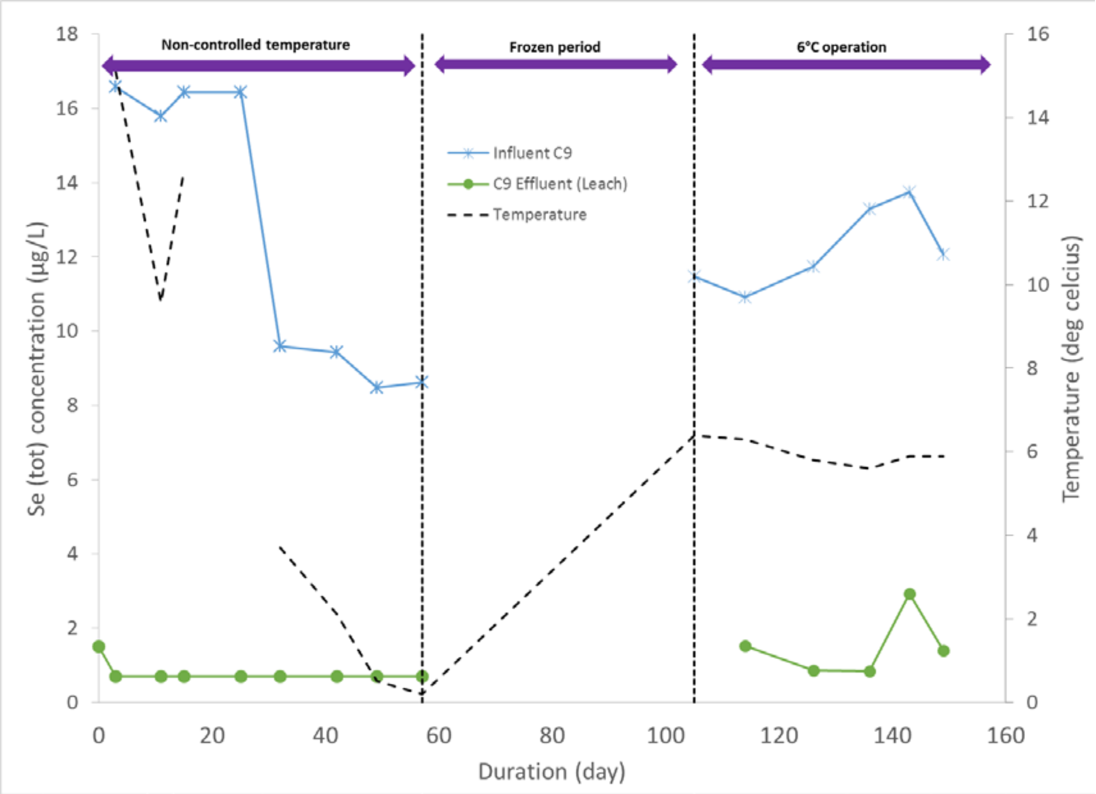

Figure 11. Se concentration in the influent and effluent from the C9 reactor (Phases 1-3; quantification limit is 0.7 ug/L, value below the limits are reported as 0.7)

3.3. TREATMENT OF THE SYNTHETIC INFLUENT

3.3.1. Impact of treatment on pH

Weekly monitoring of the pH synthetic influent, for which the pH was initially adjusted at 8 at the time of preparation, showed variations from 6.4 to 8.9, with an average of 7.8 (Figure 12). Effluents from the reactors C10, C11 and C12 had a lower pH than the synthetic influent indicating that the treatment through the bioreactor clearly decreased the pH of the water to between 5.9 and 6.5 as indicated in Figure 7 and Figure 12. The synthetic influent was reduced from an average of 7.8 down to 6.4, 6.3 and 6.5 for C10, C11 and C12, respectively.

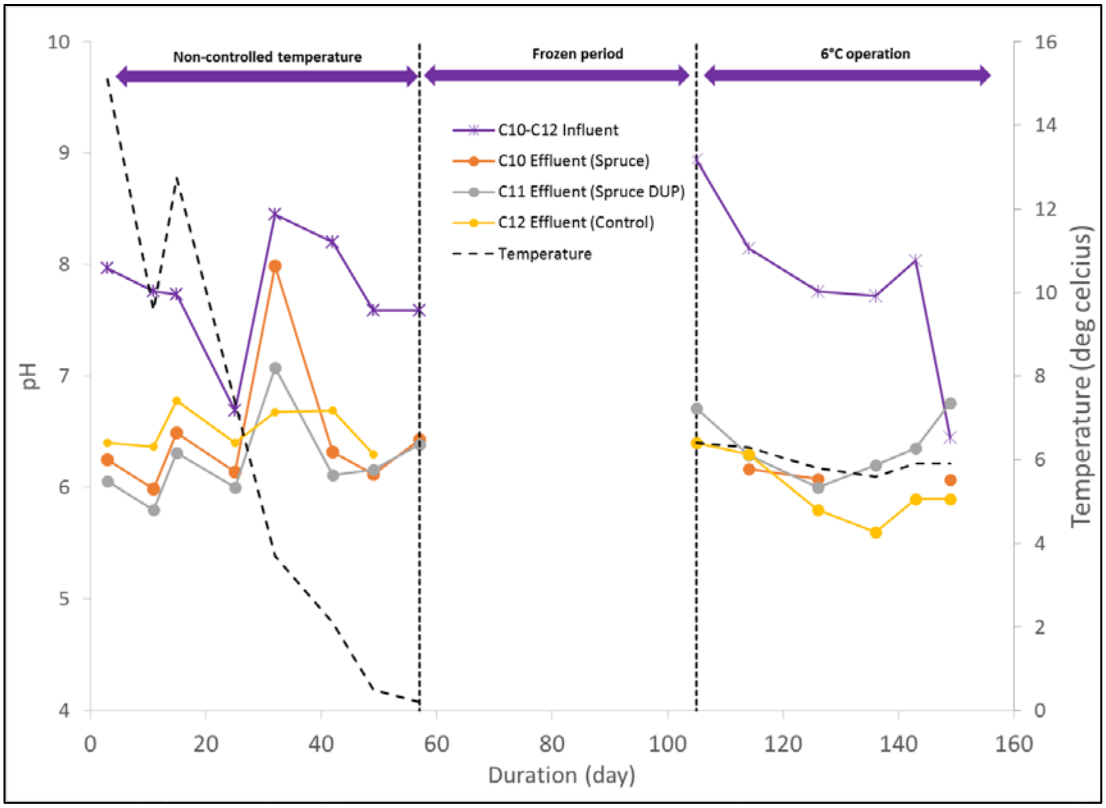

Figure 12. pH evolution for the synthetic effluent, before and after treatment by anaerobic bioreactor (C10-C12, Phases 1-3)

3.3.2. Sulfate consumption in C10, C11 and C12 bioreactors

Sulfate concentrations were reduced to less than 735 mg/L by C10 and C11 and to less than 1113 mg/L by C12. The amount of sulfate coming in and out of the three bioreactors is presented in Table 9 along with the consumption rates. Sulfate concentration was reduced by all anaerobic bioreactors, suggesting that sulfate were likely reduced by sulfate-reducing bacteria in the bioreactor. However, C10 and C11 both reduced respectively 71 and 72% of the sulfate entering the bioreactors while C12 reduced only 50% of the sulfate molecules.

Sulfate concentrations for the influents and effluents of all bioreactors are presented in Appendix A. Sulfate concentration in the synthetic influent varied from an average of 1997 ± 971 mg/L in Phase 1 before freezing, to an average of 782 ± 304 mg/L during Phase 3 after freezing. The C10 and C11 reactors decreased sulfate concentrations to 462 ± 220 and 367 ± 292 mg/L, respectively. As for metal reduction, the control C12 reactor which is not amended, reduced sulfate concentrations to a lesser extent, with an average effluent concentration of 677 ± 258 mg/L. Table 9 presents the load of sulfate in (influent concentration x volume) and out (effluent concentration x volume) from all four bioreactors. It was observed that 71% and 72% of sulfate was reduced by C10 and C11 respectively, while only 50% was reduced by C12.

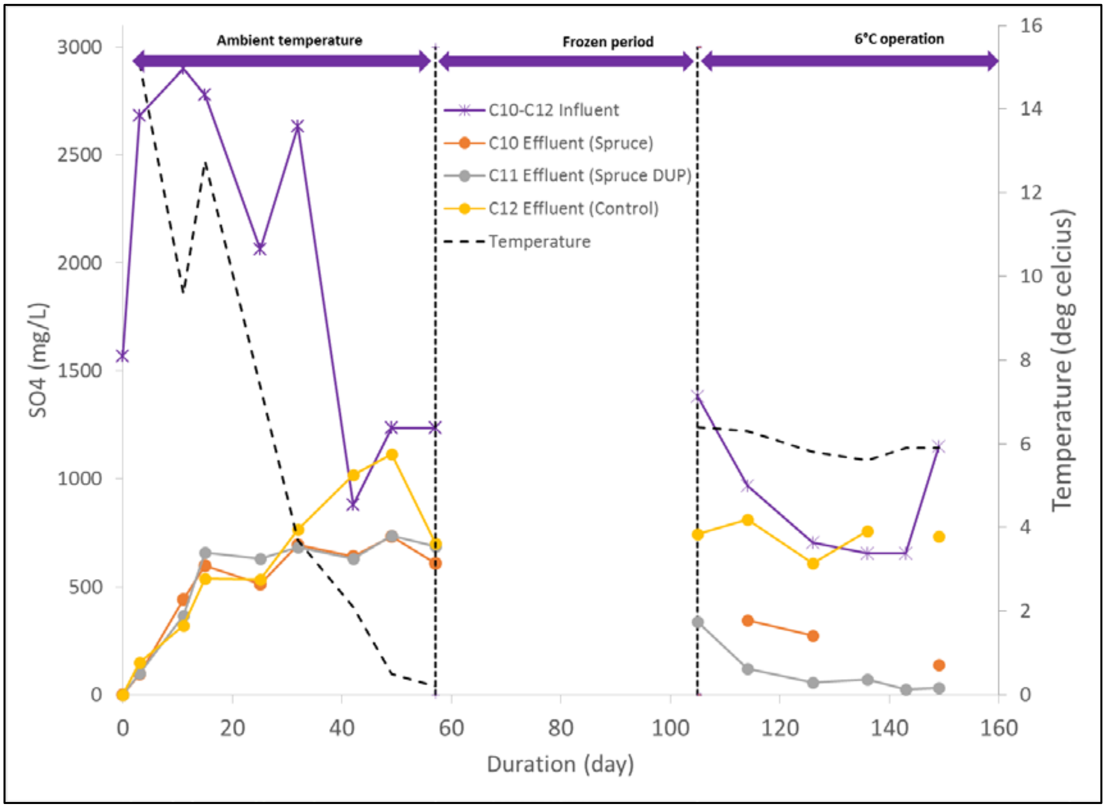

Figure 13. Sulfate concentration in influent and effluent from C10, C11 and C12 (Phases 1-3)

Table 9. Sulfate consumption rates and sulfate amounts in influent and effluent for the C10, C11 and C12 bioreactors (Phases 1-3)

	C10 (Spruce)	**C11(Spruce Dup)**	**C12 (Control)**
$SO_{4\ in}$ (mol)	0.2800	0.3080	0.2150
$SO_{4\ out}$ (mol)	0.0820	0.0870	0.1080
Amount SO4 consumed (mol)	0.198	0.221	0.107
SO4 consumption rate (%)	**71%**	**72%**	**50%**

3.3.3. Removal of arsenic from the synthetic influent

The As concentrations in the influent for the C10-12 reactors were high, with an average of 5093 ± 1743 ug/L (Table 5). The effluent from the bioreactor C11 consistently had the lowest concentrations of effluent (95 ± 45 ug/L) while C10 has also been performing well with As concentration in the effluent of 225 ± 97 ug/L. However, plugging and low effluent volumes in the C10 reactor prevented sampling in some of the weeks after thawing. Still, As concentrations in the C10 and C11 effluents were comparable before and after freeze/thaw.

The effluent from the C12 control reactor generally had higher As concentrations than the C10 and C11 effluent (Figure 14). After freeze/thaw, the average concentration and the variability of As was clearly reduced in the reactors which were amended with wood. The impact of freeze/thaw is further discussed in section 4.2.

