THE USE OF HAY AND SAWDUST TO PROMOTE THE REMOVAL OF SELENIUM AND NITRATE IN COAL MINE DRAINAGE: A SATURATED UP FLOW COLUMN EXPERIMENT

by

Nicholas Weste Dumaresq

B.Sc. McGill University, 2006
B.A.Sc. University of Northern British Columbia, 2011

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
IN
NATURAL RESOURCES & ENVIRONMENTAL STUDIES

UNIVERSITY OF NORTHERN BRITISH COLUMBIA

June 2018

Abstract

A saturated up-flow column experiment was conducted to compare the ability of locally-available organic amendments (hay and sawdust) to foster reducing conditions and attenuate permit-exceeding concentrations of sulfate, nitrate, and selenium in effluent from a British Columbia coal mine. Mine effluent was continuously passed through columns containing one or both amendments mixed with mine-sourced rock, and indicators of organic decomposition and redox conditions were quantified in influent and effluents. Over the 180-day trial, effluent from hay-amended columns exhibited the highest removal of target parameters (up to 99.9%, 98.6%, and 77.5% removal of nitrate, selenium, and sulfate, respectively), although performance decreased over time, suggesting possible long-term performance concerns. In contrast, sawdust-amended columns fostered only partial denitrification and no sulfate removal, which could be linked to the more recalcitrant nature of the organic matrix. Effluents from all columns amended with organics would require further treatment before discharge to a receiving environment.

Table of Contents

List of Figures

List of Tables

Glossary

Symbol	**Description**
Nomenclature	
ABA	Acid Base Accounting
ALS	ALS Environmental Laboratories
ANFO	Ammonium Nitrate Fuel Oil
BC	British Columbia
BCR	BioChemical reactor
BOD	Biological Oxygen Demand
CMWR	Crushed Mine Waste Rock
CoA	Criteria of Acceptability
COC	Contaminant of Concern
CRM	Certified Reference Material
D-	Dissolved
DNRA	Dissimilatory Nitrate Reduction to Ammonia
DOC	Dissolved Organic Carbon
dw	Dry Weight
e^-	Electron
e.g.	Exempli Gratia
E. coli	*Escherichia coli*
EFL	Enhanced Forestry Lab at the University of Northern British Columbia
E_h	Oxidation/Reduction Potential
$\Delta G^{\circ\prime}$	Standard Gibbs Free Energy
HDPE	High-Density PolyEthylene
IAP	Ion Activation Product
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ID	Inner Diameter
K_{sp}	Equilibrium Solubility Constant
LCS	Laboratory Control Samples
llnl	Lawrence Livermore National Laboratory PHREEQC database
Lorax	Lorax Environmental Services
MB	Method Blank
MDL	Method Detection Limit
minteq.v4	Minteq International Inc. PHREEQC database
MoE	Ministry of Environment
MS	Matrix Spike
NIST	National Institute of Standards and Technology
NEBC	North East British Columbia

NSERC	Natural Sciences and Engineering Research Council of Canada
OD	Outer Diameter
ORP	Oxidation/Reduction Potential
PES	Polyethersulfone
PHREEQC	Geochemical Equilibrium Modelling Software
ppb	parts per billion
ppm	Parts Per Million
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
QAQC	Quality Assurance & Quality Control
Redox	Reduction-Oxidation
RPD	Relative Percent Difference
RPM	Revolutions per Minute
SI	Saturation Index
T-	Total
TN	Total Nitrogen
TOC	Total Organic Carbon
Trent	Trent University Water Quality Center
UNBC	University of Northern British Columbia
USEPA, EPA	United States Environmental Protection Agency
UV	Ultraviolet
VCB	Verified Clean Bottle
WQG	Water Quality Guideline
ZVI	Zero Valent Iron

Chemicals

Ag	Silver
Al	Aluminum
As	Arsenic
Ba	Barium
Bo	Boron
C	Carbon
Ca	Calcium
$CaCO_3$	Calcium Carbonate
Cd	Cadmium
CH_2O	Formaldehyde
$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$	Redfield Molecule
Cl^-	Chloride
CO_2	Carbon Dioxide
Co	Cobalt
Cr	Chromium

Cu	Copper
F^-	Fluoride
Fe	Iron
Fe(II)	Ferrous Iron with an oxidation number of (+2)
Fe(III)	Ferric Iron with an oxidation number of (+3)
FeOOH	Goethite
FeS_2	Pyrite
H	Hydrogen
H_2O	Water
H_3O^+	Hydronium Ion
H_2S	Hydrogen Sulfide
H_2SO_4	Sulfuric Acid
Hg	Mercury
HNO_3	Nitric Acid
HPO_4^-	Hydrogen Phosphate
Mg	Magnesium
Mn	Manganese
MnO_2	Manganese Dioxide, Mn(IV)
Mo	Molybdenum
N	Nitrogen
N_2	Nitrogen Gas
NaOH	Sodium Hydroxide
NH_3	Ammonia
NH_4^+	Ammonium
NH_4NO_4	Ammonium Nitrate
Ni	Nickel
NO	Nitrogen Monoxide
NO_2	Nitrogen Dioxide
NO_2^-	Nitrite
NO_3^-	Nitrate
N_2O	Nitrous Oxide
O	Oxygen
O_2	Oxygen Gas
P	Phosphorous
Pb	Lead
S	Sulfur
S^0	Elemental Sulfur, $S_{(0)}$
S^{2-}	Sulfide
S^2_n	Polysulfides
$S_2O_3^{2-}$	Thiosulfate
$S_nO_6^{2-}$	Polythionates

SO_3^{2-}	Sulfite
SO_4^{2-}	Sulfate
Sb	Antimony
Se	Selenium
Se^0	Elemental Selenium, $Se_{(0)}$
Se^{2-}	Selenide
SeO_3^{2-}	Selenite, $Se_{(IV)}$
SeO_4^{2-}	Selenate, $Se_{(VI)}$
Si	Silicon
Sr	Strontium
Tl	Thallium
U	Uranium
Zn	Zinc
$Zn(O_2C_2H_3)_2$	Zinc Acetate

Units of Measure

"	Inch
°C	Degree Celsius
cm	Centimeter
cm^3	Cubic Centimeter
g	Gram
kg	Kilogram
kJ	Kilojoule
km	Kilometer
L	Liter
m^2	Square Meter
mg	Milligram
min	Minute
mL	Millilitre
mm	Millimeter
mM	Millimole
mV	Millivolt
nm	Nanometer
µg	Microgram
µm	Micrometer

Acknowledgement

This research was funded jointly and generously by Walter Canadian Coal Partnership (no longer in operation), a subsidiary of Walter Energy, Inc. and the Natural Sciences and Engineering Research Council of Canada, through an Engage Grant awarded to my supervisor, Dr. Mike Rutherford. The funding of these partners, and the guidance (and patience) of Dr. Rutherford have been greatly appreciated. The help and direction of Al Martin, of Lorax Environmental, and his willingness to have Lorax technical staff provide guidance through difficult times has also been of tremendous value. The efforts of Dr. Joselito Arocena were very helpful in shaping the course of the experiment, and the availability and support of Dr. Bill McGill to help finalize the thesis have also been instrumental. The support provided by the curators of the Enhanced Forestry Laboratory, John Orlowsky and Doug Thompson, have benefited the research. The wisdom of Dr. Jack Adams in assisting with the experimental design in its early stages was appreciated. Lastly, the various technical staff at the University of Northern British Columbia who have provided laboratory access, instrument demonstrations, method explanations, and overall technical support deserve recognition.

Section 1: Introduction and Literature Review

1.1 Brule Mine and Need for Research

The Brule open-pit coal mine (Brule Mine) is located in the eastern foothills of the Rocky Mountains (Peace River Regional District) approximately 57 kilometers (km) by road south of Chetwynd, British Columbia (BC). Mine access is via Highway 29, approximately 25 km south of Chetwynd by way of the Sukunka Forest Service Road, and then 12 km along the Blind Creek Road (Walter Energy, 2015). The mine is currently owned by Conuma Coal Resources Limited and produces a premium low volatile pulverized coal injection product.

Open pit coal mining operations consist of blasting, stripping, excavating, trucking and dumping large quantities of waste rock (Dreher & Finkelman, 1992). During the mining process, large pits are created in the landscape (Hochbaum & Chen, 2000), which are then partially backfilled with fragmented waste rock. The porosity, grain size and typically unsaturated characteristics of waste rock make this material susceptible to oxidative weathering, sulfide (S^{2-}) mineral oxidation and associated metal leaching (Dreher & Finkelman, 1992). In the context of coal mines in BC, naturally-occurring, relatively insoluble selenium (Se) is associated with pyrite (FeS_2) and can oxidize to more soluble oxyanions[1] on the freshly exposed surfaces of the fragmented waste rock (Kennedy, at al., 2012). This geological weathering can produce elevated concentrations of soluble Se

---

[1] Oxyanion: an ion with the generic formula $A_xO_y^{z-}$ (where A represents a chemical element and O represents an oxygen atom)

oxyanions (selenate - SeO_4^{2-} and selenite - SeO_3^{2-}) and sulfate (SO_4^{2-}) in drainages reporting from waste rock facilities (Wellen, et al., 2015). As a result of blasting activities, elevated concentrations of nitrate (NO_3^-), an oxyanion of nitrogen (N), are also a common feature to coal mine waste rock drainages (Tiwary, 2001). The high concentrations of each of these specific contaminants of concern (COCs) pose risks to aquatic receptors through chronic and acute toxicity. In this regard, Se, SO_4^{2-}, and NO_3^- in effluents are of concern to mines, surrounding communities, First Nations, and local, provincial, and federal regulatory bodies.

Over time, the void spaces in the backfilled mining pits may be filled with water from surface and groundwater inflows. These pits are then referred to as 'saturated backfills'. Saturated backfills have been shown to attenuate soluble Se and NO_3^- from mine contact waters through microbially mediated processes, due to the long residence time of water in the pits and the presence of organic carbonaceous wastes which result in suboxic environments (Bianchin, et al., 2012). There is therefore an interest in studying conditions which promote microbial populations in suboxic saturated backfill environments and the corresponding attenuation of NO_3^- and Se from mine contacted waters. A greater understanding of biogeochemical processes occurring in mine effluents may lead to more effective Se and NO_3^- management strategies at the Brule Mine as well as in the mining industry as a whole.

This research seeks to provide a greater understanding of the processes that lead to the anaerobic attenuation of oxyanions of N, Se, and S from Brule Mine effluents with the long-term goal of helping the mine develop operational scale-technologies for lowering concentrations of these COCs in discharge effluents.

The following section will provide an overview of reduction-oxidation (redox) processes and the role of specific COCs in balancing reactions resulting from the oxidation of organic matter. Specifics of the COCs are also presented, including their source and concentration in the effluent of the Brule Mine, speciation and oxidation/reduction potential (ORP, E_h) behaviour, and behaviour in waste rock environments. Aqueous concentrations of these COCs in the downstream receiving environment of the Brule Mine have been presented based on data current to May 2015. Nitrate and S are discussed individually, with specific attention directed at the ability of S to form metal-sulfide precipitants. Selenium is the focus of the research and is presented in greater detail. A brief review of existing research into the bioremediation of these COCs, bacterially mediated organic decomposition, and column reactor design is also presented.

1.2 Redox Processes Associated with Oxidation of Organic Matter

In a balanced reaction, the gain of electrons (reduction) of a compound (or other chemical species) is offset by a corresponding loss of electrons (oxidation) of another compound, resulting in no change in total charge. In natural systems, biomass decomposition is mostly an oxidative process, and releases electrons for which acceptors must be present (Van Der Weijden, 1992). The half-reaction for the oxidation of a low molecular weight organic carbon (C) molecule is shown by **Equation (1)** below:

(1) $\{CH_2O\} + 5\ H_2O \rightarrow CO_2(g) + 4\ H_3O^+(aq) + 4\ e^-$

In aerobic aquatic systems, bacteria use oxygen (O) as their terminal electron acceptor, which balances **Equation (1)**, as shown in the corresponding reducing half reaction in **Equation (2)** (Van Der Weijden, 1992).

(2) $O_2(g) + 4\ H_3O^+ + 4\ e^- \rightarrow 6\ H_2O$

Anaerobic aquatic systems, or low O_2 environments, such as sediments, wetland soils, stratified and lentic environments, and areas with insufficient O_2 recharge, have conditions in which communities of bacteria using other electron acceptors can proliferate (Nealson & Meyers, 1992; Schlesinger & Bernhardt, 2013). These communities catalyze reactions in which electrons produced during organic decomposition (**Equation (1)**) are reduced via alternate electron acceptors. **Equations (3)** through **(7)** below show the corresponding reduction half-reactions specific to alternate electron acceptors: NO_3^- **(3)**, manganese dioxide (MnO_2) **(4)**, goethite (FeOOH) **(5)**, SeO_4^{2-} **(6)**, and SO_4^{2-} **(7)**. The stoichiometric coefficients would need to be modified to provide a balanced reaction with **Equation (1)**:

(3) $2\ NO_3^-(aq) + 12\ H_3O^+ + 10\ e^- \rightarrow N_2(g) + 18\ H_2O$[2]

(4) $MnO_2(s) + 4\ H_3O^+ + 2\ e^- \rightarrow Mn^{2+}(aq) + 12\ H_2O$

(5) $FeOOH(s) + 3\ H_3O^+ + e^- \rightarrow Fe^{2+}(aq) + 5\ H_2O$

(6) $SeO_4^{2-}(aq) + 8\ H_3O^+ + 6\ e^- \rightarrow Se(s) + 12\ H_2O$

(7) $SO_4^{2-}(aq) + 9\ H_3O^+ + 8\ e^- \rightarrow HS^-(g) + 13\ H_2O$

While numerous other electron acceptors exist, the ones depicted in **Equations (3)** through **(7)** are distinct because they undergo a phase change during reduction (Martin, et al., 2013).[3] This attribute is important; aqueous concentrations of N, Se, and S will decrease as conditions become more suboxic, while those of iron (Fe) and manganese (Mn) will increase.

---

[2] The reduction of NO_3^- to nitrogen gas (N_2) is referred to as denitrification.

[3] Note: it is not the conversion between redox states that drives phase change, and no phase change is absolute. Each chemical species in the system must reach thermodynamic equilibrium, which is governed principally by pressure and temperature. This equilibrium will determine its phase. For the purposes of the discussion presented herein, standard temperature and pressure conditions (298.15K, 101325 Pa) will be assumed. The relatively high melting and low boiling points of some chemical species (i.e. elemental Se melts at approximately 494 K, while N_2 boils at 77.2 K) will dictate their state. The National Institute of Standards and Technology (NIST) website provides compound-specific (but not ion-specific) constants for calculating equilibrium states at as functions of pressure and temperature.

Comparing time-sequenced ion concentrations of a liquid undergoing a chemical transformation can provide insight into ORP dynamics. In this regard, profiling for this suite of redox reaction products has been used to evaluate E*h* gradients in stratified marine and lacustrine settings, as well as within suboxic groundwater systems (Spencer & Brewer, 1971).

The order in which alternate electron acceptors are reduced is theoretically linked to the magnitude of the Gibbs free energies associated with their respective reduction potentials (Froelich, et al., 1979). In natural systems, the reduction of O_2 produces a large Gibbs free energy and will be preferentially reduced over less energetic electron acceptors. When O_2 levels are depleted, ORP will decrease, favouring the next most efficient electron acceptor (Froelich, et al., 1979). The amount of energy obtained from the reaction is proportional to the magnitude of the Gibbs free energy, and as a result, the reaction sequence follows the hierarchy of energy yields. Relative amounts of energy, obtained from the oxidation of hydrogen (H) as O_2, NO_3^-, SeO_4^{2-}, SeO_3^{2-}, and SO_4^{2-} are reduced, are displayed in **Table 1.1.**[4] According to this data, NO_3^- should be reduced after O_2, but before SeO_4^{2-}.