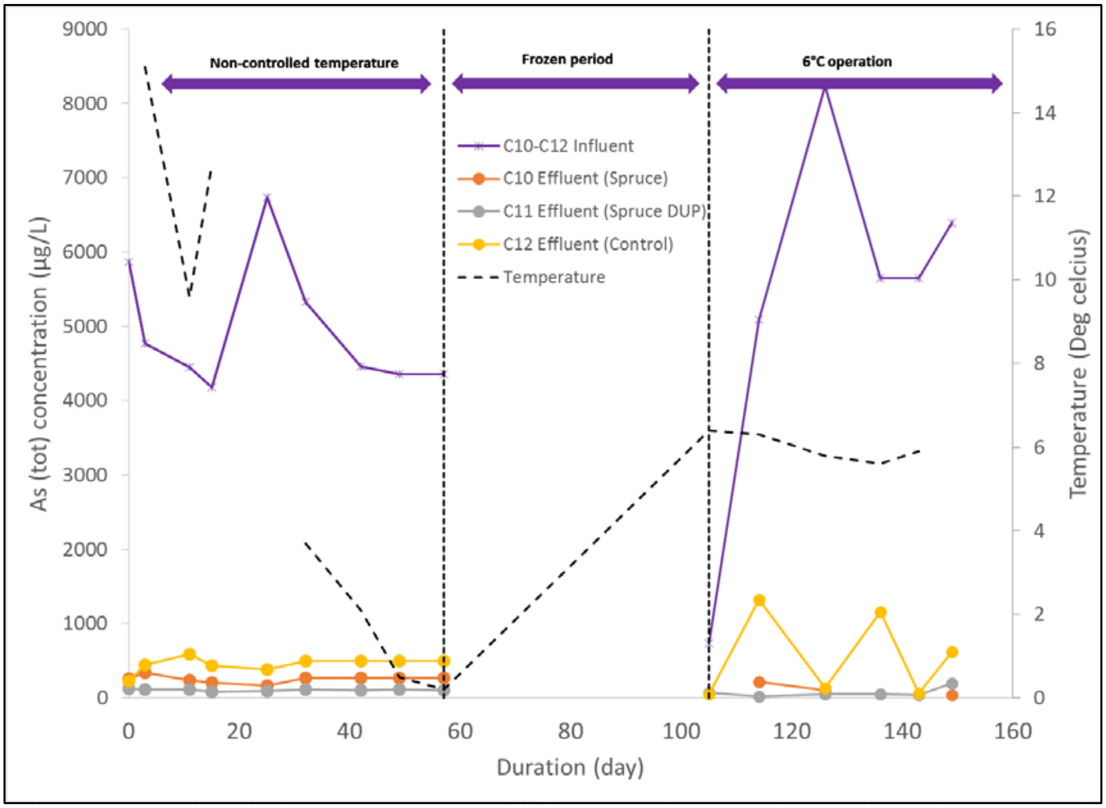

Figure 14. As concentrations before and after treatment by the bioreactors C10 and C11 (duplicates, wood-amended) and C12 (control, no organic amendment) (Phases 1-3; quantification limit is 0.8 ug/L, value below the limits are reported as 0.8)

3.3.4. Removal of antimony from the synthetic influent

The average concentration of Sb in the C10-12 influent was 31 ug/L and much lower than the target concentration likely due to the low solubility of Sb salts. Still, the effluents produced by the C10, C11 and C12 bioreactors were much lower than the influent Sb concentration (Figure 15). Sb concentrations in the effluents were consistently close to or at the 4.3 ug/L quantification limit despite fluctuations in the concentration of the influent.

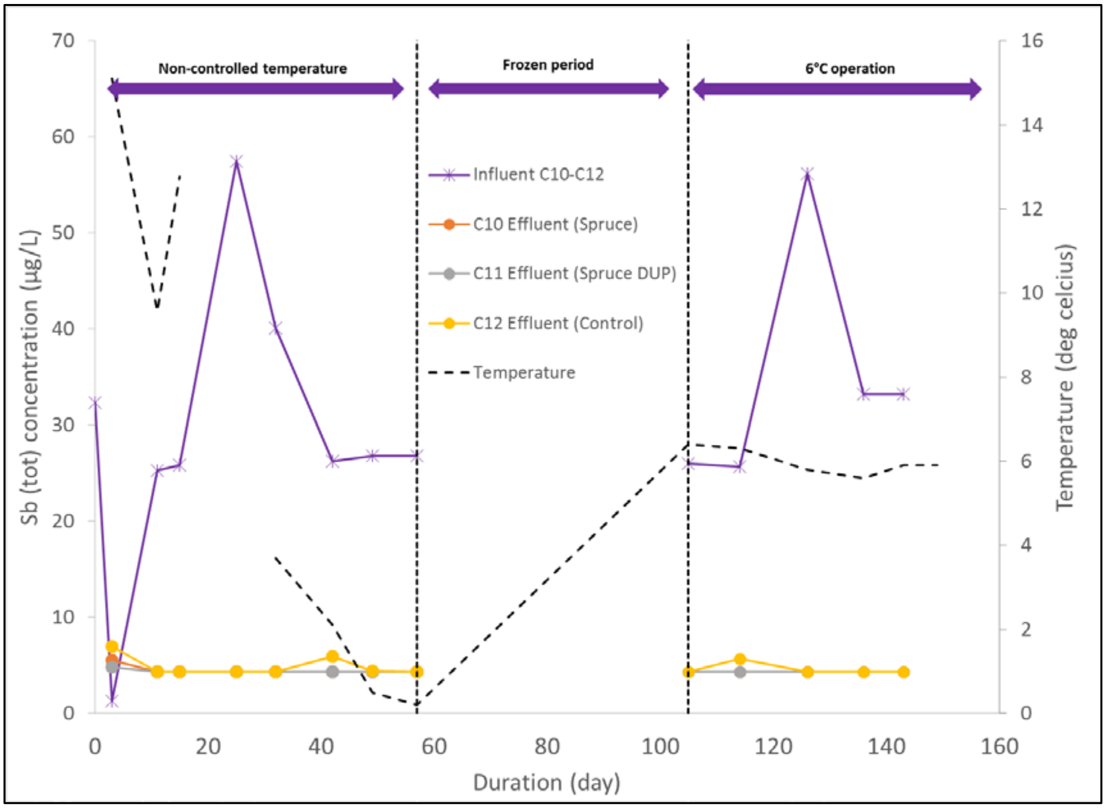

Figure 15. Sb concentrations in influent and effluents from the C10-12 reactors (Phases 1-3; quantification limit is 4.3 ug/L, value below the limits are reported as 4.3)

3.3.5. Removal of selenium from the synthetic influent

The average Se concentration in the C10-12 influent was 552 ± 68 ug/L. Se concentrations in the effluent of all reactors were consistently very low with the lowest average concentration in C11 (1.4 ug/L) and 2.0 ug/L and 3.8 ug/L for C11 and C12, respectively (Figure 16).

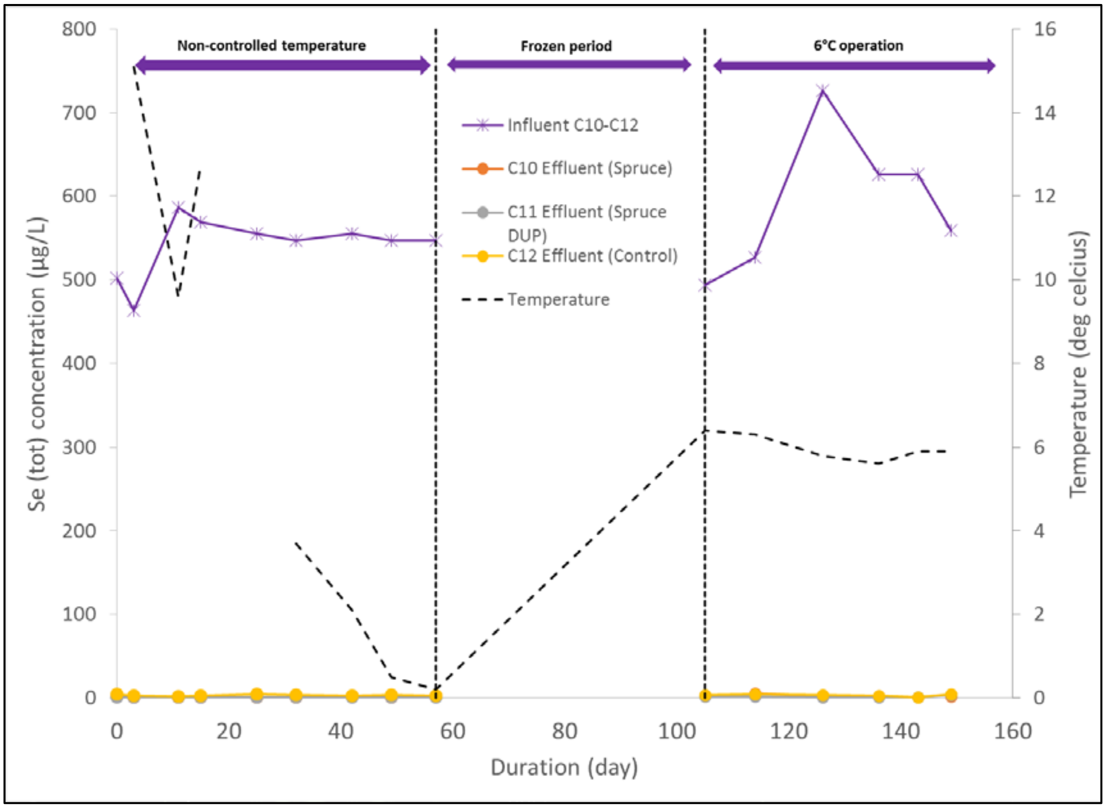

Figure 16. Se concentration in the influent and effluents from the C10-12 reactors (Phases 1-3; quantification limit is 0.7 ug/L, value below the limits are reported as 0.7)

3.4. ORGANIC CARBON CONSUMPTION AND RELEASE

As described earlier, ethanol was added to the influent to support microbial growth. As a result, TOC concentrations were relatively high and the C9 influent (barrel leachate) ranged from 131 to 2545 mg/L with an average of 1929. The C10-12 influent ranged from 475 to 2615 mg TOC/L with an average of 1959 mg/L. High variability in the concentration of carbon was likelydue to evaporation of the ethanol in the influent buckets.

TOC, as represented by the measurement of TOC, in the effluents was on average 1889 mg/L in the effluent of C9 (Figure 17); 2140 mg/L and 1926 mg/L, respectively, for the wood-amended reactors C10 and C11, and 1915 mg/L for the control reactor not amended with organic material (Figure 18).

Before freezing on day 57, TOC concentrations in the effluents were generally lower than in the synthetic influent, indicating that the organic carbon was likely consumed. This was observed in both configurations: the reactor fed with influent from site (lower metal concentration) and the reactors fed with synthetic influent (higher metal concentrations) (Figure 17 and Figure 18). Reduction in organic carbon concentrations between 15% and 20% were observed in the initial operation of the bioreactors before freezing (Table 16).

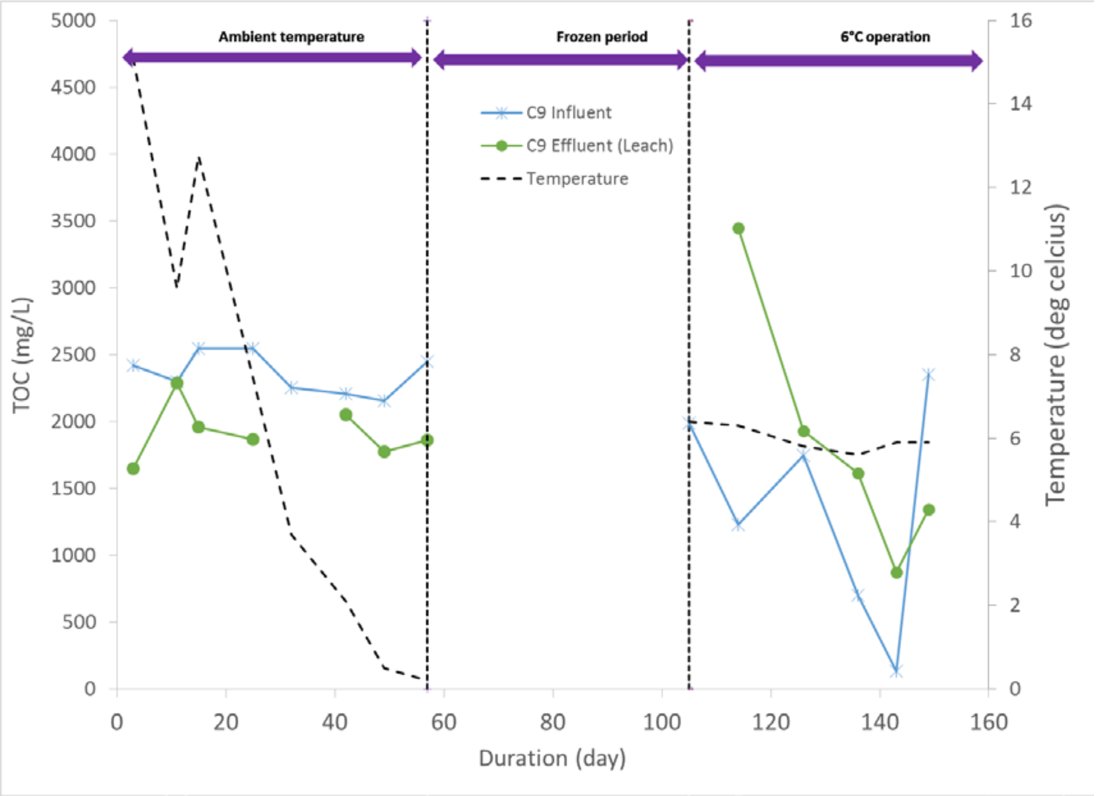

Figure 17. Total Organic Carbon concentrations in the influent and effluent of the C9 bioreactor (Phases 1-3)

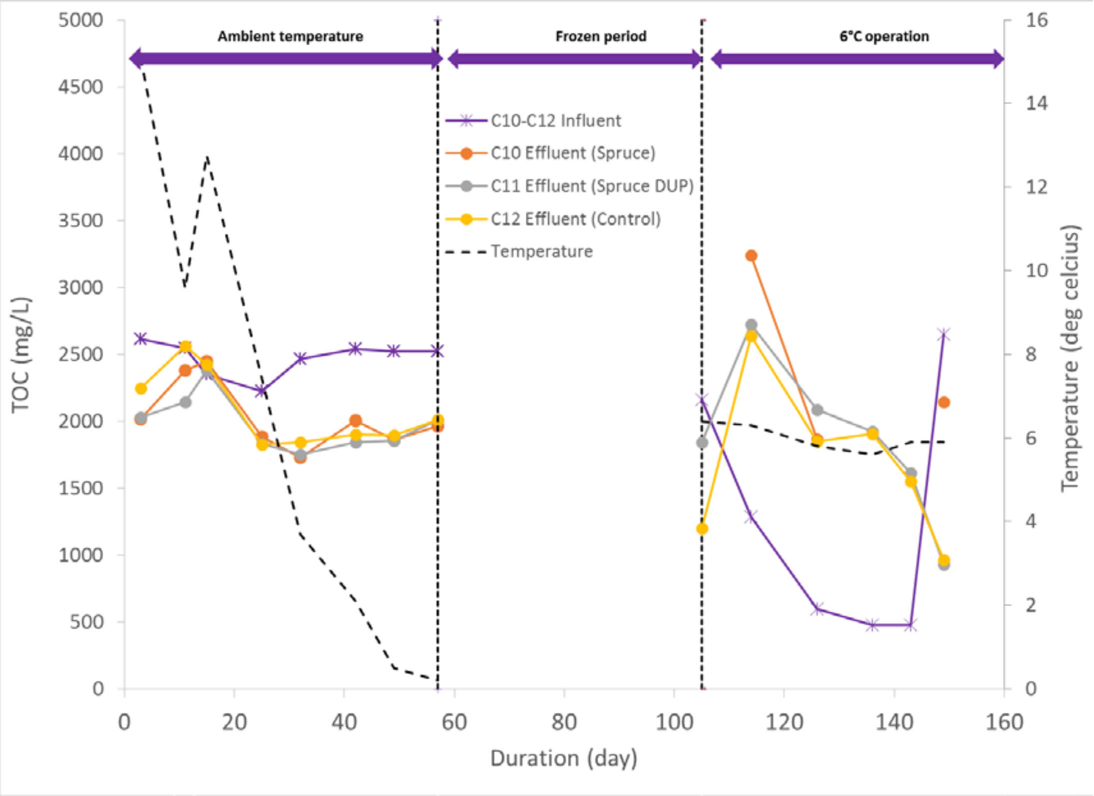

Figure 18. Total Organic Carbon concentrations in the influent and effluent of the C10, C11 and C12 bioreactors (Phases 1-3)

4. DISCUSSION: ANAEROBIC BIOREACTORS PERFORMANCES

4.1. METAL REMOVAL EFFICIENCIES

Metal removal efficiencies are shown in Table 10 below and take into account the load of metal that was fed in and discharged from each reactor during Phases 1 and 3.

Table 10. Metal removal efficiencies as calculated using total amount of metals feeding in and discharging from the C9-C12 reactors (Phases 1 and 3)

	C9 (Leach)	C10 (Spruce)	C11 (Spruce Dup)	C12 (Control)
As_{in} (mmol)	0.0173	1.3712	1.5448	1.3831
As_{out} (mmol)	0.0106	0.0544	0.0351	0.1762
As removal efficiency (%)	**38.6***	**96.0**	**97.7**	**87.3**
Se_{in} (mmol)	0.0027	0.1080	0.1372	0.1168
Se_{out} (mmol)	0.0003	0.0004	0.0004	0.0010
Se removal efficiency (%)	**90.2**	**99.7**	**99.7**	**99.1**
Sb_{in} (mmol)	0.0141	0.0038	0.0096	0.0041
Sb_{out} (mmol)	0.0007	0.0005	0.0014	0.0006
Sb removal efficiency (%)	**95.2**	**86.0**	**85.4**	**86.6**

Arsenic removal rates varied from 38.6% (C9, leach) to 97.7% (C11, spruce duplicate). The C10, C11 and C12 bioreactors showed significantly higher efficiency (87.3 to 97.7%) than the C9 bioreactor (38.6%). It is thought that this difference is due to the very different As concentrations of the barrel leachate (88.6 ± 39.7 ug/L As) and the synthetic influent (5093 ± 1742 ug/L), as illustrated in Figure 19.

Interestingly, the bioreactors amended with 20% wood (C10 and C11) showed good performances in Phase 1 (>96% removal As) when the influent concentrations were very high. The C12 control reactor had a slightly lower removal efficiency (87.3%) suggesting that wood enhances removal of As. This observation aligns well with the study reported by Neculita and Zagury (2008) who observed higher SRB activities when cellulosic waste (either woodchips or sawdust) was used in their bioreactors. This observation may be explained by: 1) wood provides an additional carbon source to the microorganisms, 2) As adsorbs to the wood chips, and 3) wood provides a suitable habitat to support microorganisms and biofilm growth.

In this case however, where ethanol, a very bioavailable liquid carbon source, is already provided to the microorganism in excess, the limited amount of soluble organic compounds provided by the wood is probably not a driver. Thus, the first hypothesis does not likely explain the improved performances of the C10 and C11 bioreactors. On the other hand, sorptive capacity of the spruce chips for As has been observed in a previous study conducted in the YRC lab and reported by Janin and Harrington (2013). A maximal adsorption capacity of 0.675 ug As/g of spruce chips was observed at pH 6. Other authors have observed As sorption on wood chips, including Keng et al. (2014), Argun et al. (2008) and O'Connell et al. (2008).

Finally, wood chips might provide a good substrate for the growth of biofilms. Yamashita et al (2011) found clear indications that different species of SRB are able to grow attached to the wood, at the surface of wood chips (0-5mm) and inside the wood (>5mm deep inside the wood) and that each of these three regions provides an ecological niche hosting a different community. Hence, the wood chips might provide a suitable habitat for a more diverse community of SRB.

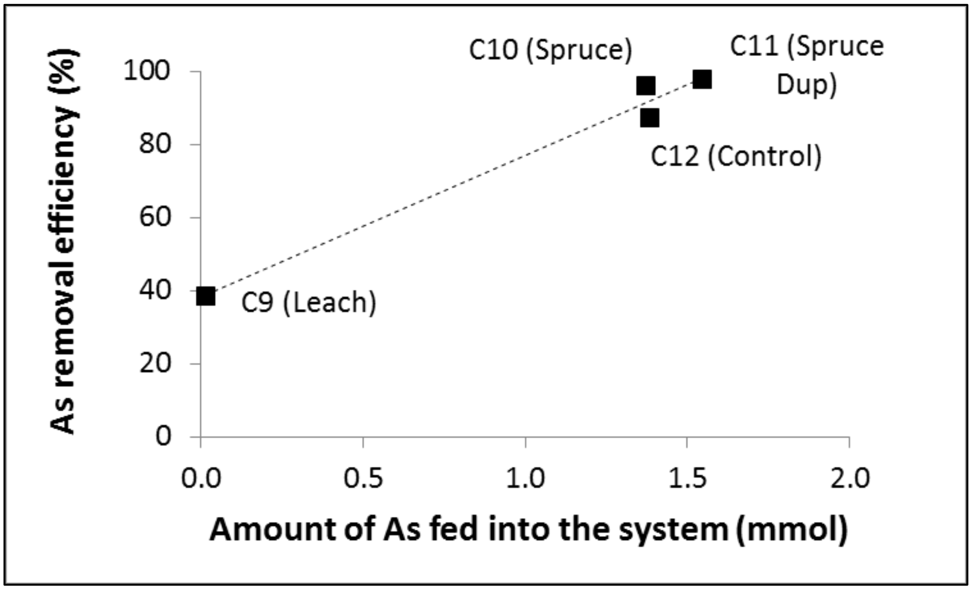

Figure 19. As removal efficiency versus the amount of As feeding into the four bioreactors (Phases 1-3)

These results indicate that the bioreactors are highly efficient for selenium removal. This aligns with results observed previously in the laboratory (Janin and Harrington 2015). The removal efficiencies of the reactors for Se removal were 90.2% (C9, leach), 99.7% (C10, spruce), 99.7% (C11, spruce duplicate) and 99.1% (C12, control). The lower removal efficiency for C9 reflects the lower concentrations of Se in the influent (0.7 to 16.6 ug Se/L). Otherwise, all three reactors fed with synthetic influent which contained 463 to 725 ug Se/L yielded relatively high performances, bringing Se concentrations down to less than 10 ug Se/L in the effluent from the C10, C11 and C12 reactors; thus, the wood amendment does not appear necessary to achieve high Se removal from the synthetic effluent. Still, Figure 20 presents the same data as in Figure 16, but the graph is presented with a much smaller y-axis scale to highlight the differences observed in Se concentration in the effluent from the wood-amended (C10 and C11) and the non wood-amended reactor (C12). Although the differences are very small and in the order of a few ug/L, it seems that the amendment with wood is somewhat beneficial to Se removal too, likely for the same reasons as discussed earlier for As.

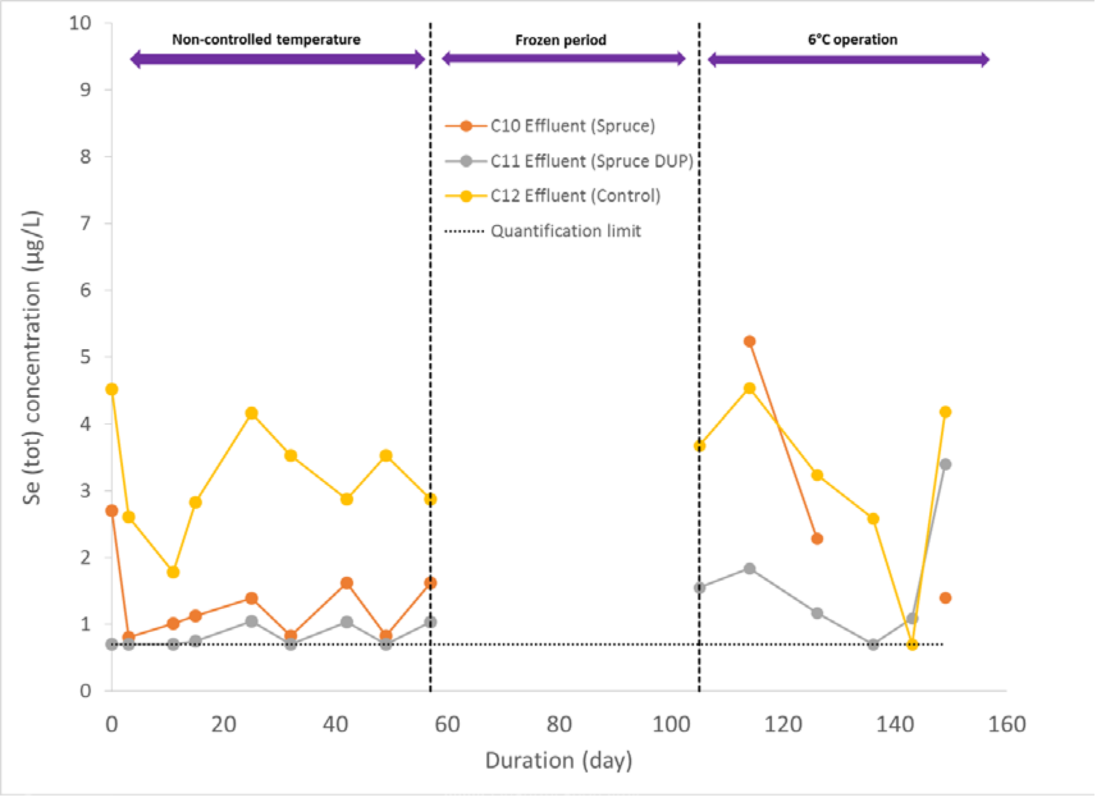

Figure 20. Se concentration in the effluents from the C10-12 reactors (results previously presented in Figure 16)

The performance of the reactors for removal of Sb was also very high, at 95.2% in C9 (initial Sb concentrations between 87 and 126 ug Sb/L), 86.0%, 85.4% and 86.6%, respectively, in wood-amended C10 and C11 and in the control reactor C12 (initial Sb concentrations between 4 and 57 ug Sb/L). The higher removal efficiency of the C9 reactor reflects the higher concentration of Sb in the C9 influent while the effluent concentrations in all reactors are < 7 ug/L and generally under the quantification limit over the entire monitoring period. No significant differences were observed between the wood-amended and control bioreactors.