Table 1.1: Potential reactions and Gibbs free energies for reduction of selected oxidized compounds with concurrent oxidation of H, reproduced from Nerenberg & Rittman (2004)

Compound	Probable Reduction Reaction(s)	$\Delta G°'$ (KJ $(e^-)^{-1}$)*
O_2	$O_2 + 2\ H_2 \rightarrow 2\ H_2O$	-123
NO_3^-	$2\ NO_3^- + 5\ H_2 + 2\ H^+ \rightarrow 1\ N_2 + 6\ H_2O$	-112
SeO_4^{2-}	$SeO_4^{2-} + 3\ H_2 + 2\ H^+ \rightarrow Se^0 + 4\ H_2O$	-71
SeO_3^{2-}	$HSeO_3^{2-} + 2\ H_2 + H^+ \rightarrow Se^0 + 3\ H_2O$	-65
SO_4^{2-}	$2\ SO_4^{2-} + 8\ H_2 + 3\ H^+ \rightarrow H_2S + HS^- + 8\ H_2O$	-19

* $\Delta G°'$ is the standard Gibbs free energy at pH = 7

---

[4] The table reproduced from Nerenberg & Rittman (2004) does not show the Gibbs free energies of the reductions of Fe and Mn, as they were not displayed in the referenced material. These reactions are important for the scope of this experiment and are discussed later in the thesis

Depending on the form of oxidized Mn mineral (i.e. birnessite, pryolusite) Mn reduction (not shown in **Table 1.1**) can occur preferentially or subsequently to that of NO_3^- (Froelich, et al., 1979). In a flowing aerated stream, rates of O_2 replenishment often match those of reductive consumption, and as such, redox levels necessary for the reduction of SO_4^{2-} may not be achieved.

When O_2 concentrations fall below bacteria specific thresholds, facultative bacteria can utilize NO_3^- as a terminal electron acceptor. Examples of facultative anaerobic genera which accomplish NO_3^- reduction are *Pseudomonas*, *Micrococcus*, *Bacillus*, and *Achromobacter* (Camargo, et al., 2005). Similarly, bacteria will generally reduce NO_3^- before SeO_4^{2-} (Steinberg, et al., 1992). Contrary to the above general assertions regarding the dependence of electron acceptor consumption on the energy yield, specific bacteria have been shown to reduce electron acceptors in alternate orders due to their specific affinities or inhibitions (Marietou, et al., 2009). Examples of bacteria deviating from the order suggested by the available energies include *Thiosphaera pantotropha*, which uses NO_3^- concurrently as the electron acceptor in oxygenated environments (Robertson & Kuenen, 1984), and *Thauera selenatis*, which use SeO_4^{2-} and NO_3^- concurrently (Oremlund, et al., 1999). Recent publications have also shown the existence of obligate aerobic bacteria that reduce $Se_{(IV)}$ (selenite) in the presence of O_2 (Zheng, et al., 2014).

In the above discussion, chemical speciation is discussed as a function solely of ORP (or E_h), measured in millivolts (mV), however speciation is also a function of pH. E_h-pH diagrams show the dominant aqueous and stable solid phases of an element on a plane as a function of redox potential on the vertical axis, and pH on the horizontal axis (Takeno, 2005). By knowing these variables, the oxidation state of an element can be reasonably predicted.

This can lead to greater understanding of the solute transport in groundwater, if elemental concentrations, pH, and ORP are known (Takeno, 2005). E_h-pH diagrams for Se, N, and S are shown in **Appendix A**, as found in Takeno (2005). These diagrams can be referenced in the upcoming discussion of oxidation states of these elements. Speciation in the field often differs with respect to thermodynamic predictions as a result of kinetic constraints and biological activity (Sharma, et al., 2015).

Stoichiometrically balanced reactions showing the oxidation of a representative organic molecule are shown below (Van Der Weijden, 1992). This organic molecule $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$ takes into account observed C:N: phosphorous (P) ratios in pelagic phytoplankton and is referred to as the Redfield molecule (Van Der Weijden, 1992). Parameters measured in standard laboratory analysis and used to elucidate redox conditions are displayed in bold font, while the electron acceptors in each reaction are underlined.

(8) $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ \underline{\mathbf{O_2}} \rightarrow 106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 18\ H^+ + 122\ H_2O$

(9) $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 84.8\ \underline{\mathbf{NO_3^-}} \rightarrow 7.2\ CO_2 + 98.8\ HCO_3^- + 16\ \mathbf{NH_4^+} + 42.4\ N_2 + HPO_4^{2-} + 49.6\ H_2O$

(10) $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236\ \underline{MnO_2} + 364\ CO_2 + 104\ H_2O \rightarrow 470\ HCO_3^- + 8\ N_2 + 236\ \mathbf{Mn^{2+}} + HPO_4^{2-}$

(11) $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 424\ \underline{FeO_2H} + 756\ CO_2 \rightarrow 862\ HCO_3^- + 8\ N_2 + 16\ NH_4^+ + 424\ \mathbf{Fe^{2+}} + HPO_4^{2-} + 120\ H_2O$

(12) $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ \underline{\mathbf{SO_4^{2-}}} \rightarrow 39\ CO_2 + 67\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} + 53\ \mathbf{HS^-} + 39\ H_2O$

The above reactions are important, as they show both how organics (like the Redfield molecule) can be decomposed (oxidized) and how corresponding electron acceptors are reduced. **Equations (8)** through **(12)** show that the P in the original organic molecule will be released as soluble hydrogen phosphate (HPO_4^{2-}), and as such, is an indication of organic decomposition. **Equations (9)** through **(12)** show that the suboxic diagenesis of organic matter results in the formation of bicarbonate (Herbert, et al., 2000) which will increase alkalinity (Van Der Weijden, 1992). This is simplified in **Equation (13)** which shows a low molecular weight organic C molecule being oxidized and SO_4^{2-} being reduced. Note that this bicarbonate production is a result of the reaction in **Equations (9)** through **(12)**, but not **(8)**, indicating that an increase in alkalinity is indicative of anaerobic and facultative systems. Also shown in **Equations (9)**, **(11)** and **(12)** is the production of ammonium (NH_4^+), which is an important biproduct of decomposition reactions.

(13) $2\ CH_2O + SO_4^{2-} \rightarrow 2\ HCO_3^- + H_2S$

While Se has not been shown, it could be represented similarly to S in **Equation (12)**. **Equation (14)** shows an approximation of SeO_4^{2-} reduction in the presence of the Redfield Molecule.

(14) $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ SeO_4^{2-} \rightarrow 39\ CO_2 + 67\ HCO_3^- + 16\ NH_4^+ + HPO_4^{2-} + 53\ HSe^- + 39\ H_2O$

1.3 Nitrogen

1.3.1 Overview and Source at the Brule Mine

Nitrogen is an important element which affects the species composition, diversity, dynamics, and functioning of aquatic and terrestrial ecosystems (Vitousek, et al., 1997). Nitrogen is used in many industrial processes ranging from fertilizer manufacture to explosives manufacturing. It is a main component in the commonly used mining explosive Ammonium Nitrate Fuel Oil (ANFO). Both pure phase ANFO and ANFO slurries were used at the Brule Mine to fracture consolidated rock and access the coal deposits (source: site investigations). ANFO is composed of more than 90% prilled ammonium nitrate (NH_4NO_3), the remainder being fuel oil, and the exact mix varies by producer (Orica, 2015). Slurries are composed of NH_4NO_3 and other chemicals held in suspension. Ammonium nitrate is extremely soluble in water (1183 g L^{-1}), with the dissolved product potentially becoming an aqueous mixture of NH_4^+ and NO_3^- ions that can be toxic to aquatic organisms (Pommen, 1983). Nitrate and ammonia (NH_3) effects are similar in their toxicity to salmonids and are likely to be found together as a result of explosive use (Pommen, 1983).

Nitrate toxicity to aquatic invertebrates is correlated positively to both concentration and exposure times (Camargo, et al., 2005), and negatively to body size (Camargo & Ward, 1992). Nitrate sensitivity is greater in freshwater aquatic organisms than marine animals and its main toxic effect on freshwater invertebrates is due to its conversion of O_2 bearing pigments (e.g., hemoglobin, hemocyanin) to forms that can no longer bind O_2 (e.g., methemoglobin) (Camargo, et al., 2005). Nitrate, nitrite (NO_2^-), and NH_3 resulting from explosive use can affect aquatic life in multiple ways which are not mutually exclusive: they can serve as nutrients for aquatic organisms (including plants), they can have direct toxic effects on animals, or they can directly or indirectly lower dissolved oxygen (DO) levels (e.g. through eutrophication or nitrification) (Pommen, 1983).

During detonation, trace amounts of unconsumed ANFO are deposited on waste rock and ore. Under complete combustion (ideal) conditions, all N in ANFO and slurries will become gaseous N_2. But, under normal, less ideal conditions, an equivalent of 6% of explosive-sourced N can be available for leaching in the form of NO_3^-, NO_2^- and NH_3 (Pommen, 1983). Small concentrations of intermediary compounds, resulting from incomplete combustion or detonation, can also be produced as nitrogen monoxide (NO), nitrous oxide (N_2O), and nitrogen dioxide (NO_2). Nitrogen oxides and NH_4^+ are expected to be released as gas into the air, but a small fraction will likely stay in the waste rock and become dissolved in the water. These compounds and NO_2 then either oxidize directly or indirectly (via intermediary compounds) to NO_3^- in water. Incomplete combustion can result from several factors including explosive wetness, poor handling and spillage, and faulty detonation sequences resulting in missed holes (Morin & Hutt, 2009).

1.3.2 Speciation and Redox Behaviour

Nitrogen can occur in many oxidation states, each with varying levels of toxicity. The states that are relevant to this experiment are primarily: NO_3^- (+5), NO_2^- (+3), and NH_4^+ (-3), with less important states being, NO (+2), N_2O (+1), and N_2 (0) (Camargo, et al., 2005). In biological material, N is almost exclusively found in its fully reduced state, N (-3) (Cabello, et al., 2004).

In the presence of high concentrations of S^{2-}, an alternate NO_3^- reduction pathway may take place. It has been suggested that dissimilatory nitrate reduction to ammonium (DNRA) results from the inhibition of regular denitrification (Soomo & Gardner, 2002). Recent research indicates that using acetate as the substrate (electron donor), NO_3^- limiting conditions result in a proliferation of DNRA activities, whereas in substrate limiting conditions, denitrification bacteria dominate. In conditions of limited NO_3^- and substrate, both processes are possible, and co-occurrence will result in complete reduction of NO_3^- (Van den Berg, et al., 2016).

Studies have shown that *Desulfobulbus propionicus*, a species of chemoautotrophic bacteria, and the facultative chemolithoautotroph *Thioploca* species are able to oxidize S^{2-} in the presence of NO_3^- and NO_2^- in controlled laboratory experiments (Dannenberg, et al., 1992; Otte, et al., 1999). When hydrogen sulfide (H_2S) was tested for its ability to enhance NO_3^- reduction, its presence resulted in greater NH_4^+ production (Brunet & Garcia-Gil, 1996). The direct coupling of Fe oxidation to denitrification and or NO_3^- reduction to NH_3 as a result of anaerobic enzymatic action has also been observed (Weber, et al., 2006). Conversely, NH_3 oxidation to NO_2^- can be paired with Fe (or alternatively Mn) reduction (Kuypers, et al., 2018). The same freshwater sediment bacteria that reduce ferric iron (Fe(III)) can subsequently oxidize it coupled with NO_3^- reduction (Weber, et al., 2006).

1.3.3 Behaviour in waste rock environments

Cumulative explicit N mass balances cannot easily be verified for ANFO explosions, as these are open systems and the atmosphere (79% N_2) provides a large source and sink of N. Multiple processes also occur simultaneously, often rapidly, making it challenging (if not impossible) to use changes in the concentration of any particular species to quantify individual processes and sources of various N constituents (Morin & Hutt, 2009).

A study of ANFO and slurry use at a BC open pit coal mine found that approximately 95% of the N discharged in mine effluents could be traced back to explosive use and that wet conditions increased explosive-N losses to the environment (Ferguson & Leask, 1988). Another study of these explosives, also in BC open pit coal mines, found that most of the effluent N was in the form of NO_3^--N (87%), with NH_3-N (11%) and NO_2^--N (2%) concentrations comparatively small (Pommen, 1983).

An assessment of the behaviour of N at a BC open pit coal mine found that the majority of explosive related N released into the environment came from waste rock. Waste rock sourced N accounted for 60-100% of N found in the receiving river, depending on the season, and an estimated 45% of the total N entering groundwaters and rivers (Pommen, 1983).

Nitrate concentrations in the receiving waters of the Brule Mine have been increasing, peaking at 40.6 milligram (mg) per liter (L) in the month of August 2014, exceeding maximum BC Water Quality Guideline (WQG) for the protection of freshwater life of 32.8 mg L^{-1}, and the 30-day average WQG of 3.0 mg L^{-1} (Nordin, et al., 2009; Walter Energy, 2015). At the Brule Mine, a NO_3^- management plan was developed in 2013 at the request of regulators, but its implementation did not, over the course of 2013 and 2014, halt the increasing annual average concentrations noted at the mine (Walter Energy, 2015). A photo provided in **Appendix B** shows ANFO dripped on the ground between blast holes on an active blasting pattern at the mine.

Average NO_2^- concentrations have been increasing in the receiving water of the mine on an annual basis since 2006 (Walter Energy, 2015), but did not exceed the WQG which is calculated as a function of chloride (Cl^-) concentration (Nordin, et al., 2009):

1.4 Sulfur

1.4.1 Overview

Sulfur, a chalcogen, is present in igneous and sedimentary rocks in its reduced form, S^{2-} (Meays & Nordin, 2013). Sulfur occurs in coal deposits in inorganic forms typically including S^{2-} and SO_4^{2-} (Calkins, 1994). Sulfur is also present in coal in organic forms, which are mostly components of the macromolecular network (Calkins, 1994). The S contained in coal originates from seawater, fresh water, vegetation and extraneous mineral matter (Ryan & Ledda, 1997). Different exposures to these sources is a factor leading to the variability of S content in coals formed at different times and different locations. Sulfur present in concentrations greater than a few tenths of a percent likely results from a depositional environment where brackish or sea water, containing SO_4^{2-}, has permeated the formation (Calkins, 1993). Bacterial reduction produces H_2S, which then reacts with the metals in the water to produce metal-sulfides. An example of this is Fe reacting with S^{2-} in the water to produce FeS_2. Hydrogen sulfide can also react with organics to produce organic S compounds (Calkins, 1994). Pyrite can also be formed synergistically in the early stages of coal formation (Diehl, et al., 2012). Pyrite can be locally enriched in potentially toxic trace elements such as Se, arsenic (As), mercury (Hg), lead (Pb) and nickel (Ni) (Diehl, et al., 2012).

Unweathered FeS_2-containing rock and coal surfaces are exposed to geoclimatic forces after blasting and stripping. Oxidized S enters the water table as a result of the reaction shown in **Equation (15)**. This reaction shows a S^{2-} (in this case FeS_2) combining with oxygen to yield SO_4^{2-}, which occurs predominantly at neutral pH (Neculita, et al., 2007):

(15) $FeS_2\ (s) + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$

Factors such as pH, temperature, surface area and the presence of Fe and S oxidizing bacteria can affect the rate of FeS_2 oxidation (Nordstrom, 1982). The conversion of SO_4^{2-} to S^{2-} is reversible and governed by biological, physical, and chemical factors (Meays & Nordin, 2013). In reducing conditions, the presence of aqueous S^{2-} complexes with Fe(II) and the Fe-S^{2-} compounds precipitate quickly out of solution (Couture, et al., 2010).

Anthropogenic sources of SO_4^{2-} are not limited to mining; the ion is released to aquatic environments through wastes from other industries including smelting, kraft pulp and paper and textile production, tanneries, agriculture, and waste water treatment (Meays & Nordin, 2013). Studies have noted a link between elevated SO_4^{2-} concentrations and increased catharsis in humans, but the World Health Organization has not proposed a health-based guideline for SO_4^{2-} in drinking water (World Health Organization, 2004).

1.4.2 Speciation and Redox Behaviour

Sulfur can occupy a large range of oxidation states between -2 to +6, which makes it important in a variety of biogeochemical processes (Luther, et al., 1985). Bacterially mediated S reduction has been studied extensively. In O_2 depleted aquatic systems, SO_4^{2-} is usually the most abundant water-soluble electron acceptor (Knossow, et al., 2015). Sulfide oxidation can occur in aqueous systems either microbially or abiotically and result in the formation of SO_4^{2-} or numerous intermediary oxidative compounds including polysulfides (S^{2-}_n), elemental S (S^0), thiosulfate ($S_2O_3^{2-}$), polythionates ($S_nO_6^{2-}$), and sulfite (SO_3^{2-}) with S oxidation states of 0, 0, jointly -2 and +6, variable depending on *n*, and 4, respectively (Knossow, et al., 2015).