Sulfate reducing bacteria are capable of producing sulfides, a strong reducing species, which allows for reduction of Sb(V) into Sb(III). Sb(III) then readily forms a complex ($H_2Sb_2S_4$) with sulfides produced by SRB and finally this complex is transformed into Sb_2S_3, also known as stibnite. (Wang et al 2013; Polack et al. 2009). This mechanism is well described in a study where Total Sb, Sb(V) and Sb (III) were monitored daily and a reduction in Sb(V) was observed, followed by an increase in Sb(III) a few days later which indicates reduction of Sb(V) into Sb(III). Finally, Wang et al (2013) reported reduction of total Sb from 20 mg/L in a synthetic solution down to 0.16 mg/L at pH 7, corresponding to a 99.2% removal in small 0.3L batch SRB bioreactors. Another study reported evidence for Sb(V) being microbially reduced into Sb(III) and suggested that it was achieved by a dissimilatory respiratory pathway in an anoxic environment, meaning that the microorganisms use Sb(V) as an electron acceptor for anaerobic respiration to produce useable energy (Abin and Hollibaugh 2014; Kulp et al 2014). More recently, Trumm et al (2015) presented the results from a pilot-scale SRB bioreactor for the treatment of Sb in mine drainage in New Zealand. The authors observed removal efficiencies for Sb of 29% at the beginning of the trial increasing up to 98% after 71 days of monitoring. Sampling of the substrate after the experiment confirmed that stibnite was produced by this SRB bioreactor.

4.2. COMPARISON WITH PROPOSED DISCHARGE LIMITS

Arsenic and selenium, and to a lesser extent antimony are generally included in effluent quality criteria (EQC) for the major mines in Yukon. The limits are site-specific and presented in Table 11 for the Bellekeno, Minto and Wolverine mine along with the proposed limits for Eagle Gold. It should be noted that the EQC cannot be directly compared between mines due to differences in receiving water characteristics. Thus, the values are only relative to potential efficiencies of the bioreactors.

Table 11. Existing effluent quality criteria for the Bellekeno, Minto and Wolverine mines and proposed limits for Eagle Gold.

Mine	Licence number	Licence date	Receiving environment	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Sb (mg/)	Se (mg/L)	Zn (mg/L)
Bellekeno	QX07-078	2011	Any watercourses	0.1	0.01	0.1	N/A	N/A	0.5
Minto	QZ96-006	2012	Minto Creek	N/A	0.0002	0.05	N/A	0.003	0.15
Wolverine	QZ04-065	2007	Go Creek	0.05	0.002	0.015	N/A	0.02	0.5
Eagle Gold	Proposed	N/A	Haggart Creek/Dublin Gulch	0.15	0.001	0.012	0.2	0.06	0.05

4.2.1. Arsenic

Discharge limits for As vary between 50 ug/L at the Wolverine mine, where As is generally not present in high concentrations in the receiving environment, to 150 ug/L proposed for Eagle Gold where As is found at higher concentrations. Figure 21 compares the concentrations from all four reactors with the discharge limits. Influent concentrations were not presented in this figure for clarity, but one should keep in mind that C10 to C12 were fed with approximately 5000 ug/L As, while C9 was fed with approximately 100 ug/L.

Interestingly, although the bioreactors C10 and C11 are duplicates and have both performed well with reductions of 96.0 and 97.7% respectively, only C11 was able to lower As concentrations to under the limit of 150 ug/L (grey dots in Figure 21). The concentration of As in the effluent of C10 was usually higher than this limit. However, it is interesting to note that C9, which was fed with effluent that had an average of 88.6 ug/L and was built with the exact same substrate as C10 and C11 was able to produce effluent closer to the limit of 50 ug/L. In other words, it is not due to lower efficiencies of the C10-C12 bioreactors that they are not complying with the 150 ug/L limit but because of a very high influent concentration (~5000 ug/L).

This presents an interesting option to produce compliant effluent. Two bioreactors could be setup in series: the first bioreactor removing the bulk of the As (from thousands ug/L down to a few hundreds); and the second bioreactor as the polishing step to bring the As concentrations down to below the discharge limit. Another option would be to increase the residence time of the bioreactor by either lengthening the reactor to increase its volume or by decreasing the flow rate.

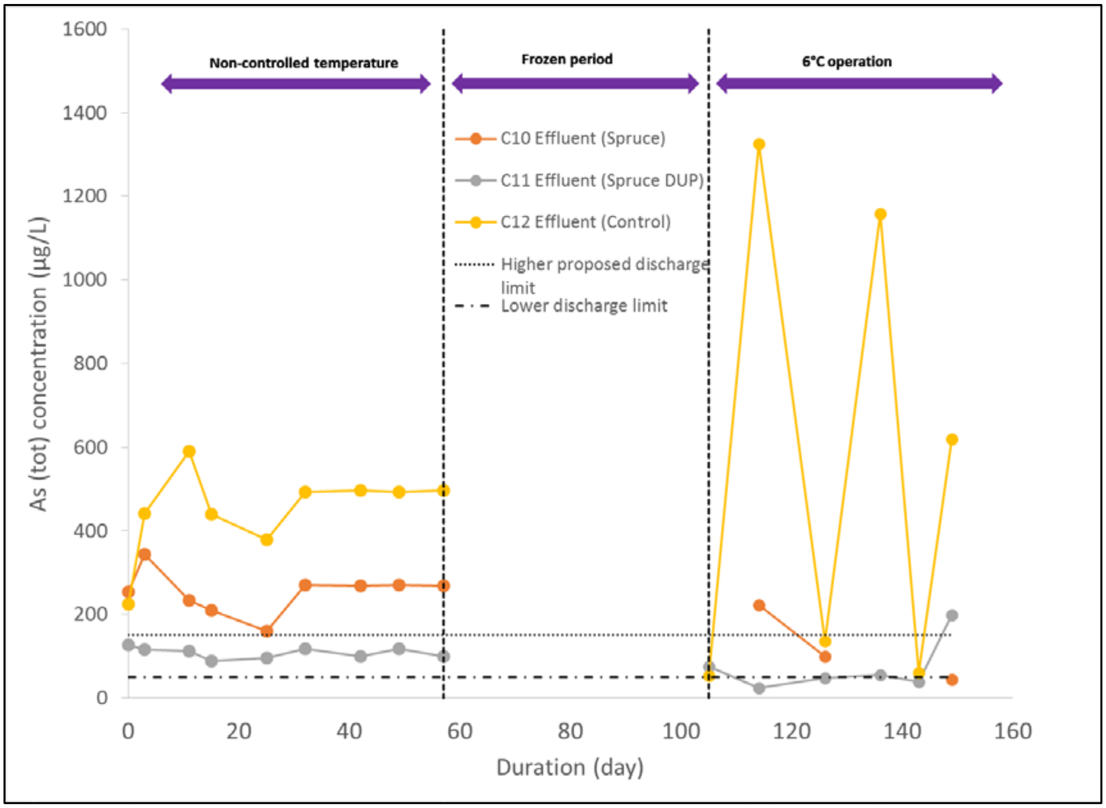

Figure 21 As concentrations in effluents from C9 to C12 bioreactors with relatively low (Wolverine mine) and high discharge limits (Eagle Gold).

4.2.1. Antimony

Antimony has not yet been regulated for major mines, however Victoria Gold has proposed a discharge limit of 200 ug/L. As discussed in section 3.2.4 and 3.3.4, the bioreactors produced effluents well below 200 ug/L and under 10 ug/L in all effluent samples analyzed.

4.2.2. Selenium

Discharge limits for selenium vary between 3 and 60 ug/L (Table 11) and Figure 22 shows the selenium concentrations in the effluent of the four reactors as they compare to the discharge limit of 3 ug/L (Minto). The effluent concentrations were generally under this limit of 3 ug/L, except the effluent of C12 (control) which was slightly above the limit (between 3 and 5 ug/L). Needless to say, these effluents would comply with the discharge limit of 20 ug/L which currently applies to the Wolverine mine, as well as with the proposed discharge limit of 60 ug/L for the Eagle Gold site. Both of these limits are beyond the scale of the axis in Figure 22 below.

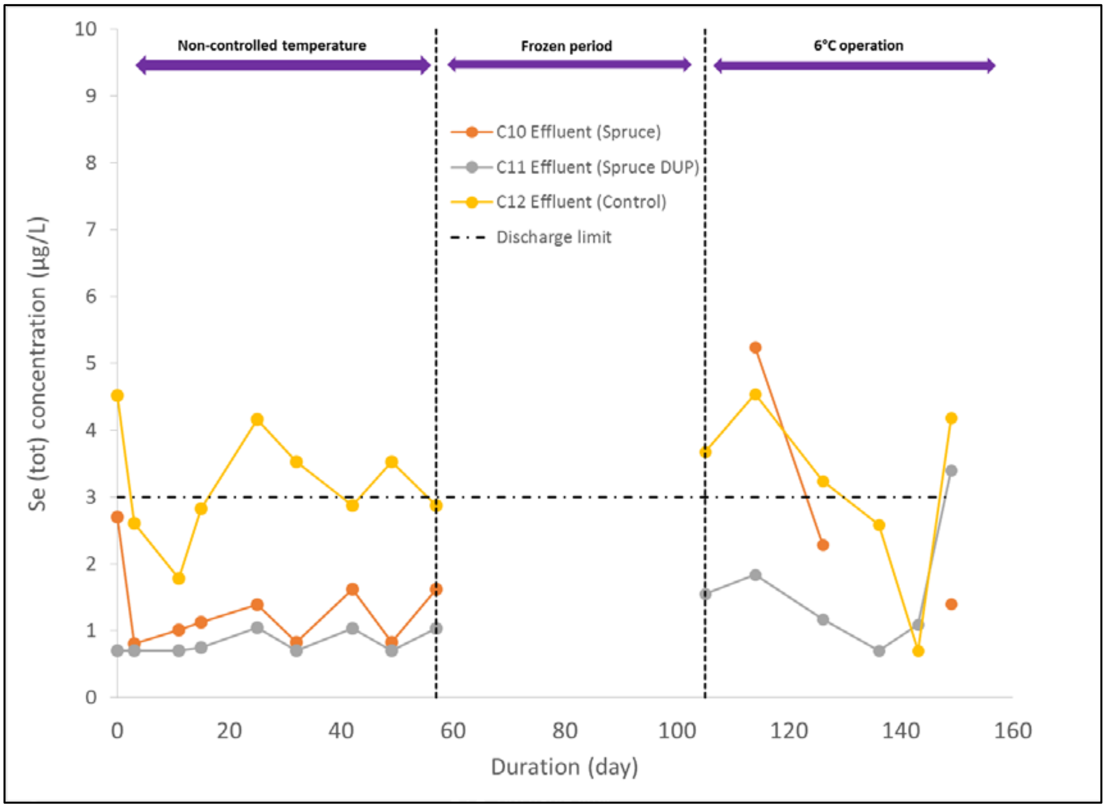

Figure 22. Se concentrations in effluents from C9 to C12 bioreactors with the lowest discharge limit currently in effect at Minto mine.

4.3. IMPACT OF FREEZE/THAW

4.3.1. Impact of freeze/thaw on metal concentrations

Table 12, Table 13 and Table 14 present the min, max, average and standard deviation before and after freeze/thaw for the three metals monitored. Due to column clogging, monitoring of C10 is missing a few samples after freeze/thaw. As expected, the average concentration after freeze/thaw in the control reactor C12 was higher than before, by 32%. However, it is surprising to see that the trend was opposite for C10 and C11, which were amended with wood. Notably, the freeze/thaw increased the variability in As concentration as indicated by the standard deviation. When the bioreactor was not wood-amended, the standard deviation increased by about 406% (from 113 to 572 ug/L). When using wood, the standard deviation increased by 44% (from 18 to 26 ug/L). On the other hand, no significant differences were observed between the average and variability of the Sb and Se concentrations before and after freezing.

In conclusion, freeze/thaw affected all of the bioreactors to some extent, but the addition of wood chips as part of the composition of the bioreactor seems to have been beneficial and to have reduced the impact of the freeze/thaw on the performances of the bioreactors. First, it improved the removal of As and Se and secondly, it decreased the variability of As concentrations following the freeze/thaw cycle.

Table 12. Min, Max, Average and standard deviation for As concentrations before (Phase 1, Day 0-57; n=8 for C10; C11 and C12) and after freeze/thaw (Phase 3, Day 105-154; n=4 for C10 and n=7 for C11 and C12)

		Total As (µg/L)		
		C10	**C11**	**C12**
Before freeze (Day 0-57)	**Min**	160.7	87.5	223.5
	Max	372.1	141.0	590.2
	Average	264.1	113.9	423.6
	Standard Deviation	68.5	18.0	113.3
After freeze/thaw (Day 105-154)	**Min**	44.4	24.0	54.1
	Max	221.8	209.4	1326.5
	Average	129.9	93.6	646.1
	Standard Deviation	75.9	26.7	570.3

Table 13. Min, Max, Average and standard deviation for Sb concentrations before (Phase 1, Day 0-57; n=8 for C10; C11 and C12) and after freeze/thaw (Phase 3, Day 105-154; n=4 for C10 and n=7 for C11 and C12)

		Total Sb (µg/L)		
		C10	**C11**	**C12**
Before freeze (Day 0-57)	**Min**	4.3	4.3	0.7
	Max	5.5	4.8	1.7
	Average	4.5	4.4	0.9
	Standard Deviation	0.4	0.2	0.4
After freeze/thaw (Day 105-154)	**Min**	4.3	4.3	0.7
	Max	4.3	4.3	3.5
	Average	4.3	4.3	1.8
	Standard Deviation	0.0	0.0	0.4

Table 14. Min, Max, Average and standard deviation for Se concentrations before (Phase 1, Day 0-57; n=8 for C10; C11 and C12) and after freeze/thaw (Phase 3, Day 105-154; n=4 for C10 and n=7 for C11 and C12)

		Total Se (µg/L)		
		C10	**C11**	**C12**
Before freeze (Day 0-57)	**Min**	0.8	0.7	1.8
	Max	3.3	1.7	8.2
	Average	1.6	0.9	3.8
	Standard Deviation	0.9	0.4	2.0
After freeze/thaw (Day 105-154)	**Min**	1.4	0.7	0.7
	Max	5.2	3.5	6.8
	Average	2.8	1.8	3.7
	Standard Deviation	1.7	0.4	1.9

4.3.2. Impact of freeze/thaw on removal efficiencies

In the Yukon, there is a distinct possibility of an on-site bioreactor freezing solid and the effect this will have on the ongoing performance of the bioreactor or on the microbial processes within it is not well understood. One of the objectives of this study was to assess the impact of freeze/thaw and compare the performance before and after a freeze/thaw cycle. In some cases freezing has been found not to affect SRB activity (Nordwick et al, 2006), however, in others it has been found that SRB do not develop at temperatures below 6°C (Panos et al, 2013). Observation of the results obtained so far clearly indicates that the bioreactors were still efficient after freeze/thaw, indicating that the microbial community was still alive and active. In his literature review, Chattopadhyay (2006) describes various mechanisms and explains how microorganisms are capable of surviving in sub-zero temperatures. Removal efficiencies before and after freeze/thaw were calculated and compared (Table 15) to assess the impact of freeze/thaw on the performances. Small differences (<10% variation) in performances were observed for As, Se and Sb in all four bioreactors except As in C9, for which removal efficiency was improved from 20% before freezing to 54% after freezing.

As discussed earlier (Section 3.3.2, page 26), sulfate consumption was not significantly affected by freeze/thaw in all the bioreactors containing spruce chips (C9, C10 and C11) but was reduced by 48% in C12, the non-amended bioreactor. This may indicate that the wood amendment helped to maintain sulfate reduction rates after freeze/thaw.

On the other hand, TOC reduction rates were very much affected by the freeze/thaw process. This is discussed in the next section.

Table 15. Removal efficiencies for As, Sb, Se, SO4 and TOC during operation before freezing (Phase 1, Day 0-57) and after freezing (Phase 3, Day 105-154) (Initial concentrations are presented in Table 4 and Table 5; <10% change are highlighted in green, >10% change are highlighted in yellow)

		Before freeze/thaw	**After freeze/thaw**	**Change**
		(Phase 1, Day 0-57)	**(Phase 3, Day 105-149)**	
As	C9	20%	54%	**+34%**
	C10	94%	98%	**+4%**
	C11	97%	99%	**+2%**
	C12	90%	88%	**-2%**
Sb	C9	95%	96%	**+1%**
	C10	85%	90%	**+5%**
	C11	85%	86%	**+1%**
	C12	85%	88%	**+3%**
Se	C9	91%	89%	**-2%**
	C10	100%	100%	**0%**
	C11	100%	100%	**0%**
	C12	99%	99%	**0%**
SO4	C9	96%	98%	**+2%**
	C10	70%	76%	**+6%**
	C11	72%	73%	**+1%**
	C12	65%	17%	**-48%**
TOC	C9	18%	-54%	**-72%**
	C10	17%	-39%	**-56%**
	C11	20%	-81%	**-101%**
	C12	15%	-34%	**-49%**

4.3.3. Impact of freeze/thaw on carbon retention and release

Addition of liquid organic carbon has been suggested by several authors to sustain SRB activities in cold temperatures (Alexco 2012, Gould et al 2012, Sobolewski 2010). Organic carbon is used by the SRB as a source of electron donor to perform the reduction of sulfate, leading to the production of sulfide (S^{2-}) and inorganic carbon (such as HCO_3^-) (Tsukamoto et al 2014). After freeze/thaw, carbon reduction was no longer observed and concentrations of carbon were generally higher in the effluents compared to the influents, although the carbon concentration in the influents was lower when the columns were operated in the fridge at 6°C due to the air circulation causing more evaporation.. Calculation of the loads of carbon into the columns ($[TOC]_{in}$ x V_{eff}) and being released by the columns ($[TOC]_{out}$ x V_{eff}) indicates that carbon was released by the bioreactors during Phase 3 (Table 16). It is suspected that the freeze/thaw might have impacted the structure of either the wood chips or the sediment used as the inoculum and this produced small particles that were transported with the water flowing in the first bed volume after it was restarted (between 20 and 30 days depending on the reactor). After the first bed volume flowed through the column, it appears that TOC concentrations followed the same decrease as the TOC concentration in the influent, except that it was delayed by a few weeks. Again, this closely relates to the time it takes for water to flow from the entrance to the exit of the column. Further operation and monitoring of the carbon levels will indicate if carbon is released on the long-term or just after thawing and if a portion of the carbon is consumed, as observed before freezing.

If TOC in the effluent originates from the ethanol which is not consumed by the microorganisms (i.e. ethanol is in excess), then the concentration of ethanol in the feed should be reduced. If the TOC measured originates from organic compounds released by the degradation of wood chips or sediments, then a polishing treatment such as an aerobic bioreactor might be required to lower the carbon content of the effluent and facilitate compliance with Biological Oxygen Demand (BOD) and toxicity tests criteria.

Table 16. Loads of carbon entering and exiting the bioreactors before freeze (Phase 1, Day 0-57) and after freeze/thaw (Phase 3, Day 105-149)

		Total Organic Carbon			
		C9	**C10**	**C11**	**C12**
Before freeze	TOC_{in} (mol)	2.34	2.51	2.48	1.54
(Day 0-57)	TOC_{out} (mol)	1.92	2.08	1.98	1.31
	% removal	18%	17%	20%	15%
After freeze/thaw	TOC_{in} (mol)	0.74	0.60	0.87	1.06
(Day 105-149)	TOC_{out} (mol)	1.13	0.83	1.60	1.42
	% removal	-54%	-39%	-81%	-34%

4.4. IMPACT OF WOOD CHIPS AMENDMENT

Following trends observed in previous reactor experiments conducted at YRC with bioreactors containing wood chips as a substrate (Janin 2014a, b), inclusion of wood in the substrate tends to lower the pH of the effluent. This study initially led to similar observations with the pH of the effluent from the wood-amended reactors (C10 and C11) being generally lower than the pH of the control reactor (C12). This is likely due to acidification of the water by the wood which releases protons and organic acid (Janin 2014a). However this trend changed after freeze/thaw, when the effluent from C12 tended to be lower than the effluent from C10 and C11 although some monitoring data are missing for C10 after freezing, when no flow was produced by the column C10 due to clogging issues.

In addition, the comparison between the spruce chip amended bioreactors C10 and C11 and the control, non-amended, bioreactor C12 allowed for the following observations:

- Unlike what was expected, the integration of 20% wood chips in the substrate did not increase the amount of carbon released by the bioreactors as indicated by the measure of TOC in the effluent (Figure 17, page 32). Either the potential release of organic acid by the wood was enough to lower the pH but not a significant quantity of organic carbon, or organic carbon consumption was slightly higher in the wood-amended bioreactor due to higher microbial activity.

- Comparison of the sulfate consumption might indicate that inclusion of wood may have promoted microbial growth and/or microbial activity in the bioreactor: 71% and 72% of sulfate was reduced by C10 and C11 respectively while only 50% was reduced by C12 (Section 3.3.2, page 26).
- Lower As concentrations in the effluent and overall higher As removal efficiency was observed when wood chips were used as part of the bioreactor filling composition, as indicated by Figure 14 (page 29) and by Table 10 (Page 34). C10 and C11 (wood-amended bioreactors) exhibited 96 and 98% removal As while C12 (non-amended) reduced As by 87%.
- Wood chips in the bioreactor did not notably affect removal efficiencies for Sb and Se (Table 10, page 34)
- As discussed in Section 4.3.1 (page 42), addition of wood chips as part of the composition of the bioreactor seems to have reduced the impact of the freeze/thaw on the performance of the bioreactors, lowering the variability of As concentrations in the effluent. The inclusion of wood may have promoted microbial growth and/or microbial activity in the bioreactor.

Overall, although minimal improvement was observed for Se and Sb removal, the use of wood appeared to have the most significant improvement on As removal. This aligns with the observations made in another study of lab-scale bioreactors reported by Janin (2014b). As discussed initially in a previous study (Janin and Harrington, 2013), it is thought that adding material with some adsorption capacity improves the reliability of bioreactors as the temperatures get colder since sorption mechanisms are not very temperature dependent. In a similar study, Janin and Harrington (2015) observed that addition of biochar, a material which displayed adsorption capacity for Cd, Cu and Zn, improved the performances of removal of these divalent metals by anaerobic bioreactors, again suggesting that integration of a porous material with sorption capacity helped with the reliability of the reactors when the temperature decreased.

5. CONCLUSIONS

Anaerobic bioreactors have been efficient at removing As, Sb and Se at cold temperatures and more importantly even after freezing and subsequent thawing and continued operation. However, the freezing and subsequent thawing of the columns may have disrupted the performance of the bioreactors to some extent, although the inclusion of wood in the composition of the substrate seemed to limit the impact of freeze/thaw on the efficiency of metal removal. TOC concentrations also became more erratic following freezing and the effluent concentrations were generally higher than the influent concentrations. Continued monitoring of the columns during the next phase will provide additional data to evaluate bioreactor stabilization following freezing and subsequent thawing.

Removal efficiencies of 87% to 97% of As and >99.1% of Se were observed with the C10-C12 bioreactors treating “worst case scenario” synthetic influent. This suggests that anaerobic bioreactors might be capable of handling a wide array of effluents ranging from low to high concentrations of As and Se.

While antimony is ubiquitous in the environment, its biogeochemical behavior is not well understood, especially in potential treatment technologies. This study demonstrated that bioreactors are capable of reducing Sb concentrations from water containing up to 0.1 mg/L. Further tests should focus on treatment of effluent with higher levels of Sb to better define the conditions for bioreactor performance. In the C9-12 reactors, Sb removal efficiencies were quite high particularly at higher influent concentrations. Sulfides were likely reacting with aqueous Sb in the effluent to form insoluble Sb. The C10-12 reactors had very similar removal efficiencies suggesting that perhaps sorption may be a less important removal mechanism for Sb; however, precise interpretation of the data was limited as most of the numbers were at or near the QL (4.3 ug/L) which masked the variability between the amendments.

6. RECOMMENDATIONS

This study has shown that anaerobic bioreactors have the potential to remove metalloids such as As, Se and Sb with high efficiency in laboratory-scale units over 5 months. Further testing and monitoring would strengthen this conclusion and further support the development of this technology for application in northern locations. Continued monitoring of the C9-C12 bioreactors is planned for an additional 4 months (March to June 2015) in the same conditions at 6°C except that liquid carbon addition will be stopped in May to assess the impact of ethanol on the performances in cold temperature.

Going beyond this study, various avenues would need further investigation, including:

- Testing of these bioreactors with higher Sb concentration in the influent
- Completion of the carbon mass balance to get a better understanding of where the liquid carbon provided to the system is used and how, and whether it is required or not
- Distinction between Particulate Metals (>0.45 um particles) and Dissolved Metals (<0.45 um particles) would help understand which fraction of the metals are best removed and this would provide additional information about the metal removal mechanisms
- Speciation of metal inside the substrate of a SRB bioreactor to characterize the products and better understand the mechanisms by which the metals are removed
- Characterization of the microbial community and its activity over a wide range of temperature to better understand how the temperature affects it and why metal removal rates are not so affected by temperatures
- Enlargement of the scale of this experiment and operation in the field would provide a more applicable suite of results

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APPENDIX 1 – MONITORING DATA

Table 17. pH in influents and effluents of C9-12 reactors over 154 of weekly monitoring

Sampling date	Duration	pH					
	(day)	C9 Influent	C10-C12 Influent	C9	C10	C11	C12
2-Oct-14	3	7.55	7.97	6.12	6.25	6.06	6.40
10-Oct-14	11	7.78	7.76	5.89	5.99	5.80	6.37
14-Oct-14	15	8.00	7.73	6.28	6.49	6.31	6.78
24-Oct-14	25	8.00*	6.69	5.86	6.14	6.00	6.40
31-Oct-14	32	7.95	8.45	6.25	7.99	7.08	6.68
10-Nov-14	42	7.67	8.20	5.81	6.32	6.11	6.69
17-Nov-14	49	7.38	7.59	5.89	6.12	6.16	6.30
25-Nov-14	57	7.68	7.59*	6.17	6.43	6.39	N/A
12-Jan-15	105	7.85	8.94	N/A	N/A	6.71	6.96
21-Jan-15	114	7.76	8.15	5.72	6.17	6.29	6.32
2-Feb-15	126	7.52	7.76	5.84	6.08	6.00	6.25
12-Feb-15	136	7.76	7.72	5.31	N/A	6.20	6.12
19-Feb-15	143	7.70	8.04	6.53	N/A	6.35	N/A
25-Feb-15	149	7.63	6.45	5.70	6.07	6.76	6.56
3-Mar-15	154	7.40	7.39	6.28	6.32	6.32	6.29
Min		**7.38**	**6.45**	**5.31**	**5.99**	**5.80**	**6.12**
Max		**8.00**	**8.94**	**6.53**	**7.99**	**7.08**	**6.96**
Average		**7.69**	**7.77**	**5.98**	**6.37**	**6.30**	**6.47**