1.4.3 Behaviour in waste rock environments

Pyrite oxidation to soluble S compounds occurs in unsaturated backfill and can be a significant source of groundwater and surface water contamination (Molson, et al., 2005). The rate of FeS_2 oxidation in waste rock environments is often limited by both S^{2-} supply and O_2 at the mineral grain surface (Molson, et al., 2005). In saturated, lentic environments, FeS_2 oxidation is limited as the rate of O_2 diffusion in water is approximately four orders of magnitude less than in air. Fine grain sizes in the waste rock environments can retain moisture after precipitation events, limiting O_2 permeation, and in turn FeS_2 oxidation, while larger grain size fragments tend to dry quicker (Molson, et al., 2005). Conversely, fine grain sizes have significantly more reactive surface areas (per unit volume) than coarse fragments, which increase FeS_2-O interactions. Another factor affecting the rate at which contaminants flow to the environment in saturated environments is the development of preferential flow paths through the waste rock environment, as backfills likely display heterogenous physical characteristics.

Sulfate concentrations in the receiving waters of the Brule Mine increased leading up to 2014 and peaked at 406 mg L^{-1} in the month of July 2014 but did not exceed the WQG (Walter Energy, 2015). The WQG 30-day average concentration for the protection of freshwater life is an increasing stepped function proportional to hardness levels (mg L^{-1} $CaCO_3$) (Meays & Nordin, 2013). Hardness levels observed in the receiving water of the mine correspond to a SO_4^{2-} WQG of 429 mg L^{-1} (Walter Energy, 2015).

1.4.4 Metal-Sulfide Precipitation

Metal-sulfide precipitation is a process that has been studied at length for its applications in hydrometallurgical treatment of ores and effluents (Lewis, 2010). In engineered systems, S^{2-} precipitation can be induced using solid, liquid, and gaseous S^{2-} sources, (Lewis, 2010). Metal-sulfide compounds can be present as complexes, nanoclusters, or colloids. **Equation (13)** which is shown again below, shows the production of both bicarbonate and H_2S (Herbert, et al., 2000).

(13) $2\ CH_2O + SO_4^{2-} \rightarrow 2\ HCO_3^{-} + H_2S$

Aqueous H_2S and other dissolved metals and non-metals including ferrous iron (Fe(II)), As, Cadmium (Cd), Cobalt (Co), Copper (Cu), Ni, Pb, and Zn may react together and precipitate as thermodynamically stable sulfides with low solubilities, (Herbert, et al., 2000; Jong & Parry, 2003) as shown in **Equations (16)** through **(19)** for a metal M^{2+} (Lewis, 2010):

(16) $H_2S \leftrightarrow HS^- + H^+$

(17) $HS^- \leftrightarrow S^{2-} + H^+$

(18) $M^{2+} + S^{2-} \leftrightarrow MS(s)$

(19) $M^{2+} + HS^- \leftrightarrow MS(s) + H^+$

pH largely governs the concentrations of the various S species in the above equations (H_2S, HS^-, and S^{2-}). The combination of a high H_2S vapour pressure and Fe-S^{2-} precipitation precludes a mass balance of aqueous components in an open system from occurring due to S losses to both gaseous and solid phases.

Reducing conditions which drive the solubilisation of reduced Mn, Fe, and As species (discussed further in **Section 1.6**) also result in increased S^{2-} concentrations. Reduced Fe(II) will consume the available soluble S^{2-} species initially, and other metals may be sequestered through co-precipitation with, or adsorption onto Fe-S^{2-} minerals (Couture, et al., 2010). In the case of As specifically, only when all available Fe(II) has become complexed with S^{2-} will reduced As ions become available to complex the remaining aqueous S^{2-}, forming As-S^{2-} minerals (Couture, et al., 2010). Couture, et al. (2010) discuss a comprehensive list of studies that point to the importance of As adsorption onto Fe oxyhydroxides, but also point out that temperature and the presence of natural organic matter can greatly reduce rate of adsorption of the former onto the latter. Hydrogen sulfide, bacteria and other reductants can also increase concentrations of metals adsorbed to Fe hydroxides via reductive dissolution of Fe(III) to the more soluble Fe(II).

1.5 Selenium

1.5.1 Overview & Presence in Geologic Material

Selenium is a metalloid that occurs in four oxidation states (-2, 0, +4, and +6), all of which can be found in soils (Lussier, et al., 2003). Selenium and S have similar chemistries and are both located in group 16 of the periodic table (Seby, et al., 2001). The higher two oxidation states of Se are commonly found as oxyanions SeO_3^{2-} (+4) and SeO_4^{2-} (+6). Selenium is found in both organic and inorganic forms (Hansen, et al., 1998). At high ORP (above 450 mV) and neutral pH, SeO_4^{2-} predominates (Masscheleyn, et al., 1990). Selenate, the most oxidized form, has high solubility and low adsorption capacities (Seby, et al., 2001), and exists as a tetrahedral oxyanion in solution as biselenate or SeO_4^{2-} (Peak, 2006). At moderate redox potentials, SeO_3^{2-} is the dominant species, and its mobility is governed by adsorption/desorption on metal hydroxide surfaces (Seby, et al., 2001). Selenite (+4) exists as a weak diprotic acid (H_2SeO_3, $H_2SeO_3^{1-}$, $H_2SeO_3^{2-}$) depending on the solution pH (Peak, 2006).

In **Section 1.4.1**, the inclusion of FeS_2 during coal formation was discussed, and its re-oxidization was linked to the presence of SO_4^{2-} in the mine effluents. In the following section, a similar correlation will be established between the presence of FeS_2 and the presence of aqueous Se. Selenium concentrations in FeS_2 can vary over many scales, from microscopic to regional, due to varying concentrations of Se distributed in the different morphologies of FeS_2. Selenium concentrations vary also because of the multiple S oxidation and reduction cycles during formation of the FeS_2 (Diehl, et al., 2012). These cycles are based on changing biotic, chemical and physical conditions (Diehl, et al., 2012). In an examination of the distribution and origin of trace elements in coal samples from the United

Kingdom, a ratio of 0.566:1 (Se to FeS_2) was established between concentration increases of Se and concentrations of FeS_2 (Spears, et al., 1999). The presence of Se in the absence of FeS_2 also indicated that not all of the Se was contained within FeS_2 (Spears, et al., 1999). The chemical oxidation of Se-bearing FeS_2 produces SeO_4^{2-} and SeO_3^{2-}, which are highly soluble and exist primarily as ions in solution or adsorbed to charged surfaces of clay minerals (Kulp & Pratt, 2004).

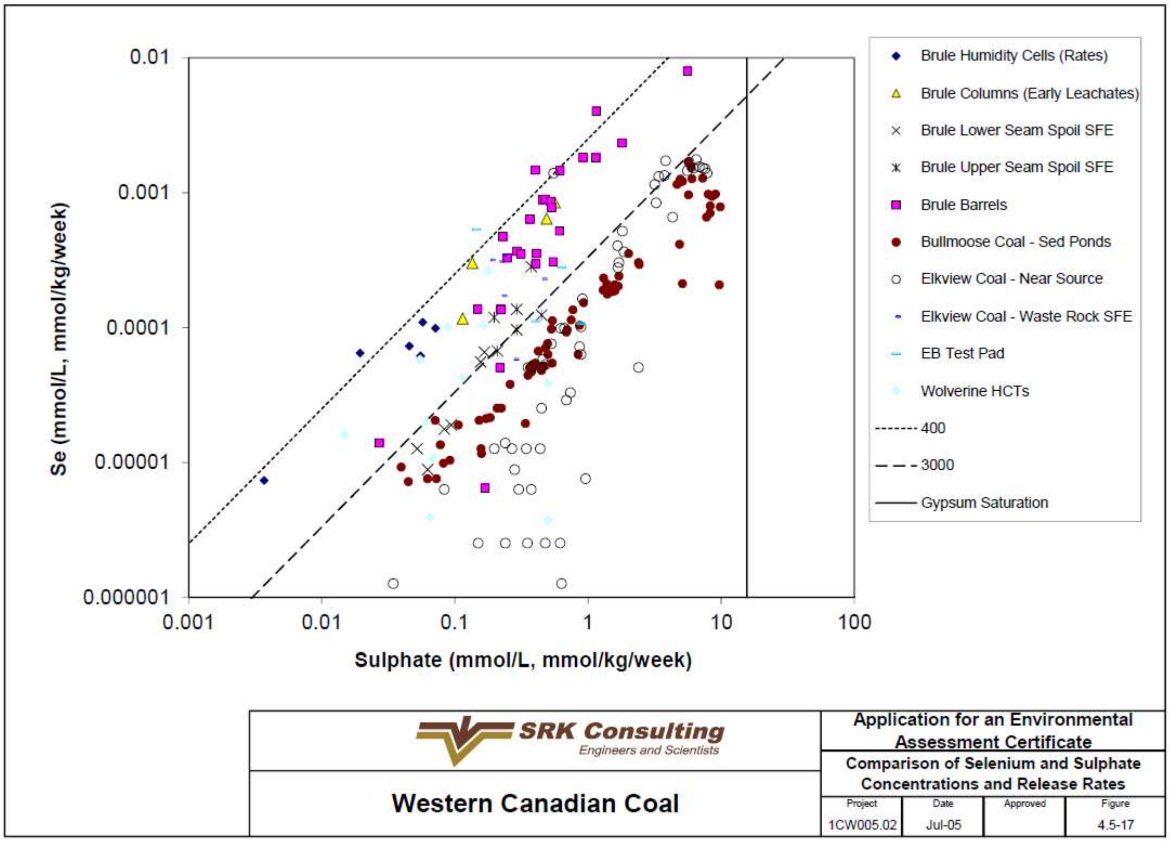


Figure 1.1: Se-SO_4^{2-} correlation in multiple Brule Mine test and discharge effluents, reproduced from Western Canadian Coal (2006)

The almost linear correlation between SO_4^{2-} and Se in various test and discharge locations was documented in the Brule Mine's Environmental Assessment Application, shown in **Figure 1.1** (Western Canadian Coal, 2006), which suggest oxidation of S and Se at the mine occurs concurrently.

In coal samples taken from Kentucky, Alabama and West Virginia, Se concentrations in FeS_2-filled veins had concentrations of 200 parts per million (ppm), 80 ppm, and 270 ppm, respectively (Diehl, et al., 2012), but whole ore concentrations were not given. Brule Mine Se concentrations range from 1.6-4.2 ppm in rocks and 0.5-2.1 ppm in coal, based on 2012-2013 analyses (Walter Energy, 2015), which are substantial given the 0.05 ppm crustal abundance of the earth (Lakin, 1973; Taylor, 1964). These concentrations are not unique to north east British Columbia (NEBC); a mine in southeastern BC has an average Se concentration in coal of 1.9 ppm. By comparison, the global Se average in coal is 1.0-1.6 mg Se kg^{-1}, and some mines in Russia and China have concentrations of up to 43 mg Se kg^{-1} (Lussier, et al., 2003; Sharma, et al., 2015). Other sources of Se mobilization include agricultural practices in previously submerged areas. Anthropogenic modification of hydrologic regimes has caused substantial changes in the biogeochemical cycle of naturally occurring soil trace elements (Lemly, et al., 1993). As shales erode and oxidize, Se-rich soils can form, and subsequent large-scale irrigation practises can mobilize oxidized Se into surface waters. In California, the collection of low-Se concentration irrigation drainage in a reservoir where evaporative losses were significant led to a concentration of Se in which teratogenic effects on wildlife were observed in the early 1980s (Green, et al., 2003).

Elemental Se usually remains in the form of nanoparticles in colloidal suspension, resulting from the presence of extracellular polymeric substances and or proteins (Buchs, et al., 2013; Jain, et al., 2017)

1.5.2 Toxicity

Bioavailability and toxicity of Se depend heavily on the oxidation state, with SeO_3^{2-} being 5-10 times more toxic than SeO_4^{2-} (Amweg, et al., 2003). Organic-Se^{2-} is taken up by algae 1000 times more easily than inorganic forms, making it the most bioavailable form of Se (Pahler, et al., 2007).

The environmental ecotoxicology of Se is complicated because it has a narrow margin of safe concentrations between deficiency and toxicity (to aquatic organisms). Selenium has three levels of bioactivity: (i) trace levels which are required for growth and development, (ii) incremental levels which are stored while homeostatic functions are maintained, and (iii) elevated levels which result in toxic effects (Hamilton, 2004). The primary pathway of Se into fish tissue is absorption through the gut, however it can also be absorbed through the gill and epidermis (Hamilton, 2004). Selenium bioaccumulates and this property makes it especially dangerous; concentrations of 5 parts per billion (ppb) in the lentic environment of Belews Lake, North Carolina, resulted in detrital food pathways that were 510 – 1395 times greater, and planktonic food pathways that were 770 times greater than water borne concentrations (Lemly, 1999). Biomagnification has resulted in approximately 1.5 to 6-fold increases of Se concentrations between plankton, invertebrates and fish, but this effect has not been detected between forage and predatory fish (Muscatello & Janz, 2009). Pairing the above facts with the heightened bioavailability of organic-Se^{2-} suggests that the presence of reduced organic Se in aqueous systems is a concern. An evaluation of the ecological risk of Se based solely on aqueous concentrations is difficult, due to the redox condition sensitivity and significantly different properties associated with each redox state of the metalloid (Sharma, et al., 2015).

In the previously described Kesterson Reservoir, Se concentrations in the food chain were linked to death and deformity of embryos of nesting waterfowl (Wu, 2004). Birds and fish excrete excess dietary Se into eggs with possible consequences of reduced egg hatchability, teratogenicity, and increased juvenile mortality (Lemly, 1998).

At Se levels slightly exceeding those where homeostatic functions are maintained, toxicity presents itself in carcinogenesis, cytotoxicity, and genotoxicity (Santos, et al., 2015). Selenosis (poisoning due to chronic excessive Se intake), has been also associated with neurological impairment (Sharma, et al., 2015). Deficient levels have caused symptoms of liver necrosis to present in rats, metabolic diseases such as ‘white muscle disease’ and ‘ill-thrift’ to present in calves, and liver damage and exudative diathesis in pigs and chicks, respectively (Hartikainen, 2005). In Finland, inadequate Se intake was shown to be the cause of nutritional disorders in pigs (affecting profitability) and as a result, all commerical animal feeds have been supplemented with SeO_3^{2-} since 1969 (Hartikainen, 2005)

1.5.3 Attenuation Pathways and Remobilization

Treatment of Se containing waters can be achieved by physical, chemical and biological technologies (Tan, et al., 2016). These include chemical reduction, membrane separation and coagulation-based processes, and microbial methods (Santos, et al., 2015). Ion exchange and adsorption are also viewed as simple and low costs methods, using organic synthetic resins, oxides, carbon-based adsorbents, and biosorbents and adsorbents derived from natural wastes (Santos, et al., 2015). Multiple commercial systems have been tested at various scales ranging from bench scale to full field scale (and developed for immediate commercial use). A comprehensive list of technologies, showing their development stage, key design considerations, advantages/disadvantages, and capital and operating costs is presented in CH2M Hill (2010). Variations in water characteristics make it difficult to identify a single best treatment option.

Biological removal of aqueous Se can be achieved by phytoremedial and microbial treatments. The bioavailability of Se to plants and organisms, and not the Se content, is responsible for the element's uptake in plants and organisms and dictates its entrance into food chains (Winkel, et al., 2012) Soluble Se concentrations have been reduced via phytoremediation by species including *Polypogon monspeliensis*, *Typha angustifolia*, *Typha domingensis*, and *Typha latifolia*. These species have biologically volatilized selenides (Se^{2-}) from oil refinery wastewaters near San Francisco Bay (Hansen, et al., 1998). Selenium-volatilization rates by *Brassica juncea* were shown to be 2-3 times higher for plants supplied with SeO_3^{2-} compared to SeO_4^{2-} (de Souza, et al., 1998). In a vegetated wetland analysis where 62.9% of the total Se inflow mass was removed, most of the Se was retained in the sediment, and less than 5% was retained in the plant tissues (Lin & Terry, 2003). The same study reported that different plant species had different volatilization rates, and rates were seasonally dependant. Microbial enhancements of the phytoreductive effects facilitate 35% of plant Se volatilization and 70% of plant tissue accumulation in Indian Mustard (*Brassica juncea*) (de Souza, et al., 1999). Phytoremediation of both SeO_4^{2-} and SeO_3^{2-} has been shown to be effective, but volatilization rates reported for one study ranged from less than 5 $\mu g\ m^{-2}\ day^{-1}$ to 274.4 +/- 99.9 $\mu g\ m^{-2}\ day^{-1}$ (Lin & Terry, 2003). In another study, plant volatilization of Se oxyanions was reported in the order of μg Se $day^{-1}\ m^{-2}$ leaf area (Terry et al., 1992). These rates of Se attenuation suggest that this mechanism is applicable in low flow conditions where significant space is available for wetland development.