Table 18. Sulfate concentrations in the influent and effluents from reactors C9- C12 over 154 days of weekly monitoring (Detection limit 4 mg/L)

Sampling date	Duration	SO_4 concentrations (mg/L)					
(dd-mm-yy)	(day)	C9 Influent	C10-12 Influent	C9	C10	C11	C12
29-Sep-14	0	369.42	1566.25	N/A	N/A	N/A	N/A
2-Oct-14	3	410.93	2681.26	14.32	97.74	100.86	149.14
10-Oct-14	11	403.10	2899.2	20.29	441.6	368.26	320.27
14-Oct-14	15	445.75	2778.01	6.81	599.76	657.84	539.04
24-Oct-14	25	445.75	2062.13	4.19	512.32	629.38	534.79
31-Oct-14	32	281.98	2632.96	N/A	692.65	682.68	765.87
10-Nov-14	42	175.13	880.41	4.32	641.79	631	1019.76
17-Nov-14	49	195.37	1236.29	4	732.02	735.39	1113.28
25-Nov-14	57	176.83	1236.29	6.45	610.35	688.82	700.42
12-Jan-15	105	211.17	1380.17	N/A	N/A	338.3	745.29
21-Jan-15	114	175.60	967.094	7.98	346.92	120.24	811.52
2-Feb-15	126	198.99	704.18	5.49	273.79	58.52	607.53
12-Feb-15	136	224.8	655.39	224.8	N/A	69.55	760.15
19-Feb-15	143	109.1	655.39	109.1	N/A	24.13	4.48
26-Feb-15	149	233.31	1148.61	233.31	139.27	30.99	735.24
3-Mar-15	154	178.82	177.12	38.4	351.82	124.54	926.19
Min		**109.10**	**655.39**	**4**	**97.74**	**24.13**	**4.48**
Max		**445.75**	**2899.2**	**233.31**	**732.02**	**735.39**	**1113.28**
Average		**270.48**	**1565.58**	**53.42**	**462.56**	**366.85**	**629.06**
Standard Deviation		**113.18**	**825.09**	**87.11**	**220.88**	**292.04**	**306.27**

Table 19. Total carbon concentrations of influents and effluents from C9-12 reactors over 154 days of monitoring

Sampling date	**Duration**	**TOC concentrations (mg/)**				**Influent**	
(dd-mm-yy)	**(day)**	**C9**	**C10**	**C11**	**C12**	**C9**	**C10-12**
2-Oct-14	3	1647.0	2014.7	2029.4	2243.9	2416.7	2615.7
10-Oct-2014	11	2288.3	2376.4	2145.3	2561.8	2298.7	2546.1
17-Oct-2014	15	1955.9	2449.1	2376.6	2422.5	2545.1	2352.0
24-Oct-2014	25	1868.3	1885.6	1835.0	1823.8	2545.1*	2225.2
31-Oct-2014	32	n/a	1728.0	1751.4	1844.8	2250.4	2464.6
10-Nov-2014	42	2051.8	2003.0	1845.9	1902.8	2203.4	2541.3
17-Nov-2014	49	1775.7	1860.3	1853.7	1894.3	2155.2	2523.4
25-Nov-2014	57	1863.5	1966.5	2007.6	2011.4	2446.2	2523.4*
12-Jan-2015	105	n/a	n/a	1843.0	1198.3	1989.6	2161.0
21-Jan-2015	114	3447.9	3242.5	2723.0	2637.3	1229.5	1283.7
2-Feb-2015	126	1931.1	1868.4	2087.4	1847.9	1743.9	597.5
12-Feb-2015	136	1612.8	n/a	1924.5	1905.9	698.8	474.7
19-Feb-15	143	873.5	n/a	1614.1	1552.4	131.0	474.7*
25-Feb-2015	149	1345.6	2141.4	932.2	966.7	2350.3	2647.8
3-Mar-2015	154	1974.3	2175.2	2098.7	2341.4	1422.7	1352.6
Min		**873.52**	**1728.04**	**932.24**	**966.74**	**131.00**	**474.68**
Max		**3447.87**	**3242.52**	**2723.04**	**2637.28**	**2545.14**	**2647.84**
Average		**1888.46**	**2139.65**	**1926.38**	**1915.27**	**1928.86**	**1959.35**
Standard Deviation		**610.33**	**426.38**	**399.22**	**470.49**	**738.08**	**853.25**

Table 20. Total metal concentrations of C9 (leach) effluent over 154 days of weekly monitoring

Sampling date	Duration	Total metal concentrations in C9 effluent (µg/L)			SO_4	pH
	(Day)	As	Sb	Se	(mg/L)	
QL		0.8	4.3	0.7	4	
2-Oct-14	3	110.5	4.30	0.7	14.32	6.12
10-Oct-14	11	41.4	4.30	1.5	20.29	5.89
14-Oct-14	15	32.1	4.30	0.7	6.81	6.28
24-Oct-14	25	36.2	4.30	0.7	4.19	5.86
31-Oct-14	32	59.8	4.30	0.7	N/A	6.25
10-Nov-14	42	38.0	4.30	0.7	4.32	5.81
17-Nov-14	49	47.9	4.30	0.7	4.00	5.89
25-Nov-14	57	43.6	4.30	0.7	6.45	6.17
12-Jan-15	105	N/A	N/A	N/A	N/A	N/A
21-Jan-15	114	86.3	4.30	1.52	7.98	5.72
2-Feb-15	126	36.5	4.30	0.85	5.49	5.84
12-Feb-15	136	67.9	4.30	0.83	224.8	5.31
19-Feb-15	143	N/A	4.77	2.92	109.1	6.53
25-Feb-15	149	44.7	4.30	1.41	233.31	5.70
3-Mar-15	154	33.9	4.30	N/A	38.4	6.28
Min		**33.9**	**4.3**	**0.7**	**4.0**	**5.3**
Max		**110.5**	**4.8**	**2.9**	**233.3**	**6.5**
Average		**53.7**	**4.3**	**0.9**	**48.4**	**5.9**
Standard Deviation		**23.8**	**0.1**	**0.6**	**87.1**	**0.3**

Table 21. Total metal concentrations of C10 (spruce) effluent over 154 days of weekly monitoring

Sampling date	Duration	Total metal concentrations in C10 effluent (µg/L)			SO_4	pH
	(Day)	As	Sb	Se	(mg/L)	
QL		0.8	4.3	0.7	4	
29-Sep-14	0					
2-Oct-14	3	372.11	5.54	3.27	97.74	6.25
10-Oct-14	11	254.26	4.30	2.70	441.6	5.99
14-Oct-14	15	344.68	4.30	0.80	599.76	6.49
24-Oct-14	25	233.16	4.30	1.01	512.32	6.14
31-Oct-14	32	210.50	4.30	1.13	692.65	7.99
10-Nov-14	42	160.69	4.30	1.39	641.79	6.32
17-Nov-14	49	269.85	4.30	0.83	732.02	6.12
25-Nov-14	57	267.79	4.30	1.62	610.35	6.43
12-Jan-15	105	N/A	N/A	N/A	N/A	N/A
21-Jan-15	114	221.78	4.30	5.25	346.92	6.17
2-Feb-15	126	99.06	4.30	2.29	273.79	6.08
12-Feb-15	136	N/A	N/A	N/A	N/A	N/A
19-Feb-15	143	N/A	N/A	N/A	N/A	N/A
25-Feb-15	149	44.44	N/A	1.40	139.27	6.07
3-Mar-15	154	154.51	4.30	2.08	351.82	6.32
Min		**44.4**	**4.3**	**0.8**	**97.7**	**6.0**
Max		**372.1**	**5.5**	**5.2**	**732.0**	**8.0**
Average		**219.4**	**4.4**	**2.0**	**453.3**	**6.4**
Standard Deviation		**94.5**	**0.4**	**1.3**	**213.0**	**0.5**

Table 22. Total metal concentrations of C11 (spruce duplicate) effluent over 154 days of weekly monitoring

Sampling date	Duration	Total metal concentrations in C11 effluent (µg/L)			SO_4	pH
	(Day)	As	Sb	Se	(mg/L)	
QL		0.8	4.3	0.7	4	
29-Sep-14	0					
2-Oct-14	3	141.0	4.81	1.7	100.86	6.06
10-Oct-14	11	127.0	4.30	0.7	368.26	5.80
14-Oct-14	15	115.2	4.30	0.7	657.84	6.31
24-Oct-14	25	112.9	4.30	0.7	629.38	6.00
31-Oct-14	32	87.5	4.30	0.7	682.68	7.08
10-Nov-14	42	95.9	4.30	1.1	631	6.11
17-Nov-14	49	117.8	4.30	0.7	735.39	6.16
25-Nov-14	57	98.9	4.30	1.0	688.82	6.39
12-Jan-15	105	75.5	4.30	1.5	338.3	6.71
21-Jan-15	114	24.0	4.30	1.8	120.24	6.29
2-Feb-15	126	48.3	4.30	1.2	58.52	6.00
12-Feb-15	136	54.5	4.30	0.7	69.55	6.20
19-Feb-15	143	39.3	4.30	1.1	24.13	6.35
25-Feb-15	149	198.7	4.30	3.4	30.99	6.76
3-Mar-15	154	209.4	4.30	3.5	124.54	6.32
Min		**87.5**	**4.3**	**0.7**	**100.9**	**5.8**
Max		**141.0**	**4.8**	**1.7**	**735.4**	**7.1**
Average		**95.5**	**4.3**	**1.2**	**366.9**	**6.3**
Standard Deviation		**46.0**	**0.1**	**0.7**	**292.0**	**0.3**

Table 23. Total metal concentrations of C12 (control) effluent over 154 days of weekly monitoring

Sampling date	Duration	Total metal concentrations in C12 effluent (µg/L)			SO_4	pH
	(Day)	As	Sb	Se	(mg/L)	
QL		**0.8**	**4.3**	**0.7**	**5**	
29-Sep-14	0					
2-Oct-14	3	326.51	6.97	8.2	149.14	6.40
10-Oct-14	11	223.48	4.30	4.5	320.27	6.37
14-Oct-14	15	441.31	4.30	2.6	539.04	6.78
24-Oct-14	25	590.17	4.30	1.8	534.79	6.40
31-Oct-14	32	439.08	4.30	2.8	765.87	6.68
10-Nov-14	42	379.11	5.90	4.2	1019.76	6.69
17-Nov-14	49	492.37	4.36	3.5	1113.28	6.30
25-Nov-14	57	496.99	4.30	2.9	700.42	N/A
12-Jan-15	105	54.06	4.30	3.7	745.29	6.96
21-Jan-15	114	1326.5	5.64	4.5	811.52	6.32
2-Feb-15	126	135.48	4.30	3.2	607.53	6.25
12-Feb-15	136	1158.78	4.30	2.6	760.15	6.12
19-Feb-15	143	60.73	4.30	0.7	4.48	6.56
25-Feb-15	149	620.18	4.30	4.2	735.24	6.29
3-Mar-15	154	1167.01	4.30	6.8	926.19	6.29
Min		**54.1**	**4.3**	**0.7**	**4.5**	**6.1**
Max		**1326.5**	**7.0**	**8.2**	**1113.3**	**7.0**
Average		**527.45**	**4.68**	**3.75**	**648.86**	**6.46**
Standard Deviation		**398.8**	**0.8**	**1.9**	**304.9**	**0.2**

Table 24. Sulfate concentrations of C9-C12 influents and effluents over 154 days of monitoring

Sampling date	**Duration**	**SO_4 concentrations (mg/L)**					
(dd-mm-yy)	**(day)**	**C9 Influent**	**C10-12 Influent**	**C9**	**C10**	**C11**	**C12**
29-Sep-14	0	369.42	1566.25	N/A	N/A	N/A	N/A
2-Oct-14	3	410.93	2681.26	14.32	97.74	100.86	149.14
10-Oct-14	11	403.10	2899.2	20.29	441.6	368.26	320.27
14-Oct-14	15	445.75	2778.01	6.81	599.76	657.84	539.04
24-Oct-14	25	445.75	2062.13	4.19	512.32	629.38	534.79
31-Oct-14	32	281.98	2632.96	N/A	692.65	682.68	765.87
10-Nov-14	42	175.13	880.41	4.32	641.79	631	1019.76
17-Nov-14	49	195.37	1236.29	4	732.02	735.39	1113.28
25-Nov-14	57	176.83	1236.29	6.45	610.35	688.82	700.42
12-Jan-15	105	211.17	1380.17	N/A	N/A	338.3	745.29
21-Jan-15	114	175.60	967.094	7.98	346.92	120.24	811.52
2-Feb-15	126	198.99	704.18	5.49	273.79	58.52	607.53
12-Feb-15	136	224.8	655.39	224.8	N/A	69.55	760.15
19-Feb-15	143	109.1	655.39	109.1	N/A	24.13	4.48
26-Feb-15	149	233.31	1148.61	233.31	139.27	30.99	735.24
3-Mar-15	154	178.82	177.12	38.4	351.82	124.54	926.19
Min		**109.10**	**655.39**	**4**	**97.74**	**24.13**	**4.48**
Max		**445.75**	**2899.2**	**233.31**	**732.02**	**735.39**	**1113.28**
Average		**270.48**	**1565.58**	**53.42**	**462.56**	**366.85**	**629.06**
Standard Deviation		**113.18**	**825.09**	**87.11**	**220.88**	**292.04**	**306.27**

APPENDIX 2- METAL ANALYSIS QUALITY CONTROL

YRC AA QC Report

VGC Columns 9-12 Influent and Effluent

Conditions	GF AAS	**Standards source**	SCP
Element	Se 196.03	**QC Source**	Perkin Elmer Mixed Std
Date	24/10/2014	**QC Frequency**	every 10 samples
Operator	HM	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9993
Detection Limit	0.68		

Sample ID	Absorbance (Corr)	Conc (ug/L)	QC Recovery (%)
blank	0.000487194		
1 ppb	0.001961169		
2 ppb	0.004667266		
5 ppb	0.012688935		
10 ppb	0.025438482		
25 ppb	0.062104194		
50 ppb	0.122908614		
Blank	-0.000453045	-0.193247163	
low level	0.002183181	0.929696067	92.96960668
high level	0.135461216	53.22381444	106.4476289
Oct 2 CM9	0.001604671	0.68358949	
Oct 2 CM10	0.007700376	3.267824999	
Oct 2 CM11	0.00392586	1.669976341	
Oct 2 CM12	0.019366302	8.158859919	
Oct 10 CM9	0.00350696	1.492178235	
Oct 10 CM10	0.006355031	2.699173867	
Oct 10 CM11	0.001555458	0.662645064	
Oct 10 CM12	0.010671745	4.520372014	
Oct 17 CM9	0.000553834	0.236089368	
Oct 17 CM10	0.00188331	0.802148977	
Blank	-0.000363187	-0.1549092	
low level	0.001921821	0.818532094	81.85320938
high level	0.12951122	51.06232636	102.1246527
Oct 17 CM11	-0.000668983	-0.285395047	
Oct 17 CM12	0.006143235	2.609564592	
Blank	0.00054505	0.232345917	
low level	0.002539448	1.081168375	108.1168375
high level	0.132814986	52.26434969	104.5286994

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VGC Columns 9-12 Influent and Effluent

Sample ID	Absorbance (Corr)	Conc (ug/L)	QC Recovery (%)
Conditions	GF AAS	**Standards source**	SCP
Element	Se 196.03	**QC Source**	Perkin Elmer Mixed Std
Date	4/11/2014	**QC Frequency**	every 10 samples
Operator	HM	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9999
Detection Limit	0.68		
Sample ID	**Absorbance (Corr)**	**Conc (ug/L)**	**QC Recovery (%)**
blank	-0.002802662		
1 ppb	0.002658879		
2 ppb	0.004365738		
5 ppb	0.011676684		
10 ppb	0.0229815		
25 ppb	0.056874798		
50 ppb	0.10424614		
Blank	0.000902398	0.374223465	
low level	0.002104646	0.873755863	87.37558625
high level	0.100796212	48.43828435	96.87656871
Sep 29 Infl CM9	0.001718889	0.713353959	
Sep 29 Infl CM10-12	0.012497926	524.0523522	
Oct 2 Infl CM9	0.001033625	42.86943041	
Oct 2 Infl CM10-12	0.011750188	492.3323888	
Oct 10 Infl CM9	0.000392621	16.27439471	
Oct 10 Infl CM10-12	0.011979719	502.0641706	
Oct 17 Infl CM9	0.000479547	19.87912583	
Oct 17 Infl CM10-12	0.01106481	463.300802	
Blank	-0.000387625	-0.160559783	
low level	0.002226799	0.924572743	92.45727433
high level	0.104372252	50.59757564	101.1951513
Oct 17 Infl 9	0.03991632	17.2597369	
Oct 10 Infl CM9	0.039128949	16.9025765	
Oct 2 Infl CM9	0.040757872	17.64237383	
Blank	0.001022961	0.373615941	
low level	0.002965261	1.086448726	108.6448726
high level	0.107521248	47.53908199	95.07816397
Oct 17 Infl 9	0.042002095	16.44082571	
Oct 10 Infl CM9	0.040443222	15.7875579	
Oct 2 Infl CM9	0.042328022	16.5778606	
Blank	0.000825489	0.301396166	
low level	0.002685849	0.983624026	98.36240264
high level	0.107963363	47.7763211	95.55264221

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VGC Columns 9-12 Influent and Effluent

Conditions	GF AAS	**Standards source**	SCP
Element	As 193.70	**QC Source**	Perkin Elmer Mixed Std
Date	18/12/2014	**QC Frequency**	every 10 samples
Operator	HM	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9998
Detection Limit	0.79		

Sample ID	Absorbance (Corr)	Conc (ug/L)	QC Recovery (%)
blank	-0.000246488		
1 ppb	0.003544172		
2 ppb	0.007967494		
5 ppb	0.020520018		
10 ppb	0.039929768		
25 ppb	0.106178294		
50 ppb	0.213156283		
blank	-0.000246736	-0.063675615	
low level	0.003544936	0.911725707	91.17257071
high level	0.204849043	47.65681623	95.31363245
CM10-12 infl Oct 24	0.141727288	6730.718367	
CM9 infl Oct 31	0.219970288	101.9312783	
CM10-12 infl Oct 31	0.110728021	5325.445834	
CM9 infl Nov 10	0.231210062	106.8318077	
CM10-12 infl Nov 10	0.190637559	4453.283836	
CM9 infl Nov 17	0.220843111	102.3123708	
blank	-0.000201417	-0.05197807	
low level	0.003737324	0.961041901	96.10419013
high level	0.205109077	47.71384414	95.42768827
CM10-12 infl Nov 17	0.186006474	4351.16068	
CM9 infl Nov 25	0.217946857	101.0474441	
blank	-0.000118282	-0.030521627	
low level	0.003981278	1.023552378	102.3552378
high level	0.204655625	47.61439477	95.22878955
CM9 infl Sep 29	0.194130212	45.30195196	
CM9 infl Oct 2	0.199078421	46.39005844	
CM9 infl Oct 10	0.209208435	48.61226917	
blank	-0.000238984	-0.061674765	
low level	0.003639135	0.935874371	93.58743708
high level	0.196781755	45.88524414	91.77048829
CM9 infl Oct 17	0.200115347	46.61785449	
CM10-12 infl Sep 29	0.122572327	5865.246976	
CM10-12 infl Oct 2	0.205163786	4772.584175	
CM10-12 infl Oct 10	0.190155789	4442.667655	
CM10-12 infl Oct 17	0.1781119	4176.682691	
CM9 Oct 2	0.044309799	110.4529886	
CM10 Oct 2	0.157611647	372.111714	
CM11 Oct 2	0.057004441	140.9570389	
CM12 Oct 2	0.137270345	326.5055083	
blank	0.000131766	0.033993494	

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VGC Columns 9-12 Influent and Effluent

Conditions	GF AAS	**Standards source**	SCP
Element	As 193.70	**QC Source**	Perkin Elmer Mixed Std
Date	18/12/2014	**QC Frequency**	every 10 samples
Operator	HM	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9998
Detection Limit	0.79		

Sample ID	Absorbance (Corr)	Conc (ug/L)	QC Recovery (%)
low level	0.003785058	0.973275226	97.32752255
high level	0.20617941	47.94853006	95.89706013
CM9 Oct 10	0.016267779	41.39091364	
CM10 Oct 10	0.1054851	254.2622124	
CM11 Oct 10	0.05118654	127.0285956	
CM12 Oct 10	0.092129359	223.4770219	
CM9 Oct 17	0.012568809	32.07635353	
CM10 Oct 17	0.145354692	344.6833002	
CM11 Oct 17	0.046266353	115.1819022	
CM12 Oct 17	0.188816017	441.3135437	
CM9 Oct 24	0.014185098	36.15301497	
CM10 Oct 24	0.096318364	233.1635682	
blank	-0.000336104	-0.086746317	
low level	0.003710598	0.954191925	95.41919251
high level	0.206190318	47.9509215	95.901843
CM11 Oct 24	0.045325231	112.9085517	
CM12 Oct 24	0.123376143	590.1745309	
CM9 Oct 31	0.023632214	59.7818647	
CM10 Oct 31	0.086537086	210.4990261	
CM11 Oct 31	0.034858208	87.45579304	
CM12 Oct 31	0.187803014	439.0796968	
CM9 Nov 10	0.014915242	37.99122974	
CM10 Nov 10	0.0653069	160.6938109	
CM11 Nov 10	0.038316457	95.90055677	
blank	-0.00017085	-0.04408863	
low level	0.003656225	0.940255211	94.02552105
high level	0.207023084	48.13346299	96.26692598
CM12 Nov 10	0.160750579	379.1120116	
CM9 Nov 17	0.01884978	47.86156753	
CM10 Nov 17	0.112292887	269.8492671	
CM11 Nov 17	0.047366225	117.8356956	
CM12 Nov 17	0.21206423	492.3749138	
CM9 Nov 25	0.017143522	43.58839993	
CM10 Nov 25	0.111393983	267.7949743	
CM11 Nov 25	0.039531463	98.85905337	
CM12 Nov 25	0.214173146	496.9885799	
blank	0.000100337	0.025885954	
low level	0.004013965	1.031926204	103.1926204
high level	0.206101826	47.93152129	95.86304259

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VGC Columns 9-12 Influent and Effluent

Conditions	GF AAS	**Standards source**	SCP
Element	Sb 217.58	**QC Source**	Perkin Elmer Mixed Std
Date	18/12/2014	**QC Frequency**	every 10 samples
Operator	HM	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9993
Detection Limit	4.3		

Sample ID	Absorbance (Corr)	Conc (ug/L)	QC Recovery (%)
blank	-0.000165333		
5 ppb	0.006001296		
10 ppb	0.012220544		
25 ppb	0.030033333		
50 ppb	0.060591024		
75 ppb	0.082955997		
100 ppb	0.107182522		
blank	0.000234876	0.189687214	
low level	0.00668589	5.438810771	108.7762154
high level	0.110499911	101.7934175	101.7934175
CM12 Oct 31	0.004812971	3.906993242	
CM9 Nov 10	0.002975901	2.410749024	
CM10 Nov 10	0.003924206	3.182347229	
CM11 Nov 10	0.00386235	3.131966872	
CM12 Nov 10	0.007243019	5.895721916	
CM9 Nov 17	0.001816003	1.46921439	
CM10 Nov 17	0.004381615	3.555110495	
CM11 Nov 17	0.00299485	2.426150491	
CM12 Nov 17	0.005363793	4.356827782	
CM9 Nov 25	0.002099764	1.699328328	
blank	0.00024037	0.194125541	
low level	0.006066114	4.931195369	98.62390738
high level	0.113130314	104.5674497	104.5674497
CM10 Nov 25	0.002058242	1.665647585	
CM11 Nov 25	0.000943363	0.762471082	
CM12 Nov 25	0.003425986	2.776760054	
CM9 infl Aug 27	0.068775097	120.308587	
CM10-12 infl Aug 27	0.004354904	35.33331909	
CM9 infl Sep 29	0.067509453	117.9138333	
CM10-12 infl Sep 29	0.005254647	42.67648121	
blank	0.000458535	0.370408753	
low level	0.006101482	4.960143203	99.20286406
high level	0.110147622	101.4233054	101.4233054
CM10-12 infl Oct 2	0.003106442	25.16866936	
CM9 infl Oct 10	0.067984344	118.8115244	
CM10-12 infl Oct 10	0.003462272	28.06284297	
CM9 infl Oct 17	0.066641461	116.275717	
CM10-12 infl Oct 17	0.003821162	30.98424331	
CM10-12 infl Oct 24	0.005897547	47.93256074	
CM9 infl Oct 31	0.092509393	83.3084516	

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VGC Columns 9-12 Influent and Effluent

Conditions	GF AAS	**Standards source**	SCP
Element	Sb 217.58	**QC Source**	Perkin Elmer Mixed Std
Date	18/12/2014	**QC Frequency**	every 10 samples
Operator	HM	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9993
Detection Limit	4.3		

Sample ID	**Absorbance (Corr)**	**Conc (ug/L)**	**QC Recovery (%)**
CM10-12 infl Oct 31	0.006745667	54.87807354	
blank	-0.000456408	-0.368313859	
low level	0.006067887	4.932646533	98.65293066
high level	0.292831766	351.5227324	351.5227324

Conditions	GF AAS	**Standards source**	SCP
Element	As 193.70	**QC Source**	Perkin Elmer Mixed Std
Date	6/2/2015	**QC Frequency**	every 10 samples
Operator	HM	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9998
Detection Limit	0.79		