A concern of biological processes, including phytoremediation of oxidized Se compounds, is the possibility of generating more highly toxic compounds, such as seleno-methionine, which is 10,000 times more toxic than SeO_4^{2-} (Murphy, 1988).

Microbial reduction of Se oxyanion concentrations is achieved via assimilatory and dissimilatory processes. In assimilation, oxyanions are transported into the cells by different permeases, then reduced (Eswayah, et al., 2016). In seliniferous environments, assimilitory reduction is expected to contribute minimally, while dissimiltory reduction is considered to be the dominant form of removal (Eswayah, et al., 2016). Dissimilatory reduction occurs when anaerobic microbial respiration reduces oxyanions of Se while a variety of electron donors are utilized (Eswayah, et al., 2016), as described in **Section 1**. Selenate is reduced to SeO_3^{2-}, which is then reduced to Se^0, with further reduction to organic and inorganic Se^{2-} possible. Selenium-reducing bacteria have been identified and tested in both water (Losi & Frankenberger, 1997) and sediments (Siddique, et al., 2007; Fujita, et al., 2002). Specific strains of bacteria are more effective at reducing SeO_4^{2-} to SeO_3^{2-}, while others are more effective at reducing SeO_3^{2-} to Se^0 (Fujita, et al., 2002). Concentrations of Se in water can affect the development of *Azospirillum brasilense* (Se-reducing microbial) which stalls in the lag phases of growth as concentrations of SeO_3^{2-} increased from 1 to 5mM (Vogel, et al., 2018). Bacillus sp. SF-1 is an effective reducer of SeO_4^{2-} to elemental Se but not further (Fujita, et al., 2002).

Adsorption experiments at neutral pH have shown that SeO_3^{2-} readily adsorbed to wetland sediments, while SeO_4^{2-} did not (Baldwin & Al, 2003). In another adsorption experiment, at least 50% of SeO_3^{2-} adsorbed onto different oxy-hydroxides of Fe in the first 10 minutes, with equilibrium being reached in about 2 hours, and adsorption decreased as temperature increased from 298-308 Kelvin (Parida, et al., 1997). Parida, et al., (1997) also found a sharp decrease in percent adsorbed in multiple trials as pH increased past approximately 7.25-7.50 standard units. Another study has shown adsorption to decrease with increasing pH but noted no specific significance of the 7.25-7.50 pH range (Balistrieri & Chao, 1987). The decrease in adsorption at increasing pH is due to the balance shown in **Equations (20)** and **(21)** below (S-OH being the surface hydroxyl group and S-SeO_3^- and S-$HSeO_3$ being the adsorbed SeO_3^{2-} species) (Parida, et al., 1997; Balistrieri & Chao, 1987):

(20) $S\text{-}OH + H^+ + SeO_3^{2-} \leftrightarrow S\text{-}SeO_3^- + H_2O$

(21) $S\text{-}OH + 2\ H^+ + SeO_3^{-2} \leftrightarrow S\text{-}HSeO_3 + H_2O$

Adsorption of Se^{-2} and $Se_{(IV)}$ onto Fe minerals (FeS_2 and Fe-oxyhydroxides) has been observed at pH less than 8, and these behaviours may be explained by the oxidation of the FeS_2 surface (Naveau, et al., 2007; Tachi, et al., 1998).

The reduction of SeO_3^{2-} to Se^0 can occur via numerous mechanisms, and this reaction can be catalyzed by reductases including periplasmic NO_2^- reductases and dimethyl sulfoxide reductases (Eswayah, et al., 2016). Engineered systems for the treatment of SeO_4^{2-} and SeO_3^{2-} are often designed with the reduction to Se^0 in mind, but these oxyanions are readily reduced to Se^{2-} (Herbel, et al., 2003). An important requirement in the design of any engineered removal system is the understanding of the physical and chemical properties of Se species present (Jain, et al., 2017)

Elemental Se, generally appearing in the form of Se nanoparticles (Eswayah, et al., 2016), is of little toxicity and can be more easily removed from the aqueous phase due to its insolubility compared to oxyanions (Fujita, et al., 2002). The mechanisms involved in the formation of Se nanoparticles, and their physical and chemical formations have not been fully characterized (Eswayah, et al., 2016).

Aqueous concentrations of Se can be measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), but differentiating between the various forms (oxygenated and reduced) requires additional measures. High-performance liquid chromatography coupled to a collision cell inductively coupled plasma mass spectrometer is a cost-effective method for quantifying selenium species to sub parts per billion levels (ALS Global).

A concern of remediation strategies that remove soluble Se through reduction is the unknown long-term stability of the reduced precipitates, which is dependent on the quality and ORP of the water. Kinetic reoxidation of Se nanoparticles will be accelerated, compared with larger particle sizes, due to the higher surface to volume ratio (Winkel, et al., 2012). Another factor affecting long term Se stability is the sloughing off of biological solids, which may contain elevated concentrations of Se (CH2M Hill, 2013). A concern with microbially reduced Se is the propensity of Se^0 to form stable colloidal suspensions, which do not settle quickly via gravity, however these can be disrupted by pH, cation concentrations, and dissolved organic matter (Buchs, et al., 2013).

The remobilization rate of reduced Se (through subsequent exposure to oxygenated conditions) was low in undisturbed columns subjected to aerated simulated groundwater (Simonton, et al., 2000). Selenium levels were however very close to the maximum concentrations established by the United States Environmental Protection Agency (EPA) Resource Conservation and Recovery Act standards for hazardous waste (1.0 mg L^{-1}) in effluents from a leaching procedure on the substrate from these columns (Simonton, et al., 2000).

While the main focus of the above text has been bioremedial attenuation pathways, reduction in Se concentrations can also be achieved by conventional desalting, adsorption, and chemical reduction schemes (Murphy, 1988). Chemical reduction methods using ferrous hydroxide are common (USA Patent No. US 6183644 B1, 2000). Chemical reduction with zero valent iron (ZVI) has also been investigated, with earlier trials resulting in quick cementation of the Fe filings (Santos, et al., 2015). Recent studies have shown the oxidized Fe products can have reduced Se embedded in their solid structure (Santos, et al., 2015). Disadvantages of ZVI include the long hydraulic residence times required (typically greater than 4 hours of contact time), pH and temperature dependence, costs related to sludge disposal, and the passivation of ZVI (CH2M Hill, 2010).

At the Brule Mine, Se concentrations in the receiving waters have been increasing, peaking at 69 $\mu g\ L^{-1}$ in the month of August 2014 (Walter Energy, 2015), a value that exceeds the WQG maximum concentration of 2 $\mu g\ L^{-1}$ (Beatty & Russo, 2014).

1.6 Other Redox Sensitive Parameters

Other redox sensitive parameters that are present in mine water include O_2, Fe, Mn, and As. The regulatory compliance sampling location at the Brule Mine is in a creek immediately downstream of a large elevation change, and the water is rapidly flowing. As a result, samples collected at this location are assumed to be exhibit high redox potentials. Groundwater in the vicinity of the mine has shown high levels of reduced Fe(II) (source: site investigations). Natural groundwaters containing Fe(II) are not stable under ambient conditions: Fe concentrations are lowered by oxidation and precipitation at rates governed by diffusion of O_2 through air (Hem & Cropper, 1962). Oxidized Fe(III) is insoluble at neutral pH ranges. The result of this behaviour is observable in the discharge of artesian wells; groundwater with low redox potentials flowing from well taps and splashing on the ground will often run clear but leave a rust layer on the ground (splashing of the water rapidly introduces O_2).

Manganese speciation behaviour is similar to that of Fe: reduced species are soluble, while oxidized species are less soluble and precipitate. These special characteristics of Fe and Mn help identify the spatial distribution of redox conditions in waters where these constituents are present (i.e. landfill leachate plumes) and also help to identify the governing redox environments (Bjerg, et al., 1995). They also identify redox zones in ocean waters and sediments, where deeper zones contain soluble species, and shallow ones contain particulate forms of the metals (Spencer & Brewer, 1971). Arsenic mobility is strongly linked to its redox state as well, with its reduced form being adsorbed much less strongly to the surfaces of metal oxides than the oxidized form (Newman, et al., 1998). Arsenic toxicity is similar to Se toxicity in the fact that it causes toxic and teratogenic effects in micromolar concentrations, and its crustal abundance is relatively low (Stolz & Oremland, 1999).

1.7 Biologically Mediated Processes for Mine Water Treatment

Mining wastes have been generated for centuries, and a variety of engineered systems have utilized bacteria to provide dissimilatory reduction of metal and organic contaminants. Techniques for using alternate electron acceptors such as NO_3^- and Fe(III) have also been developed (Lovley, 1995). Alternatively, electro-biochemical transformations can be achieved through the utilization of a charge provided from an electrode to reduce oxyanions (Opara, et al., 2014).

1.7.1 Bioremediation

In contrast to many organic molecules that can be ‘broken down’ as part of the remedial action, examples of which are some volatile organic compounds, the process of dissimilatory reduction can result in increased volatility or reduced solubility of contaminants, as presented in **Equations (9)** through **(12)**. Examples of contaminants whose reduction leads to an increase in volatility are NO_3^- and Hg, and those whose reduction leads to a decrease in solubility are uranium (U), chromium (Cr), Se, and Pb (Lovley, 1995).

Microbial treatment systems designed to enhance Se reduction can be divided into passive, semi-passive and active. Gusek (2002) defines passive treatment as a 'process of sequentially removing metals and/or acidity in a natural-looking, man-made bio-system that capitalizes on ecological and geochemical reactions. The process requires no power and no chemicals after construction and lasts for decades with minimal human help'. The benefits of these passive systems are that they can be operated in remote locations, in harsh climates, with little or no power and maintenance (Gusek, 2002). Interestingly, temperatures approaching (or below) 0°C have not been reported to have a significant effect on the performance of Se-remediating bioreactors (Baldwin, et al., 2015; Opara, et al., 2014; Luek, et al., 2014), though in the 20-50°C range, the greatest conversion of SeO_4^{2-} to SeO_3^{2-} occurred at 30°C (Hageman, et al., 2013).

The processes involved in passive and semi-passive bioreactors include the development of biologically active suboxic zones for Se-reduction, filtering of suspended material, and adsorption and exchange of Se bearing ions with plant, soil and other biological materials. Semi-passive treatments are those which require active management (e.g., ongoing fertilization or addition of organic amendment) to sustain desired conditions and processes (Martin, et al., 2009).

Many laboratory experiments have reduced soluble Se concentrations using organics such as manure (Pahler, et al., 2007), yeast extract (Oremlund, et al., 1999), glucose (Dungan & Frankenberger, 1999), ethanol (Luo, et al., 2008) protein, egg albumen, casein and gluten (Frankenberger & Arshad, 2001), hay, sawdust, and manure (Baldwin, et al., 2015), mulch, manure and bone meal (Luek, et al., 2014) among others as the source of electrons (provided via organic decomposition). Columns of organic substrate from the Wolverine River (Yukon Territory) and gravel amended with various amounts of manure, treated sewage effluent, zero valent iron, alfalfa and wood chips (including a control) achieved reductions in Se concentrations in water sourced from the Wolverine Mine (Mioska, 2012). The introduction of WQG exceedances of *Escherichia coli* (*E. coli*) into downstream environments due to the use of manure as the organic substrate has been reported (Luek, 2014).

Active treatment systems for Se reduction are design specific. One such design implements a selective screening process to isolate Se reducing bacteria, and then establishes them on a high-density biofilm in an anaerobic reactor with an ideal nutrient and sugar concentration to facilitate the development of reducing conditions. Selenium-contaminated water is passed through the reactor, and a specialized nutrient feed is metered into the reactor creating the electron donor state which facilitates Se reduction (USA Patent No. US 6183644 B1, 2000). Teck Coal commissioned an active selenium reduction treatment system on Feb 17th, 2016 near its Line Creek facility in southeastern BC. The project has an estimated capital cost of 80 million dollars and an annual operating cost of 5 million dollars (Will, 2012).

1.7.2 Role of Organic Substrate

In environmental systems, the decomposition of organic compounds provides energy for chemoorganotrophic organisms, and a pathway for the mineralization of organic molecules. As described in **Section 1.2**, the oxidation of organic molecules is coupled with the reduction of various electron acceptors. Numerous factors impacting the rate of organic decomposition include bacterial population and diversity, physical environment at both regional and microclimate scales (moisture content, pH, temperature and O_2 content), and the chemical nature of the environment and material to be decomposed (e.g., nutrient availability, and the complexity of the molecules). In low O_2 environments, decomposition rates may also be limited by availability of alternate electron acceptors. Carbon:N ratios, C:P ratios, other nutrient contents, and lignin content have been shown to affect decomposition rates. Decomposer organisms typically have high N and P contents, and this translates to high N and P nutritional requirements (Enriquez, et al., 1993). Elevated N and P contents should lead to high rates of microbial mass production, and low rates should lead to nutrient controlled remineralisation (Enriquez, et al., 1993).

The effect of O_2 on organic decomposition has been studied at length, particularly in pelagic sediments. A comparison of aerobic and anaerobic C mineralization showed that aerobic mineralization was approximately 10 times faster than anaerobic mineralization (Kristensen, et al., 1995).

Woody debris is mostly composed of cellulose, hemicellulose and lignin (Schmidt, 2006). In the early stage of decomposition of wood materials, bacteria and fungi can degrade simple soluble substrates, pectin, and easily accessible cellulose and hemi-cellulose. Once these readily available substrates are degraded, the degradation of the remaining ligno-cellulose is dominated by slow growing, saprotrophic, ligno-cellulytic fungi (van der Wal, et al., 2007). Some Actinobacteria, such as Nocardia and Streptomyces, also have a limited ability to degrade lignin (Horwath, 2015). Fungal decay of wood only occurs in the presence of O_2 (Blanchette, et al., 1989). A limiting factor in the decomposition of wood by these fungi is often N content. Much research has been devoted to the effect of N additions on litter decomposition and studies have shown both a direct correlation of N additions to mass lost or respiration and no effect between the two (van der Wal, et al., 2007). In a review of available studies, Enriquez, et al. (1993) showed that across all plant types, a positive correlation existed between decay rates and N content, decay rates and P content, and a negative correlation existed between degradation and lignin content. Bacteria are expected to demonstrate a greater response to N addition than are fungi, as fungi are thought to be more efficient in re-allocation or use of N (van der Wal, et al., 2007). Small particles of organic matter are expected to decompose faster than larger particles, due to their increased surface area providing greater access to substrates, and larger surface for bacterial growth (van der Wal, et al., 2007).

1.8 Brule Mine Stratigraphy and Mineralogy

The general stratigraphy of the mine consists of three coal seams, hosted primarily within interlayered siltstones and mudstones (Western Canadian Coal, 2006). Sandstone is the least abundant rock type. Petrography and Rietveld XRD analysis demonstrates that the waste rock mineral assemblage is composed primarily of quartz, carbonate, muscovite and kaolinite (PetraScience, 2005). Pyrite is the main S^{2-} mineral (Western Canadian Coal, 2006). With regards to carbonate mineralogy, siltstones are dominated by calcium carbonate ($CaCO_3$), while mudstones contain roughly equivalent proportions of Fe-carbonate and $CaCO_3$ (Western Canadian Coal, 2006). A sample of mudstone from the mine contained 0.2%, 3.1%, 4.0%, and 1.6% of FeS_2, calcite, siderite, and ankerite, respectively (Western Canadian Coal, 2006). A sample of siltstone contained 0.3%, 9.0%, 3.8%, and 6.3% of FeS_2, calcite, siderite, and ankerite, respectively (Western Canadian Coal, 2006).

The results of acid-base accounting (ABA) and mineralogy suggest that total S occurs mainly as S^{2-} minerals and organic S. During any oxidizing events S^{2-} and organic S are expected to oxidize rapidly and slowly, respectively. In waste rock, an acceptable assumption is that all S is bound up in FeS_2, while in coal, the greater presence of organic S invalidates the above assumption (Western Canadian Coal, 2006).