Sample ID	**Absorbance (Corr)**	**Conc (ug/L)**	**QC Recovery (%)**
blank	-0.001344738		
1 ppb	0.002579397		
2 ppb	0.006014525		
5 ppb	0.015912401		
10 ppb	0.030586221		
25 ppb	0.076031004		
50 ppb	0.151213275		
blank	0.000155032	0.052396623	
low level	0.002916609	0.98505742	98.50574196
high level	0.146711167	47.83033533	95.66067065
Jan 12 CM11	0.022457334	75.47869307	
Jan 12 CM12	0.016058927	54.05984284	
Jan 21 CM9	0.025683744	86.25334227	
blank	0.000406791	0.137475964	
low level	0.002466316	0.833068735	83.30687354
high level	0.140928844	46.00942187	92.01884374
Jan 21 CM10	0.066712773	221.7778545	
Jan 21 CM11	0.007120316	24.02294553	
Jan 21 CM12	0.100585165	1326.468896	
Feb 2 CM9	0.010836015	36.52528695	
Feb 2 CM10	0.029526381	99.06335693	
Feb 2 CM 11	0.014330248	48.26131378	
Feb 2 CM 12	0.040489201	135.4755257	
Jan 12 infl CM9	0.036019444	120.6534775	
blank	-0.000223389	-0.075506789	
low level	0.002963283	1.000809259	100.0809259
high level	0.169513377	54.96171066	109.9234213
Jan 21 infl CM9	0.027214756	91.36013432	

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VGC Columns 9-12 Influent and Effluent

Conditions	GF AAS	**Standards source**	SCP
Element	As 193.70	**QC Source**	Perkin Elmer Mixed Std
Date	6/2/2015	**QC Frequency**	every 10 samples
Operator	HM	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9998
Detection Limit	0.79		

Sample ID	Absorbance (Corr)	Conc (ug/L)	QC Recovery (%)
Feb 2 infl CM9	0.00670353	22.61912361	
Jan 12 infl CM10-12	0.021952133	737.8999884	
Jan 21 infl CM10-12	0.156526996	5090.983022	
Feb 2 infl CM10-12	0.125531094	8227.1183	
blank	0.000359341	0.121441585	
low level	0.002530387	0.854696921	85.46969208
high level	0.166538872	54.03586787	108.0717357

Conditions	GF AAS	**Standards source**	SCP
Element	Sb 217.58	**QC Source**	Perkin Elmer Mixed Std
Date	24/2/2015	**QC Frequency**	every 10 samples
Operator	HM	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9974
Detection Limit	4.3		

Sample ID	Absorbance (Corr)	Conc (ug/L)	QC Recovery (%)
blank	-0.000562564		
5 ppb	0.007036531		
10 ppb	0.014859195		
25 ppb	0.036991685		
50 ppb	0.073092463		
75 ppb	0.10960289		
100 ppb	0.143411995		
blank	6.47E-05	0.044323096	
low level	0.008405633	5.760628149	115.212563
high level	0.147717598	101.8664695	101.8664695
C10-12 infl Aug 29	0.044776361	30.73628729	
C10-12 infl Sep 29	0.047126091	32.35262299	
C10-12 infl Oct 2	0.001869517	1.280862936	
C10-12 infl Oct 10	0.036824913	25.26914315	
C10-12 infl Oct 17	0.037618131	25.81435911	
C10-12 infl Oct 24	0.083600801	57.48637456	
C10-12 infl Oct 31	0.058407024	40.11728303	
C10-12 infl Nov 10	0.038192784	26.20936906	
C10-12 infl Nov 17	0.038998417	26.76318539	
C10-12 infl Nov 25	-1.93E-05	-0.013191986	
blank	0.000275075	0.188449202	
low level	0.008365958	5.733427649	114.668553
high level	0.144909112	99.91716988	99.91716988
C10-12 infl Jan 12	0.037915184	26.01854724	
C10-12 infl Jan 21	0.037372202	25.64531655	

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C10-12 infl Feb 2	0.08170657	56.17909648	
C10-12 infl Feb 12	0.048420777	33.24335835	
C9 infl Oct 10	0.018418183	126.2814888	
C9 infl Oct 17	0.01690041	115.8672777	
C9 infl Oct 24	-0.000102018	-0.698891604	
C9 infl Oct 31	0.013835597	94.84234048	
C9 infl Nov 10	0.012811022	87.81492536	
C9 infl Nov 17	0.012991466	89.05252006	
blank	0.000148087	0.10145131	
low level	0.007646667	5.240310064	104.8062013
high level	0.143998138	99.28499109	99.28499109
C9 infl Nov 25	0.012730939	87.26567201	
C9 infl Jan 12	0.013504846	92.57369464	
C9 infl Jan 21	0.014038428	96.23360217	
C9 infl Feb 2	0.014518815	99.52878985	
C9 infl Feb 12	0.015795248	108.2850928	
C9 infl Feb 19	0.017193471	117.8780071	
C11 Jan 12	0.004090364	2.802709551	
C12 Jan 12	0.005708591	3.911796362	
C9 Jan 21	0.002555489	1.7508966	
C10 Jan 21	0.005524536	3.785642552	
blank	-0.000277891	-0.190373326	
low level	0.007517301	5.151624889	103.0324978
high level	0.140629615	96.94782029	96.94782029
C11 Jan 21	0.003007757	2.060809781	
C12 Jan 21	0.008226354	5.637717985	
C9 Feb 2	0.001659836	1.13719341	
C10 Feb 2	0.003655981	2.505022389	
C11 Feb 2	0.004137755	2.835187097	
C12 Feb 2	0.004920875	3.371897937	
C9 Feb 12	0.000987035	0.676221078	
C11 Feb 12	0.00316846	2.170933158	
C12 Feb 12	0.00277387	1.900538574	
C9 Feb 19	0.006959115	4.768980305	
blank	0.000621386	0.425706864	
low level	0.006828392	4.679370057	93.58740114
high level	0.138807143	95.68363451	95.68363451
C11 Feb 19	0.001524709	1.044608253	
C12 Feb 19	0.00141208	0.967439316	
blank	-0.000247442	-0.16951396	
low level	0.00770551	5.280649224	105.6129845
high level	0.133747285	92.17486677	92.17486677

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VGC Columns 9-12 Influent and Effluent

Conditions	GF AAS	**Standards source**	SCP
Element	Se 196.03	**QC Source**	Perkin Elmer Mixed Std
Date	2/3/2015	**QC Frequency**	every 10 samples
Operator	IN	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9993/0.9996/0.9999
Detection Limit	0.68		

Sample ID	Absorbance (Corr)	Conc (ug/L)	QC Recovery (%)
blank	0.00164061		
1 ppb	0.001604458		
2 ppb	0.00359008		
5 ppb	0.010057758		
10 ppb	0.018660144		
25 ppb	0.047794841		
50 ppb	0.092231823		
Blank	0.000751479	0.411243543	
low level	0.002105593	1.151682614	115.1682614
high level	0.097901537	51.66669329	103.3333866
Jan 12 C9 in	0.02111723	11.46746037	
Jan 21 C9 In	0.020102846	10.92079299	
Feb 2 C9 In	0.021617281	11.73679153	
Feb 12 C9 In	0.02451963	13.29801373	
Feb 19 C9 In	0.025343639	13.74063941	
Feb 26 C9 In	0.022230503	12.06693906	
Jan 12 C10-12 In	0.045838368	24.66183681	
Jan 21 C10-12 In	0.049024146	26.34445156	
Feb 2 C10-12 In	0.068020388	36.29504274	
Feb 12 C10-12 In	0.05848915	31.31999005	
Blank	0.000545904	0.298766582	
low level	0.001744835	0.95449193	95.449193
high level	0.099835054	52.64974466	105.2994893
blank	0.001015097		
1 ppb	0.001143758		
2 ppb	0.004162703		
5 ppb	0.01048497		
10 ppb	0.019803135		
25 ppb	0.050398478		
50 ppb	0.104800994		
Blank	0.000263244	0.139799914	
low level	0.001633947	0.866239938	86.6239938
high level	0.101648464	47.87158165	95.74316329
Feb 26 C10-12 In	0.075161393	36.47612275	
Jan 21 C9	0.002874508	1.521553024	
Feb 2 C9	0.001606873	0.851915552	
Feb 12 C9	0.001569014	0.831883072	
Feb 19 C9	0.005543481	2.924515956	
Feb 26 C9	0.002658814	1.407761624	
Jan 21 C10	0.009998198	5.245419424	

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VGC Columns 9-12 Influent and Effluent

Conditions	GF AAS	**Standards source**	SCP
Element	Se 196.03	**QC Source**	Perkin Elmer Mixed Std
Date	2/3/2015	**QC Frequency**	every 10 samples
Operator	IN	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9993/0.9996/0.9999
Detection Limit	0.68		

Sample ID	Absorbance (Corr)	Conc (ug/L)	QC Recovery (%)
Feb 2 C10	0.004338533	2.292288327	
Feb 26 C10	0.002651476	1.403888872	
Blank	0.000384013	0.203905283	
low level	0.001849236	0.980110514	98.0110514
high level	0.106156967	49.74447365	99.48894729
Jan 12 C11	0.002920723	1.545925806	
Jan 21 C11	0.003475934	1.838515794	
feb 2 C11	0.002211991	1.171839609	
Feb 12 C11	0.000953246	0.505797818	
Feb 19 C11	0.002051113	1.086831295	
Feb 26 C11	0.006455724	3.401896593	
Jan 12 C12	0.00699063	3.681309742	
Jan 21 C12	0.008641903	4.541518269	
Feb 2 C12	0.006157867	3.246146324	
Blank	9.09E-05	0.04828154	
low level	0.001724523	0.91415491	91.41549101
high level	0.108222825	50.59640519	101.1928104
blank	0.000370837		
1 ppb	0.001691512		
2 ppb	0.004538876		
5 ppb	0.010264936		
10 ppb	0.02036174		
25 ppb	0.053476624		
50 ppb	0.114325718		
Blank	0.000311845	0.155086519	
low level	0.001830715	0.908777766	90.87777663
high level	0.116267434	50.70084907	101.4016981
Feb 12 C12	0.016379127	7.990150911	
Feb 19 C12	0.001405576	0.698095058	
Feb 26 C12	0.008504979	4.188126149	
Blank	-0.000110866	-0.055164166	
low level	0.001937639	0.961731485	96.17314853
high level	0.109301793	48.01858845	96.0371769

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VGC Columns 9-12 Influent and Effluent

Conditions	GF AAS	**Standards source**	SCP
Element	As 193.70	**QC Source**	Perkin Elmer Mixed Std
Date	4/3/2015	**QC Frequency**	every 10 samples
Operator	IN	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9988
Detection Limit	0.79		

Sample ID	Absorbance (Corr)	Conc (ug/L)	QC Recovery (%)
blank	-0.0006882		
5 ppb	0.023252203		
10 ppb	0.047630596		
25 ppb	0.10637027		
50 ppb	0.217324605		
blank	0.000278322	0.059054971	
low level	0.004520189	0.960903578	96.09035783
high level	0.208424417	48.69913613	97.39827225
Feb 12 C9 In	0.06659834	14.5572179	
Feb 19 C9 In	0.066965066	14.63981941	
Feb 26 C9 In	0.052650969	11.43602698	
Feb 12 C10-12 In	0.125652935	56.44708715	
Feb 26 C10-12 In	0.265944926	63.92668702	
Feb 12 C9	0.149537057	67.93487197	
Feb 19 C9	0.071260065	15.60928285	
Feb 26 C9	0.19290965	44.73661766	
blank	0.001171042	0.248572452	
low level	0.004505695	0.957816453	95.78164531
high level	0.209094838	48.87171138	97.74342277
Feb 26 C10	0.191726575	44.43688998	
Feb 12 C11	0.230707121	54.4959293	
Feb 19 C11	0.171345829	39.32667355	
Feb 26 C11	0.160097133	243.6571959	
blank	0.001142123	0.242430751	
low level	0.005038934	1.071424519	107.1424519
high level	0.20911087	48.87583966	97.75167931
Feb 12 C12	0.132848837	59.88108641	
Feb 19 C12	0.014173234	3.025871506	
Feb 26 C12	0.146325204	33.18748206	
blank	0.000450398	0.095573725	
low level	0.004774702	1.015122433	101.5122433
high level	0.202784628	47.2518205	94.50364101

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VGC Columns 9-12 Influent and Effluent

Conditions	GF AAS	**Standards source**	SCP
Element	As 193.70	**QC Source**	Perkin Elmer Mixed Std
Date	4/3/2015	**QC Frequency**	every 10 samples
Operator	IN	**QC Limits**	Low level: ±20%, High level: ±10%
Calibration equation	nonlinear through zero	**Correlation coefficient**	0.9991
Detection Limit	0.79		

Sample ID	Absorbance (Corr)	Conc (ug/L)	QC Recovery (%)
blank	-0.000453828		
1 ppb	0.004999255		
2 ppb	0.00914795		
5 ppb	0.023625915		
10 ppb	0.048388478		
25 ppb	0.108815272		
50 ppb	0.224746174		
blank	0.000720363	0.150297735	
low level	0.005085253	1.06271052	106.271052
high level	0.213457446	48.33609304	96.67218609
Feb 12 C12	0.054436756	1158.780558	
blank	-6.26641E-05	-0.013070572	
low level	0.005017208	1.048464159	104.8464159
high level	0.20936774	47.33236733	94.66473466
Feb 19 C12	0.003320041	69.33654482	
Feb26 C12	0.029409346	620.1768665	
Mar 2 C12	0.05481565	1167.012689	
Feb 12 C9In	0.271663108	125.9736028	
Feb 25 C11	0.09203031	198.7190298	
Feb 19 C12	0.028804839	60.72920625	
Feb 19 C9	0.155021804	1371.993197	
blank	5.90387E-05	0.012314941	
low level	0.005459311	1.141038753	114.1038753
high level	0.206027384	46.51498828	93.02997655