1.9 Column Design Review

Many studies investigating the fate and transport of pesticides, explosives, microbes, heavy metals and non-aqueous phase liquids as well as evapotranspiration, use soil columns in both saturated and unsaturated regimes (Lewis & Sjostrom, 2010). Column design can be partitioned into two broad categories: packed (disturbed) components and monolithic columns of intact soil. Packed (and if possible screened) contents are typically more homogeneous than monoliths, which is expected to allow greater reproducibility, while monoliths will likely better reproduce field conditions at the expense of reproducibility (Lewis & Sjostrom, 2010). Multiple studies have reported that experimental results have changed as a result of the choice between packed and monolithic components. Packing may lead to homogeneous columns avoiding the formation of stratifying layers or preferential flow pathways.

Up-flow column reactors, in which water flows in an upwards direction, entering the base and exiting the top, reduce the development of preferential flow paths and last longer as they do not promote compaction of the column materials (URS Corporation, 2003). Upflow reactor fluids are driven by a pump, and this promotes complete saturation (Electric Power Research Institute, 1991). Column systems that achieve influent delivery through a small tube or port, rather than uniformly to the entire cross section, have less uniformity of flow as column size increases (Electric Power Research Institute, 1991). This issue can be overcome with the use of porous endplates (Electric Power Research Institute, 1991). Lewis & Sjostrom (2010) summarize a soil column study in which the inlet orifice had a radius less than the column radius, and the resulting effect was non-uniformity of velocity profiles at the end, and the height of the zone of influence was calculated to be up to 1.5 times the column radius.

Sidewall flow, and for soils, macropore flow, can also influence flow regimes through saturated columns. For example, flow velocity at a column wall was found to be 1.1 – 1.45 times the flow velocity in the column center, and that sidewall flow increases with larger soil particles (Lewis & Sjostrom, 2010). Ensuring complete saturation is also important to achieve uniform flow, as pockets of gas can substantially influence the flow of liquids through pore spaces. As a result, a week-long period of static saturation will allow entrapped air to dissolve and disperse in pore liquids of soils (Lewis & Sjostrom, 2010). Another method of removing air from the column in to flood the column with carbon dioxide (CO_2), as this gas is several orders of magnitude more soluble than the component gases of air, resulting in faster dissolution of CO_2 bubbles when compared with air (Lewis & Sjostrom, 2010).

Steel, acrylic, or glass accounted for over 60% of experimental setups documented in a review by Lewis & Sjostrom (2010). Factors that determine material choice include: a) whether transparency is required, b) the structural requirement of the material, c) whether the material will chemically affect the processes internal to the column (inertness), d) the ease of installing instrumentation, and e) any cost or availability considerations pertaining to the material of choice (Lewis & Sjostrom, 2010).

Saturated columns (of soil) should have a baffle zone as least as thick as the column diameter, at both the inlet and outlet of the column, to avoid non-ideal flow patterns (Lewis & Sjostrom, 2010). To avoid sidewall effects, it is recommended that a 1:4 ratio of diameter to length be applied for cylindrical columns.

1.10 Research Objectives and Approach

A saturated up-flow column reactor study was used to identify ways of promoting Se removal and denitrification (i.e. NO_3^- removal) from mine effluent. In the experiment, toe seep effluent (characterized earlier) was pumped at a metered rate through columns containing Crushed Mine Waste Rock (CMWR) and locally available organic amendments. The decomposing amendments provided the electrons required for the reduction of species of interest (O_2, NO_3^-, SeO_4^{2-}, SeO_3^{2-} and SO_4^{2-}) and fostered the necessary conditions for the proliferation of bacteria required for the experiment. The experiment was conducted at the University of Northern British Columbia (UNBC) within the Enhanced Forestry Laboratory (EFL) to control climatic interferences.

The experiment was initially set up to address the following questions:

a) Which of two easily available (to the Brule Mine) organic amendments is best suited as an electron donor for promoting Se removal from Brule Mine effluent? How do the two amendments differ in their kinetics (time to onset of reducing conditions) and longevity (how appropriate redox conditions are maintained) in regard to their ability to foster conditions conducive to denitrification and Se removal within waste rock environments?

An original subpart of the above question was ‘How does an increase in mass of a single amendment affect the reaction kinetics?’ but limitations to the scale and size of the experiment prevented this consideration to be addressed.

b) What are the biogeochemical mechanisms governing the speciation and behavior of Se and N in waste rock pore waters in response to these organic amendments?

c) How does the use of organic amendments and CMWR in a saturated low-flow, toe seep effluent environment affect column effluent water quality? i.e. in addition to Se and

NO_3^-, will the concentration of any other parameter of environmental relevance be significantly affected by the column conditions?

To address these questions, an experiment was performed comparing organic amendments in a saturated CMWR environment for their ability to foster Se reducing and denitrification conditions. The effluents of up-flow column reactors containing various treatments were collected on a weekly or bi-weekly schedule and analyzed to infer inter-column conditions, and to examine amendment effects on effluent water quality. The potential for contaminant remobilization through oxidation or complexation has not been evaluated in this research. The short-term nature of this experiment also did not allow for adequate exploration into effects from material aging, matrix clogging, or remobilization of attenuated elements.

The column experiment was designed and operated while a full-scale biochemical reactor (BCR) was constructed at the Brule Mine. Insights derived from the bench scale column study were expected to aid in overcoming some of the technical, permitting, and operational challenges encountered during future implementations of BCRs, as the Brule Mine had forecasted the need for at least two more operational scale units at the mine site.

1.11 Readily Available Organic Substrate in NEBC

Organic amendments (C sources) used in the full-scale BCR at the Brule Mine were chosen for inclusion in the column study. The following criteria were used by the mine administrators to find appropriate C sources:

- Cost: the volume required for field scale application in a bioreactor is expected to be substantial, and an annual ‘top-up’ may be required to compensate for organic decomposition and losses to throughput water. These factors put constraints on the unit cost of the amendment. While short chained organic compounds have been used in published experiments, their cost was prohibitive in the scale required at the mine;

- Abundance and proximity to the mine: Shipping amendments to the remote location of the mine was a major cost of the project. Successful Se bio-attenuation using food processing wastes as C sources had been proposed by Bioremedial Technologies Inc. (Matt Perry, personal communication, 2013), but the cost of transporting these wastes from major industrial centers was prohibitive. In addition, if the project could use a waste or by-product of a local industry, it could benefit the industry and increase the social license of the mine; and,
- Reactivity: The material must be considered relatively inert in the event of a spill or large-scale release to the sensitive surrounding watershed. The mine housed a 150-person capacity work camp, complete with sewage treatment lagoon. It was decided early on by project stakeholders that using sewage as the organic amendment would cause unnecessary logistic and regulatory complications, and possible guideline exceeding concentrations of *E. coli*.

After eliminating organic amendments which did not meet the above criteria, there were two remaining options. The first option was sawdust from a local sawmill, considered a waste stream and burned in a large beehive burner (note: the sawdust is now being burned in an electrical cogeneration plant). The second option was old bales of hay no longer suitable for livestock feed (e.g. bales of hay having been exposed to at least one winter in fields of farmers). An additional benefit of this old hay was that because of moisture and aged conditions, bacterial decomposition had likely already begun, some microbes of which were possibly anaerobic.

Multiple considerations indicated that the inclusion of CMWR as an amendment in the columns was appropriate including;

- The need to use similar volumetric ratios of tailing material to organic matter to other studies, in the event that comparison of results between experiments is necessary or appropriate (see **Table 1.2**);
- The importance of creating an experiment that was comparable and thus applicable to the bioreactor design being implemented at the Brule Mine;
- The assumed effect of CMWR would be to increase the overall porosity of the columns to achieve less clogging (due to increased particle size).
- The increased specific gravity of CMWR with respect to both the organic amendments and water, which was anticipated to result in less accumulation of fines in the upper (effluent) valves of the column (i.e. the CMWR could ‘hold’ the amendment in place).

Table 1.2: Summary of research used to determine CMWR: organics ratio

Number	Article	Author	Year	Quantity	Results
#1	Evaluation of in situ layers for treatment of acid mine drainage: a field comparison	Hulshof, et al.	2006	Tailings: organic matter (om) - 4:1 volumetric ratio	Pulp residue was more effective at generating anaerobic conditions than woodchips, likely due to composition and 'respiration rates'
#2	Microbial and nutrient investigation into the use of in situ layers for treatment of tailings effluent	Hulshof, et al.	2003	Column components - tailings: om - 4:1 volumetric ratio	High SO_4^{2-} reduction initially observed then reduced over time due to complete consumption of labile C
#3	Transport and attenuation of metal(loid)s in mine tailings amended with organic C: column experiments	Lindsay, et al.	2011	Column compositions 0, 2, & 5 vol. % amendment	Increased attenuation of certain parameters and mobilization of others at 5 vol. % (more than 2% & 0%)
#4	Managing pore-water quality in mine tailings by inducing microbial SO_4^{2-} reduction	Lindsay, et al.	2009	Field scale cell: 0.6 % weight & 5 % volume C	"Amendment of tailings with a small and dispersed mass of organic C resulted in a general decrease in mass transport of S2- oxidation products"

Section 2: Materials and Methods

2.1 Overview

In order to address the research questions outlined in **Section 1.9**, a column experiment was designed with support from Lorax Environmental Services (Lorax) and the supervisory committee. The experiment was executed with technical help from Lorax and operational support from the UNBC EFL curators. Organic amendments were collected from sources local to the mine, and inorganic materials were sourced from the mine. Laboratory materials were collected from UNBC Chemstores, equipment providers, and specialty manufacturers as needed.

To properly quantify the effect of individual column amendments on redox conditions, column influent and effluent liquids were collected and characterized for elemental and ion concentrations. Organic amendments were submitted to ALS Environmental Laboratories (ALS) for chemical characterization. Subject to funding constraints, a collection schedule was initiated and followed (the details of which are presented in **Section 2.4.5.2**). A rigorous Quality Assurance and Quality Control (QAQC) sample collection and submission plan was created.

2.2 Materials

In the following descriptions, all dimensions are provided in metric. As needed, imperial units are provided immediately after in parentheses to indicate that the original unit of measure was imperial and was converted for the thesis. An example is the size of tubing – specifications are provided by the manufacturer in standard imperial units (e.g., 1/16", 1/8") but are reported herein as metric (e.g., 1.59 mm (1/16") and 3.18 mm (1/8")). Where original measurements were metric, no imperial units follow.

2.2.1 Treatments

Attempts were made to obtain a chemical characterization of the amendments and where practical, particle size distributions. Amendment ratios were chosen at a volumetric ratio of 4 units of CMWR:1 unit of organic matter, to reflect published studies (shown in **Table 1.2**). To determine if there was a synergistic effect of a combine (hay and sawdust) application, a treatment consisting of a volumetric ratio of 8 units of CMWR:1 unit of hay:1 unit of sawdust was used, which maintained the 4 units of CMWR:1 unit of organic matter. To quantify the potential leaching effects of CMWR in the effluent water, a column consisting of only CMWR was created as well. Amendment masses and volumes were as displayed in **Table 2.1**.[5]

Table 2.1: Treatment mass[6] and volume of substrates utilized within experimental columns

	Crushed Mine Waste Rock		Sawdust		Hay		Total Solids	
Column	Mass (kg)	Volume (L)	Mass (kg)	Volume (L)	Mass (kg)	Volume (L)	Mass (kg)	Volume (L)
1	3.575	2.565			0.192	0.640	3.767	3.205
2	3.700	2.565					3.700	2.565
5	3.725	2.565	0.070	0.320	0.096	0.320	3.891	3.205
6	3.700	2.565	0.141	0.640			3.841	3.205

2.2.2 Column Design

The column design was provided Lorax and constructed by Dimension 3 Plastics Limited, of Burnaby, BC. Column specifications are provided in detail in **Appendix C**.

---

[5] Results have been dismissed from two columns, as the experimental design was not rigorous enough to properly quantify all of the variables.

[6] Treatment mass refers to mass of amendment in the state they were when added to the columns and should not be interpreted to mean dry mass.

While the columns did not match design criteria suggested in **Section 1.8**, the design and manufacturing process had been perfected by Lorax and Dimension 3 Plastics Limited through previous iterations. Six columns were received at UNBC on October 20, 2014.

The columns were modelled after up flow packed bed reactors. A 3.18-mm (1/8”) thick plastic plate, 1.59 mm (1/16”) smaller than the column inner diameter (ID), with machined flow dispersing grooves radiating from the center to small holes drilled through the plate, was placed in the bottom of each column to help minimize the development of preferential flow paths. This plate was overlain with a 1 cm layer of boil-sterilized 20-30 mesh Ottawa Sand to distribute the flow equally through the cross-sectional area of the column (please refer to **Appendix B** for an image of the sand layer). The column specific mixture of CMWR and organic amendment was placed on top of the flow dispersing media. Please refer to **Figure 2.1** for an image of a saturated column, taken after 1 week of operation.

2.2.3 Hay

Hay was sourced from the Brule Mine BCR project. The mine had accumulated approximately 1400 round bales of hay from farms in the vicinity of the mine. One contractor was responsible for the collection of hay bales sturdy enough to be handled by a forklift, but no longer suitable for livestock feed. This system of hay procurement provided ease of management as only one contractor required access to the mine. Unfortunately, this system lacked sufficient accountability to specify exactly where the hay was grown, how long it had been since its harvest, and the species distribution.

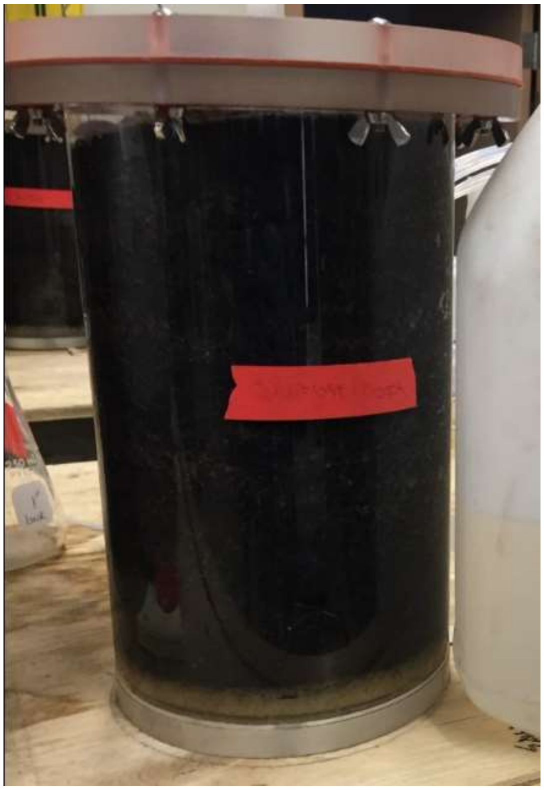


Figure 2.1: Column with 1 cm layer of Ottawa Sand overlain by organic amendment mixed with CMWR.

2.2.4 Sawdust

Spent sawdust was collected from the West Fraser Sawmill (3598 W Fraser 89, Chetwynd, BC) on June 3rd, 2013, directly from the milling process waste stream conveyor belt. According to the mill operators, the mill was processing approximately 99% White Spruce (*Picea glauca)*, all sourced from within a 200-km radius from the mill. The mill regularly ran other species including Lodgepole Pine (*Pinus contorta*) and Subalpine Fir (*Abies lasiocarpa*) (Source: Field Notes, 2013). The sawdust is assumed to be from softwood species. Samples were stored in sealed 20 L buckets and transported to UNBC in early September.

2.2.5 Crushed Mine Waste Rock

Previously mined (waste) rock was regularly crushed to make gravel for road maintenance at the Brule Mine. As part of the crushing process, gravel was screened to remove fines less than 19.1 millimeter (mm) (3/4"). These smaller diameter fraction (rejects smaller than 19.1 mm) from the 2013-2014 period were placed in 20 L sealed buckets in August 2014 and transported from the mine to UNBC, to be used as CMWR.

2.2.6 Mine Water

A 1000 L (1 m x 1 m x 1 m) polyethylene tote, previously used for transporting grape concentrate for wine production, was purchased from Hobby Brews (Prince George B.C.). The tote was cleaned with muriatic acid (31.45% strength) and triple rinsed with de-ionized water supplied by UNBC (the entire process was repeated twice). The tote was then filled with water collected from a toe seep historically characterized by high levels of mine signatures. A 51 mm (2") trash pump and hose were used to transfer the water on Friday, October 10th, 2014. Prior to filling the tote, toe seep water was pumped though the trash pump for 10 minutes to flush out any accumulated debris and contaminants in the pump housing.

The following measures were implemented to maintain a static water chemistry over the duration of the experiment:

- To prevent ultraviolet (UV) light from entering the tank, which could cause biofouling, the growth of algae, and could change the water chemistry, a black fabric tarp was wrapped around the tote, extending from the floor to the top of the tote and held in place with tape and staples; and,

- To maintain oxic conditions in the tote, a 4.5-Watt, 5.4 L min^{-1} fish tank aerator was installed and left running from Wednesday October 15th until the end of the experiment. Lines from the aerator were connected to fish tank air dispersion stones at the bottom of the tote, which resulted in a constant bubbling of O_2 through the mine water.

To accommodate the air supply and water extraction (column supply) lines, three 2.54-centimeter (cm) diameter (1") holes were drilled into the lid of the water tote. A wooden platform was fabricated to sit on top of the tote to serve as a workspace and a hole was cut in the platform to allow access to the lid (located at the center of the tote surface). In periods of no maintenance or sampling, any clear plastic exposed lines were also loosely covered with aluminum (Al) foil to further prevent light from accelerating biofouling.

2.3 Experimental Design

Lorax provided a column design template. An annotated photograph of the design (**Figure 2.2)** and descriptions of the individual elements are provided below.

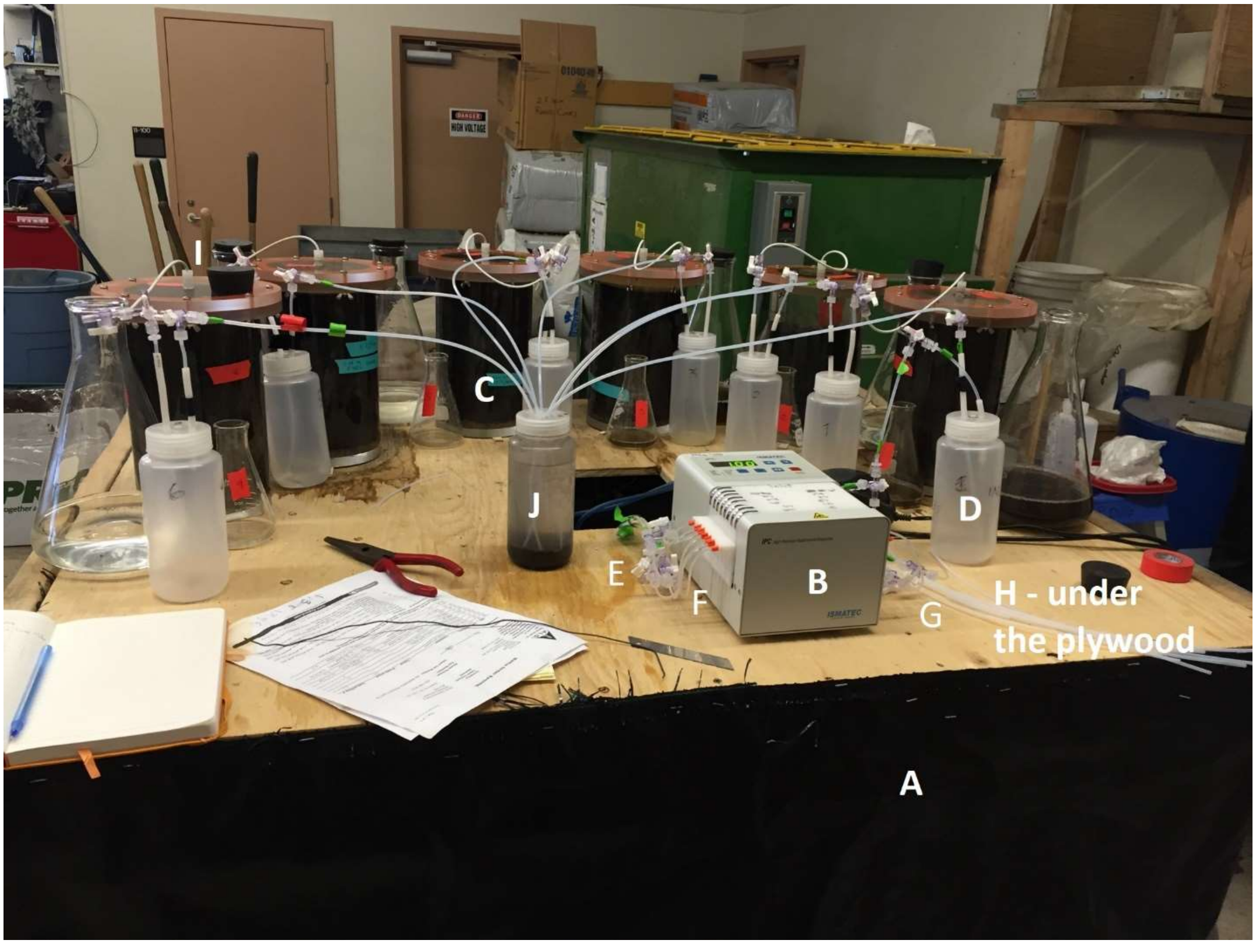


Figure 2.2: Experimental configuration during sampling events – annotated to reflect the description of **Section 2.3**.

A) 1 x 1000 L polyethylene tote of toe seep water (described in detail above in **Section 2.2.6**).

B) 1 x 8-channel standard-speed digital dispensing pump provided a consistent flow volume to each column. The pump drive and corresponding flow rates were verified by a NIST Traceable Calibration Report (provided in **Appendix C**) as part of the procurement process.

C) 6 x column (described in detail above in **Section 2.2.2**).

D) 6 x sample collection container (see **Figure 2.3**): 500 milliliter (mL) polypropylene bottle with two 5.56 mm (7/32") diameter holes drilled in the top and plugged with an inlet and an outlet line. These lines were polytetrafluoroethylene (PTFE) 1.59 mm (1/16") ID by 3.18 mm (1/8") outer diameter (OD) tubes inserted in softer C-Flex 3.18 mm (1/8") ID by 6.35 mm (1/4") OD tubing. The softer tubing created an airtight seal between the 5.56 mm ID hole and the 3.18 mm OD tube. Both inlet and outlet lines end in 4-way valves (stopcock with male Luer lock connections, shown in **Appendix B**). The inlet tubing delivered liquid into the container, and extended to the bottom of the container, while the outlet line allowed venting of displaced gas (N_2) and extended approximately 2-cm into the container.

The tubing used in the experiment was predominantly PTFE 1.59 mm (1/16") ID by 3.175 mm (1/8") OD, and this tubing is referred to as 'typical' in the following description. Special tubing was required for column attachments and the pump housing. All connections (except for the column fittings) were male or female polypropylene Luer lock 1.59 mm (1/16") hose barb adapter fittings. Four-way stopcock valves were placed between each successive piece of tubing or apparatus so that in the event of biofouling, plugging, or trouble shooting, individual sections of the system could be isolated, tested and or removed without introducing air to the otherwise saturated system. The influent delivery and effluent collection system was identical for each column, so the description below describes the path of fluid through the system and continues to reference **Figure 2.2**.

E) The collection line, consisting of typical tubing, was taped to a weight so it would hang suspended in the 1000 L tote. This prevented the line from either floating on the water surface and drawing in air or resting on the bottom and drawing in sediment. The line extended from inside the tote to a 4-way valve immediately preceding the pump.

F) Departing the 4-way valve was 0.79 mm (1/32”) ID tygon tubing which sat in a dedicated pump channel. The pump was external to the tubing, and as such, did not impact the water quality. The tygon tubing is more resistant to the wear caused by the pump than the typical tubing.

G) The next section of typical tubing conveyed water from the pump to a 4-way valve at the bottom (inlet) of the column (in **Figure 2.2** this is difficult to see as these lines were run from the pump to each column underneath the wooden workspace).

H) A small piece of 1.59 mm (1/16") ID viton tubing connected the 4-way valve to the inlet port (or bottom) of the column via a 3.18 mm x 3.18 mm (1/8" x 1/8") polyvinylidene fluoride (PVDF) compression fitting. Viton tubing was chosen for its compatibility with the compression fitting (this is clearly displayed in **Figure 2.4**, which shows an inverted column, but cannot be seen in **Figure 2.2**).

I) Upon exiting the column through the outlet (top) 3.18 mm x 3.18 mm (1/8" x 1/8") PVDF compression fitting, 1.59 mm (1/16") ID viton tubing conveyed the water to a 4-way valve.

J) During sampling events the 4-way valve was configured to direct flow into an N_2-purged sample collection container described in D) (above) and shown in **Figure 2.3**. The configuration shown in **Figure 2.2** is for sampling events. As the container was filled with the column effluent, displaced N_2 would flow out the effluent line. The end of the effluent line was submerged in a container of tap water. The submerged effluent line ensured that N_2 could bubble out, but air could not flow up the line, and the introduction of O_2 in the sample was prevented.

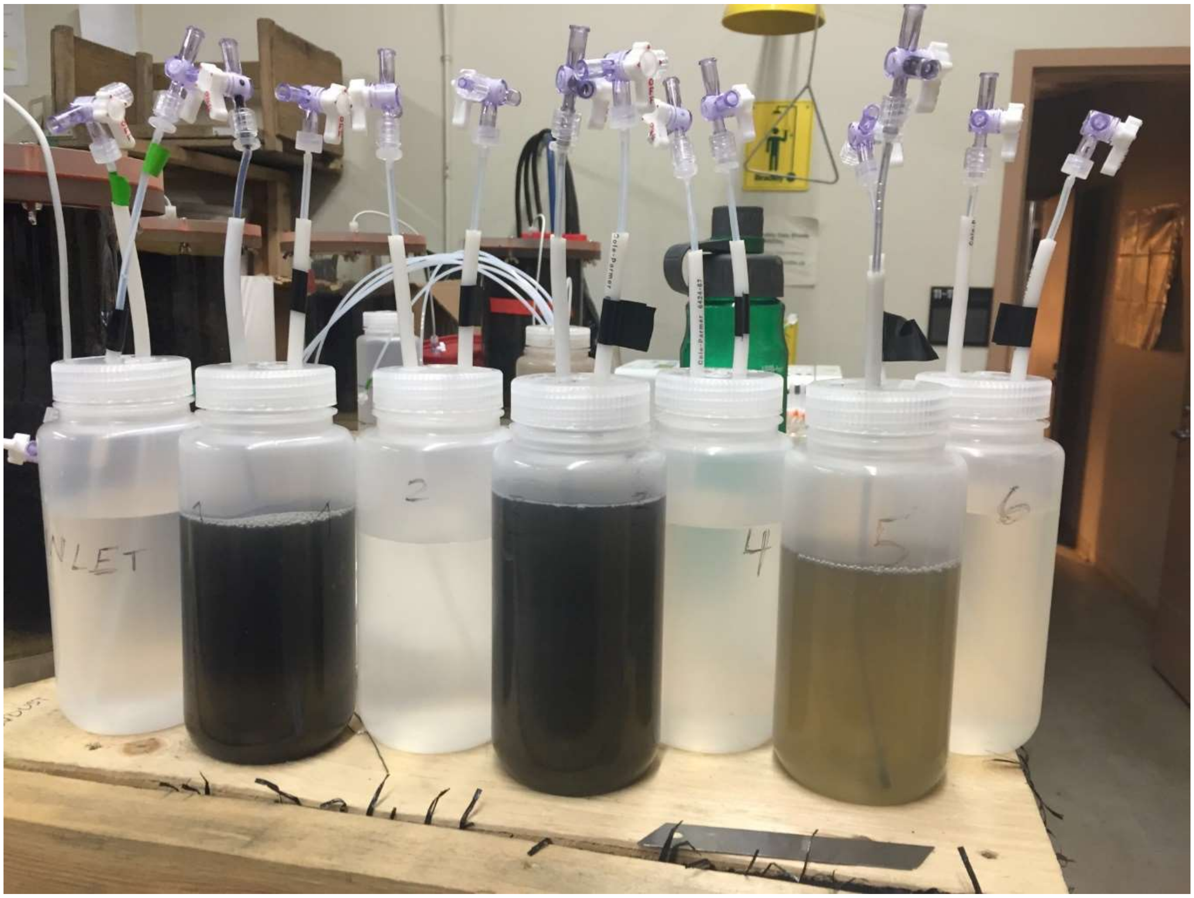


Figure 2.3: Sample collection containers, with inlet and outlet tubes individually valved to allow N_2 purging and sample collection in an O_2 depleted environment. The containers would be connected in series to a N_2 cannister and purged for 5 minutes then individually sealed (under positive N_2 pressure) and hooked up to the sampling system. A good indication that the system was working properly was bubbling out of the submerged effluent lines when the valves were opened. This system of positive pressure verification was only established after week 2.

Figure 2.4: An inverted column during maintenance - changing a leaking influent hose (on the bottom). Note the 3.18 mm x 3.18 mm (1/8" x 1/8") compression fitting on the column bottom. This allowed tubing to be firmly sealed to the column bottom. A similar fitting was attach attached to the effluent (top) side.

In order to get a representative sample for pH, ORP, and DO measurements, the connection from I) (above) was connected to the bottom of a 15 mL polypropylene vial, allowing effluent to flow up through the vial. The multimeter probe would be inserted into each vial from the top and would measure saturated liquid flow. The vials for all columns were mounted on a single board and are shown in **Figure 2.5.**

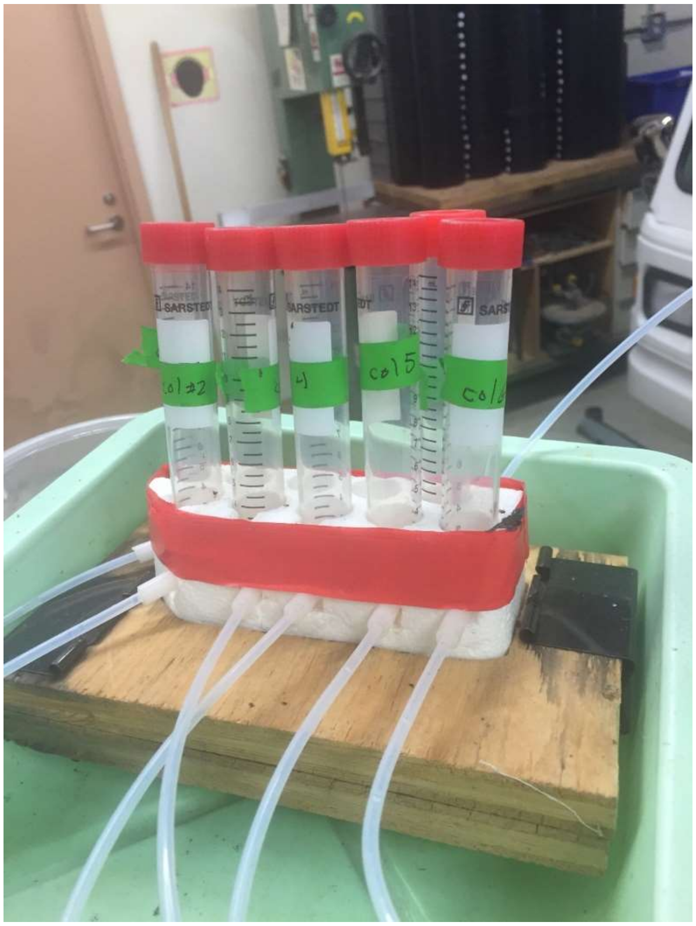


Figure 2.5: Up flow 15 mL polypropylene containers into which the multimeter probes were inserted.

During normal operations (not sampling events) typical tubing connected the 4-way valve to an overflow collection jug, as shown in **Figure 2.6**. The collection jugs were maintained at a higher elevation than the columns to prevent siphoning of column liquids. On a weekly basis, the collection jugs would be compared and drained. Any variance in the volumes of effluents from the columns would indicate tube plugging, pump tube rupture or system failure, and signalled that corrective action was required.

Figure 2.6: Experimental setup – configured for normal flow through operations (columns were not yet connected to overflow collection jugs)

2.4 Analytical Methodology

A list of the analyses performed, and the specific methods employed on liquid (water) and solid (organics and CMWR) matrices can be found in **Appendix C.**

2.4.1 Hay Preparation

On September 7th, 2014, four representative samples were pulled by hand from the bales at the mine site and transported to UNBC where 3 were shipped immediately, on September 15th, to ALS for chemical characterization.

The sample not sent away for characterization was dried for a period of 7 days at ambient temperatures in the greenhouse of the EFL at UNBC, and shredded using the hammer

& screen mill (hammer mill) of the EFL on September 30th, 2014. The hammer mill screen had 1.59 mm (1/16”) round openings. Individual pieces of hay, larger than the screen openings, were observed after milling, indicating that some pieces had passed lengthwise through the screen opening, requiring a second milling. The resulting volume of hay was insufficient for the experiment, and on October 4th, 2015 a second collection of hay occurred at the mine site. The second collection was also dried for 7 days in the greenhouse and similarly milled twice. This method of particle size normalization provided no data about the distribution of grain size. The hammer mill was disassembled and cleaned with compressed air and a vacuum immediately prior to and after each use.

2.4.2 Sawdust Preparation

Three samples of the sawdust were sent to ALS on September 7th for chemical characterization. The analysis was similar to that performed for hay, but no analysis for available NH_4^+ was requested (as per discussions with Dr. Rutherford). Wood chips were milled twice in the hammer mill on September 30th, 2014, providing a pre-treatment similar to that of the hay samples discussed above. The hammer mill was disassembled and cleaned with compressed air and a vacuum immediately prior to and after each use.

2.4.3 Crushed Mine Waste Rock Preparation

Three samples were sent to ALS for metals characterization, ABA, C content and physical tests which included SO_4^{2-}S, pH, and moisture quantification. Cone and quartering methods (USEPA, 1993) were performed on a 29.2 kg sample of CMWR to maintain similar particle size distribution in the subsamples. A starting volume eight times greater than the required column volume was placed in a pile and the coning and quartering method was performed (Schumaker et al., 1989). This involves extensively mixing the rock volume in a pile to achieve particle size distribution heterogeneity, and then quartering the pile to get representative subsamples (**Figure 2.7).** This method is not designed to provide similar masses or volumes in the subsamples and resulted in subsamples which were not comparable in size or mass.

Figure 2.7: Cone and quarter method in progress.

When performing the coning and quartering method, a criteria of acceptability (CoA) of 5% relative percent difference (RPD) between sample masses was chosen, where sample A is split into subsamples B & C and the RPD is given by **Equation (22)**:

(22) $$RPD = 100\% * (2)\frac{|subsample\ B - subsample\ C|}{subsample\ B + subsampl\ \ C}$$

Note: all subsample values indicate masses

If the RPD exceeded 5%, the subsamples would be recombined, and the cone and quartering method would be applied again. This introduced an unintended bias: the cone and quartering method was performed on 0.254 mm (10-mil) thick plastic sheeting, but due to the angularity of the rock, the sheeting was punctured during every iteration of the method, which resulted in a loss of small fines (see **Figure 2.8**). An attempt was always made to recover the fines, by sweeping under the sheeting, but if the cone and quartering method was performed numerous times to meet the CoA, successive re-handling of the rock may have influenced the particle size (e.g., particles becoming stuck in the broom on each sweep).

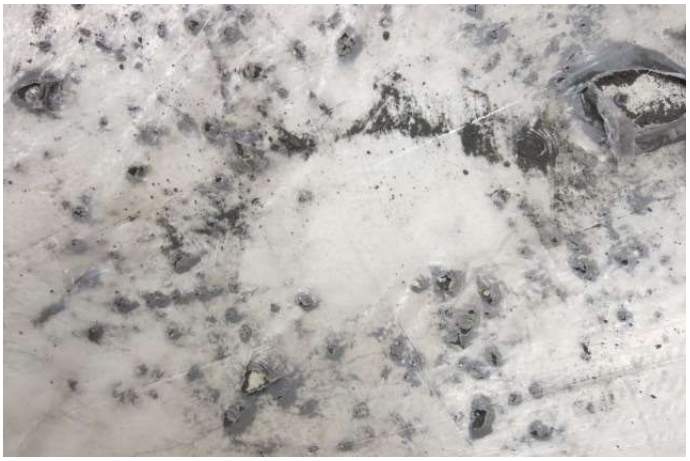


Figure 2.8: Residual fines left on the plastic sheeting after a cone and quartering event.

Sweeping above and below the sheeting resulted in most fines being recovered, but some losses resulted from each iteration of this method. The cone and quartering method was used again to split one CMWR subsample into 4 smaller samples. This sub sample splitting was performed on a clean laboratory bench using a dustpan and brush. On July 29th, 2015 these samples were submitted to ALS for particle size analysis to determine what the particle size distribution of this material was.

2.4.4 Sample Collection and Chemical Analysis

Column effluent was collected in the N_2-purged environment of the sample containers at the experiment site (see **Section 2.3**). The sample containers were then moved to a fume hood where they would be placed in a 571.5 mm (22.5”) N_2 purged inflatable glove bag[7],

---

[7] The glove bags were procured after the week 2 sampling event, and O_2 may have been introduced during filtering in the first 2 weeks,

allowing for effluent filtration and handling in an O_2 depleted environment. Filtration was achieved with plastic 50 ml Luer lock syringe, and 0.45-micrometer (µm) pore sized polyethersulfone (PES) membrane filters. In this environment the samples would be transferred into parameter specific sample shipping bottles and preserved according to ALS instructions.[8] Please refer to **Appendix C.4** for the list of preservation instructions (supplied by ALS) which were followed during the experiment. Samples stored in the 4 degree Celsius (°C) walk-in cooler in the EFL and were shipped on ice to ALS within 8 days of collection. Samples were analyzed for concentrations of parameters relevant to the project: dissolved metals, N species, S^{2-}, anions, dissolved organic carbon (DOC), and total alkalinity (a complete list of parameters and methods employed by ALS can be found in **Appendix C.3**).

Effluent samples were sent to Dr. Dirk Wallschlager at the Trent University Water Quality Center (Trent) for speciation of Se. Four species were reported: $Se_{(VI)}$, $Se_{(IV)}$, Se^0 and unidentified Se species. The samples were collected four times; on week 4, 11, 19, and 24. In week 4, samples were preserved by filtration through 0.45 µm PES filter and shipped on ice by overnight courier to Trent. The laboratory technician indicated that there was still an unacceptable presence of suspended solids in the samples, and that even after re-filtering, fine suspended solids clogged the analysis column. Subsequent preservation methods included twice centrifuging the samples at 20,000 revolutions per minute (RPM) at a force of 32 647 x gravity for 45 minutes (90 minutes total) and then filtering through 0.2 µm cellulose acetate

---

[8] In week 12, column 1 samples were not filtered, due to operator error.

filters prior to shipment on ice. This resolved the issue of fine solids clogging up the system in the Trent laboratory.

Minimum samples volumes, preservation requirements, and hold times are presented in **Table 2.2.** The target collection volume of each sample was 10 mL greater than that required by the laboratory to allow for duplicate analysis if required, mitigate losses occurring during transfer, possible spillage at ALS, and any other incidental loss of volume. ALS provided all sample containers: 125 mL high density polyethylene (HDPE) verified clean bottles (VCB), regular 125 mL HDPE bottles, and 250 mL amber glass bottles.

ALS also provided the following reagents for preserving samples:

- 1:1 Trace grade sulphuric acid (H_2SO_4): water mixture
- 3:1 Nitric acid (HNO_3): water mixture
- 1:9 Zinc acetate ($Zn(O_2CCH_3)_2$): water mixture
- 6N Sodium hydroxide (NaOH) solution

These reagents were color coded and provided in individual doses sufficient to preserve single samples.

Samples that were refrigerated for 8 days prior to shipment exceeded the EPA suggested hold times for the following parameters:

- NO_3^- (2 days)
- NO_2^- (2 days)
- S^{2-} (7 days)

Table 2.2: Hold times, preservatives, minimum volumes, and containers for parameters measured in the experiment in column influent and effluents

Parameter	Preservation method	Minimum Volume (ml)	Minimum Hold Times (days)*	Sample Container
Alkalinity	None	30	14	125 mL HDPE
Anions		5	2 – NO_3^- + NO_2^-	
S^{2-}	(1) $Zn(O_2CCH_3)_2$, shake + (2) NaOH, shake	100	7	125 mL HDPE
Total Metals	(1) Filter + (2) HNO_3, shake	50	6 months	125 mL VCB HDPE
TOC	(1) Filter + (2) H_2SO_4, shake	10	28	250 mL Amber Glass
NH3		50	28	

*Minimum hold time of all parameters (e.g., NO_3^- & NO_2^- in anions), as suggested by EPA methods.

After consultation with Dr. Rutherford, Clive Dawson (supervisor of the BC Analytical Laboratory), and technical representatives from ALS, it was determined that the samples would likely remain acceptable, so long as they were chilled to 4°C, and their exposure to light was limited. This was accomplished by placing the sample vials inside a sealed cooler, which was placed in the EFL walk-in cooler.

2.4.5 Column operation

The Natural Sciences and Engineering Research Council of Canada (NSERC) funding agreement covered a 6-month period, and this provided a fixed timeline for the completion of the experiment. The columns were filled on Jan 26th, 2015, and pumping was initiated on Feb 3rd, 2015, and completed on Jul 24th, 2015.

2.4.5.1 Flows

Flows varied from 0.212 – 0.350 mL min^{-1}. Short periods of no flow and high flow were required during the switching of pump lines, but these periods were generally less than 10 minutes in length.

2.4.5.2 Sampling Schedule

The sampling schedule was determined before starting the experiment to accommodate personnel availability Mondays and Tuesdays (and every second Wednesday), and to remain within the constraints of the funding. Effluent samples were collected from columns 1 and 6 on a weekly basis, filtered, and/or preserved (as required), and stored in sealed coolers in the EFL walk in refrigerator (4°C). Samples from all columns were sampled every second week and preserved. The appropriate QAQC samples would be prepared every second week as well, and the samples from both the current and previous week would be shipped overnight via courier to ALS as one complete sample set. This arrangement was chosen to reduce number of sample sets submitted, resulting in reduced the shipping and QAQC costs.

2.5 Quality Assurance and Quality Control (QAQC)

A comprehensive QAQC program was developed to determine accuracy and precision of results, operator error, and temporal variability in the results.

2.5.1 Field (independent of ALS)

In every bi-weekly sample set submitted, the following samples were included as part of the QAQC program:

1. Duplicate: The liquid in a randomly sampled collection container was split and submitted as a duplicate sample. The 500 mL sample collection containers (shown in **Figure 2.3**) did not permit two full suites of samples (305 mL per full suite) to be generated, so S^{2-} analysis was dropped from the duplicate suite (reducing the combined total volume of both original and duplicate sample suites

to 500 mL). The duplicate samples were labelled according to a code not provided to the lab.

2. Blank: Samples were either
    a. Filtered and preserved in the glove bag, as a measure of contamination introduced in the confined and contaminated environment inside the glove bag; or,
    b. Sampled directly from the Milli-Q meter in the lab and preserved, which hopefully provided a 'true blank'.
3. Reference: A solution containing 2 mL of Refractory Element and ICP-MS Elements standard (both containing elements at 10 μg mL^{-1}) was mixed with 396 mL Milli-Q water on January 20th, 2015 to create a reference solution. This mixture was acidified to pH<2 with 8 mL trace grade HNO_3, and stored in a 500-mL volumetric flask, which was wrapped in Al foil and refrigerated in a refrigerator at less than 5°C.

2.5.2 Laboratory

With every submitted every sample set, ALS provided data from their internal laboratory QAQC program, with the following parameters reported:

1. Replicates: Replicate analyses are measurements of the variable of interest performed as identically as possible on two subsamples of a sample. Replicate analyses were used to assess analytical variance (Clark, 2013);
2. Certified Reference Materials (CRM) . CRMs are reference materials having one or more property values that are certified by a technically valid procedure,

accompanied by a certificate or other documentation is issued by a certifying authority (Clark, 2013);

3. Laboratory Control Samples (LCS): LCSs are known matrixes spiked with compounds representative of the target analytes, and used to document laboratory performance (Clark, 2013);
4. Method Blanks (MB): MBs are analyte-free samples to which all reagents are added in the same proportions as used in sample processing. MBs must be carried through the complete sample preparation and analytical procedure. MBs are used to assess contamination resulting from the analytical process (Clark, 2013);
5. Matrix Spikes (MS): MSs are aliquots of sample spiked with known concentration of target analytes. Spiking occurs prior to sample preparation and analysis. A MS is used to document the bias of a method in a given sample matrix (Clark, 2013).

Section 3: Results

3.1 Overview

The results of the experiment are presented in this section. A detailed analysis of the QAQC measures introduced in **Section 2** are presented in **Appendix D.1** through **D.4**. Issues associated with data quality are presented in **Section 3.2**. Results of the materials characterization are presented in **Section 3.3**. The results of the column influent and effluent fluid characterizations are presented in **Sections 3.4** and **3.5**, respectively. Finally, qualitative observations are presented in **Section 3.6**.

All references to levels of NO_3^-, NO_2^-, and NH_3 refer to the N content of these measurements. Other parameters have been often prefixed with D- (dissolved) or T- (total). The concentrations of a specific parameter and column throughout the experiment (e.g., concentrations of D-Se in column 1 throughout the experiment) are referred to as a 'data set'. The following describes how means were calculated when some sample concentrations were below the method detection limit (MDL). The mean of any data set, if less than 15% of data points were less than or equal to the dilution dependent MDL, was calculated by the setting these values to 50% of the MDL (EPA, 2006). In attempting to quantify means of data sets with 15-50% of the values less than or equal to the MDL, the Cohen Method (EPA, 2006) was considered, but the data follows neither normal nor log normal distributions, and as a result, cannot be approximated by this method. As such, for data sets with greater than 15% of the results less than or equal to the MDL, no mean was calculated.

A 'field measurement' refers to a reading observed in the UNBC EFL, while a 'lab result' refers to a measurement obtained from an outside (not at UNBC) commercial or academic laboratory.

3.2 Data Quality

In addition to the QAQC CoAs used to evaluate the quality of the data in **Appendix D.1**, results were screened for inconsistency with the rest of the data set. This was noted in a few instances and the following corrective actions were taken:

- In weeks 1 and 2, procedures for sample handling (in oxygen free environments) were not fully developed. As such, the samples were not filtered in a N_2 purged glove bag. After consulting with Lorax, glove bags were procured all remaining sampling events;
- Column 1 and 2 results for anion/nutrient and dissolved metals samples from week 17 did not align with those of weeks before or after. This was noted for many parameters in this category. It appears that the samples from these columns were mislabeled. The anion/nutrient and metal results from this date were corrected, and the results now align with those immediately preceding and proceeding;
- In week 12, column 1 dissolved metal samples were not filtered due to operator error. The difference in sample preparation and analysis results in values that do not agree with those of previous and ensuing weeks, so this data point has been removed;
- In week 19, the sample for column 2 was different from other weeks: the dilution required to compensate for interference-causing analytes was much higher, and alkalinity levels were an order of magnitude greater than all other results. This casts doubt on the validity of these results, and the alkalinity result has been removed;
- In week 20, the DOC result reported for column 6 was 32.9 mg L^{-1}, while the average of the 6 closest results (preceding and following this event) was 4.47 mg L^{-1}. This data point has been removed as an outlier; and,

- Multimeter readings varied wildly for DO and ORP, and the swings in the values do not seem to coincide with changes in related parameters or each other. These data have been presented in the following sections, but their validity remains in question.

3.2.1. Data Issues Arising from Column Blockages

Column 1 effluent water quality was likely impacted by the frequent requirement to clear the effluent port of the column. Materials causing clogging or blocking were presumed to be organic (the specific gravity of CMWR would prevent it from blocking the PVDF effluent fitting located at the top of the column). They likely accumulated due to their small grain size (which allowed movement within the saturated pore volume of the column) and low density (which buoyed the pieces). These blockages were cleared by disconnecting the effluent tubing from the PVDF compression fitting and inserting a small piece of wire (approximately 2 mm in diameter) through the fitting. Blockages were often noticed during the 2-3-day sampling window each week, though they may have developed at any time during the unmonitored 4-5 days prior. Due to the blockage, the column was often under pressure from continuously pumping into a closed (blocked) system, and from gas generation. Please see **Figure 3.1** for an image of bubbles building up in top of Column 1. When the blockage was removed, discharge velocities were enough to spray foul smelling gas, liquids and organics approximately 3 m into the air. This resulted in the possible loss of organic mass in the columns, and possibly re-oxygenation of portions of the column. Collectively, these processes may have had an impact on the quality of the data from this column.

3.2.2. Operational Issues Affecting Results

After initially filling the columns, they were sealed tightly for a week, allowing entrapped air to dissolve and disperse in pore liquids of soils (Lewis & Sjostrom, 2010).

Unfortunately, there was a lack of supervision during this first week-long period, and the vapour pressure generated by the rapidly decomposing organic mass was sufficient to push liquids, gases, and organics through the upper gasketed seal (see **Figure 2.1** for an elevation profile of a column). **Table 3.1** shows the approximate void space for each column, calculated by dividing the initial mass of water required to fill each individual column by an assumed liquid density of 1 g/cm^3. The mass of amendment and liquid that was lost as a result of this initial pressurization is also shown. There is no direct correlation between lost mass and lost organics, as each column may have vented a unique mixture of gas, liquid, and organics.

Figure 3.1: Gas bubbles building up at the top of column 1. Rapid discharge of gas at specific periods during the column operation (at higher than average liquid flow velocities) may have contributed to organics plugging the column discharge port.

Table 3.1: Initial void space and estimated combined liquid and solid mass lost in first 5 days

Column	Void space	Mass lost in first 5 days
	cm^3	g
1	1415	434
2	1612	0
5	1459	447
6	1440	56

3.3 Amendment Characterization

3.3.1 Waste Rock

3.3.1.1 Particle Size Distribution

The average particle size of the CMWR samples is shown in **Table 3.2**. Please see **Appendix D.5** for a table of the individual results of each of the three samples.

Table 3.2: Average particle size distribution of three CMWR samples

Parameter	Average % of Total Sample	Standard Deviation
% Gravel (>2mm)	55.2	3.15
% Sand (2.00mm – 1.00mm)	14.3	0.45
% Sand (1.00mm – 0.50mm)	9.8	0.98
% Sand (0.50mm – 0.25mm)	6.2	0.67
% Sand (0.25mm – 0.125mm)	3.5	0.39
% Sand (0.125mm – 0.063mm)	2.2	0.25
% Silt (0.063mm – 0.0312mm)	2.3	0.30
% Silt (0.0312mm – 0.004mm)	3.9	0.32
% Clay (<4µm)	2.5	0.20

3.3.1.2 Elemental Abundance, Acid Base Accounting, and pH

The results of the chemical characterization of the CMWR are presented in tabular format in **Appendix D.6.** The CMWR was composed of the following dominant constituents: Calcium (Ca) (2.013%), Fe (1.527%), Al (0.757%), and P (0.243%). These values compare to upper continental crustal abundances of 2.945%, 3.089%, 7.744%, and 0.066%, respectively (Wedepohl, 1995). Given the purview of this thesis, concentrations of other elements of note are 119.3 ppm (Mn), 1233 ppm (S) and 2.833 ppm (Se), which contrast with the upper continental crustal averages of 527 ppm, 953 ppm, and 0.083 ppm, respectively (Wedepohl, 1995).

The results of the ABA Test on the CMWR showed an average acid generating potential of 7.53, and an average neutralizing potential of 56.3, resulting in a net neutralizing potential of 49 (all values are reported in tonnes $CaCO_3$ per kiloton of rock). The CMWR had an average paste pH of 8.1.

3.3.2 Organic Substrates

The result of the chemical characterization of the hay and the sawdust are presented in **Appendices D.7** and **D.8**, respectively. The hay was characterized by an average Total Organic Carbon (TOC) of 44.3%, and an average Total N (TN) of 1.15%, resulting in a TOC: TN ratio (% based) of 38: 1. The sawdust was characterized by an average TOC of 47.8% and an average TN of 0.054%, resulting in a TOC: TN ratio of 890: 1.

3.4 Influent Characterization

3.4.1 Overview

The results of field measurements and the chemical characterization of influent and individual column effluents are presented in raw tabular form in **Appendix D.9**. These results are plotted, separated by parameter, including both the influent and the effluent of each column in **Appendix D.10**. Dissolved-Se is presented in **Appendices D.9** and **D.10**. Selenate, SeO_3^{2-}, and any unidentified Se species detected are presented in tabular form in **Appendix D.11**, and graphically in **Appendix D.12** in two ways:

- Concentrations of $Se_{(IV)}$, $Se_{(VI)}$, and unknown species of Se, shown as percent of the cumulative Se total, are plotted in species-specific graphs to compare values between columns, an example of which is displayed in **Figure 3.2**; and,
- Species concentrations, shown as percent of the cumulative Se total, are plotted in column-specific graphs to demonstrate the dynamic conditions as a function of time. An example of this presentation is displayed in **Figure 3.3**.

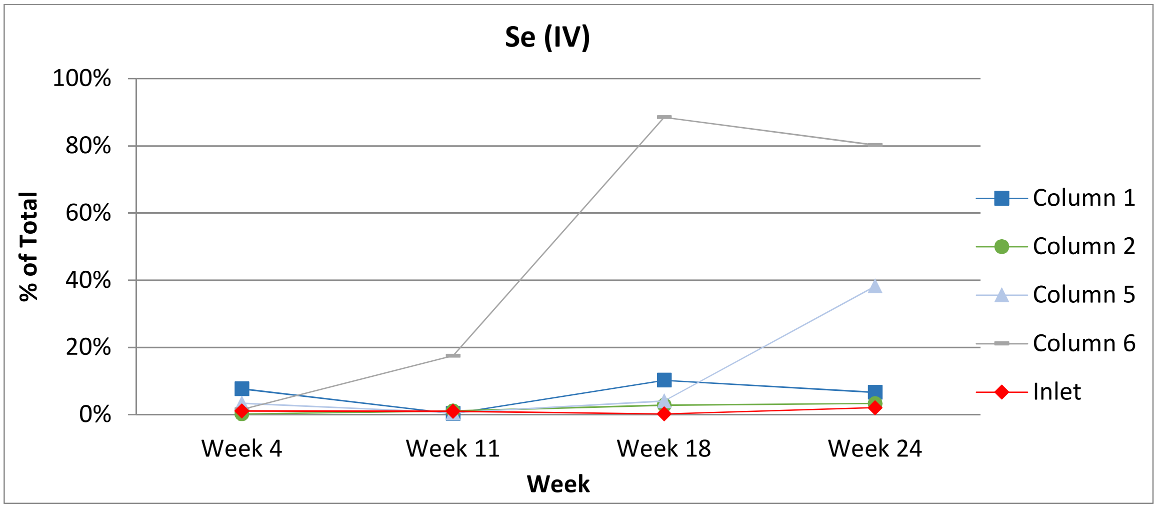


Figure 3.2: Column influent and effluent $Se_{(IV)}$ concentrations, presented as a percentage of total Se, plotted as a function of time.

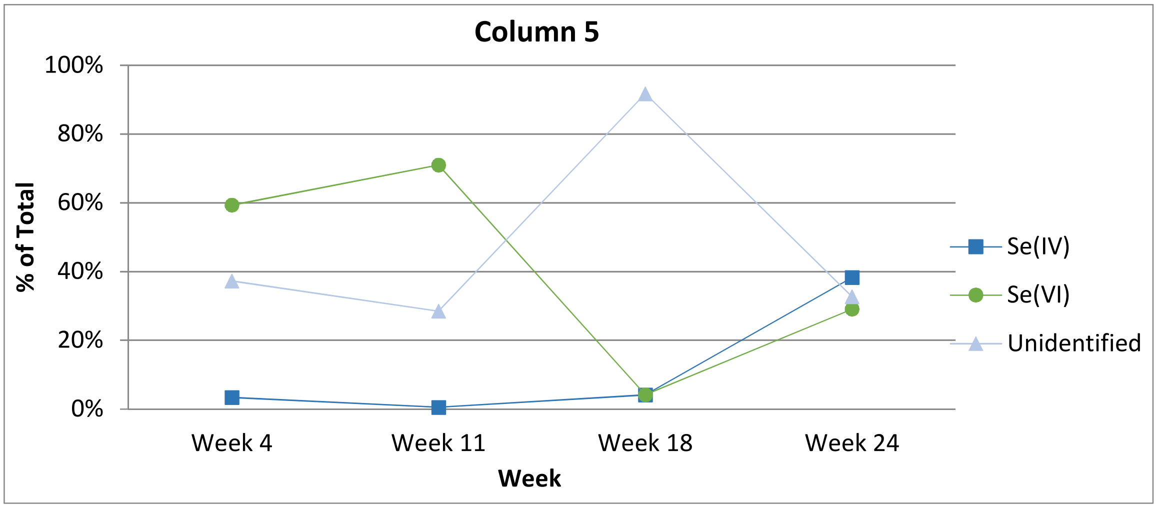


Figure 3.3: Column 5 effluent Se species concentrations presented as a percentage of total Se, plotted as a function of time.

The influent water used in the column experiment was sampled and chemically characterized on a biweekly basis as a measure of consistency. The results of this characterization are presented in raw form in **Appendix D.9**.

The results of the chemical characterizations have been input into PHREEQC using both the Lawrence Livermore National Laboratory (llnl) and Minteq International Inc. (minteq.v4) databases to determine the saturation index (SI) for specific minerals. The SI is useful to help determine whether the water is saturated, undersaturated, or supersaturated (corresponding SIs of 0, less than 0, and greater than 0, respectively), with respect to the mineral in question, where the SI is defined as:

$$SI = \log_{10}(IAP/K_{sp})$$

And where:

IAP = ion activity product

K_{sp} = equilibrium solubility constant

The SIs for individual parameters have been combined to a single set of results using the following methodology:

- if a valid result (not a SI of -999.9999) was obtained from the llnl database, the result was accepted as an input for the graph;
- if no valid llnl database result was obtained, but a valid result was obtained from the minteq.v4 database, the result was accepted as an input for the graph; and,
- if both database results produced invalid results, no result was presented on the graph.

The above approach allowed the maximum number of values to be used in generating the graphs. The input files, selected output parameters and graphed data are all provided in **Appendix D.13**. Consultation with members of the committee yielded the following CoA for SI results: saturation indices were only considered relevant if they were between -2.0 and 2.0, as values outside of this range may not be important in governing solute concentrations.

---

[9] A value of -999.999 is indicative of an undefined phase, or one or more of the constituent elements not in solution (Parkhurst & Appelo)

In the following presentation of influent water chemical analysis, and subsequent presentation of column effluent analysis, the information is laid out in subsections:

1) Major ions and pH, and these include alkalinity, D-Ca, D-Mg, Fluoride (F^-) and Cl^-;
2) Nitrogen species including NO_3^-, NO_2^-, and NH_3;
3) Parameters relevant to redox chemistry (unless shown in other sections) including DO, ORP, D-Fe, D-Mn, SO_4^{2-}, and S^{2-};
4) Selenium species; and
5) Trace elements and DOC.

Trace elements to be included in item 5) above were chosen after reviewing the Brule Mine 2014 Annual Water Quality Report (Walter Energy, 2015). Parameters that exceeded the WQG in 2014 are scrutinized to determine if column amendments influenced concentrations. These parameters are D-Al, D-Cd, D-Cu, D-Pb, D-Ni, and D-Zn.[10] Dissolved silver (Ag) samples had concentrations less than or equal to the MDL for all columns, so this parameter will not be discussed further.

3.4.2 Consistency of Influent Water

Influent water quality results were analyzed to determine if the water was chemically constant. The analysis consisted of calculating the RPD between the minimum and maximum concentrations reported over the duration of the experiment. The RPDs exceeded 100% for

---

[10] Fluoride exceeded the WQG in the Brule Mine's effluent in 2014, but this parameter is reported in Major ions and pH.

the following parameters (if the minimum value was less than 500% of the MDL, the result is not included):

- Dissolved Al, 126%;
- Dissolved Mn, 162%; and
- Dissolved Tl, 103%.

Influent water characterization results are summarized in **Section 3.4.3**. The results are also discussed in **Section 3.5** and are important as they present a baseline from which amendment effects can be evaluated. As evidenced by the few parameters with large RPDs (shown above) and by the following sections, influent water chemistry was rather static over the course of the experiment.

3.4.3 Influent Water Chemical Characterization

3.4.3.1 Major Ions and pH

Total alkalinity concentrations in the influent water ranged from 97.8 mg L^{-1} in week 24 to 121 mg L^{-1} in weeks 2 and 3. The average for the experiment was 114 mg L^{-1}. Influent D-Ca concentrations ranged from 178 mg L^{-1} in week 7 to 195 mg L^{-1} in week 19 and averaged 188 mg L^{-1}. Dissolved magnesium (Mg) concentrations ranged from 107 mg L^{-1} in week 9 to 115 mg L^{-1} in week 2 and averaged 110 mg L^{-1}. Chloride concentrations ranged from 9.5 mg L^{-1} in week 7 to 12.0 mg L^{-1} in week 2.

Influent pH generally increased throughout the experiment, and the minimum value was observed in week 4 (7.16) and the maximum in week 22 (8.14). When results were approximated by a linear slope ($R^2 = 0.32$) the slope is as shown in **Equation (23)**.

(23) $\mathrm{pH} = 0.0164x^{*} + 7.4666$

*where x is the number of weeks elapsed

Fluoride concentrations were always less than or equal to the dilution dependant MDL (which ranged from 0.2 mg L^{-1} to 0.4 mg L^{-1}).

3.4.3.2 Nitrogen Species

Influent NO_3^- concentrations averaged 73.5 mg L^{-1} over the experiment and ranged from 70.9 mg L^{-1} in week 7 to 75.6 mg L^{-1} in week 19. Nitrite concentrations only exceeded the MDL (0.01 mg L^{-1} or 0.02 mg L^{-1} depending on the dilutions required) in week 3 (0.011 mg L^{-1}). The influent NH_3 concentrations exceeded the MDL (0.005 mg L^{-1}) in weeks 1 and 9 only (0.0069 mg L^{-1} and 0.0063 mg L^{-1}, respectively).

3.4.3.3 Redox Chemistry

Influent DO levels generally increased over the life of the experiment, with a minimum being observed in week 1 (57.7% saturation), peaking in week 14 (172% saturation), and averaging 103.2%. Oxidation/reduction potential readings ranged from -122 mV to 288 mV in weeks 14 and 15 these results cast doubt on the calibration and accuracy of the instrument. Concentrations of D-Fe were below MDL (0.03 mg L^{-1}) throughout the entire experiment. Concentrations of D-Mn were above the dilution dependant MDL (0.05 - 0.1 μg L^{-1}) for only the first four sampling events. The maximum D-Mn concentration was observed in week 2 (0.472 mg L^{-1}). Sulfate concentrations ranged from 746 mg L^{-1} in week 7 to 801 mg L^{-1} in week 19 and averaged 778 mg L^{-1}. No sample had a S^{2-} concentration exceeding the MDL (0.02 mg L^{-1}). Dissolved U concentrations ranged from 17.5 μg L^{-1} to 22 μg L^{-1} in weeks 19 and 13, respectively. Dissolved antimony (Sb) concentrations ranged from 1.72 μg L^{-1} to 1.98 μg L^{-1} in weeks 19 and 7, respectively. Dissolved Mo concentrations ranged from 3.9 μg L^{-1} to 4.5 μg L^{-1} in weeks 19 and 13, respectively.

3.4.3.4 Selenium Species

Dissolved Se in column influents, as measured by ICP-MS analysis, ranged from a minimum in week 1 to a maximum in week 9 (104 µg L^{-1} and 118 µg L^{-1}, respectively). Speciation results from Trent indicate that Se$_{(VI)}$ ranged from 87-94% of the cumulative Se. Concentrations of Se$_{(IV)}$ ranged from a minimum in week 18 (less than 0.2 µg L^{-1}) to a maximum in week 24 (2 µg L^{-1}). Concentrations of Se$_{(VI)}$ ranged from a minimum in week 4 (87.1 µg L^{-1}) to a maximum in week 18 (91.5 µg L^{-1}). Unidentified Se species concentrations dropped from week 4 to week 24 (11.7 µg L^{-1} and 3.61 µg L^{-1}, respectively).

3.4.3.5 Trace Elements, DOC, and Solubility Controls

Concentrations of D-Al were at or below the MDL (3.0 µg L^{-1}) for every week of the experiment except weeks 9 and 22 (13.2 µg L^{-1} and 11.1 µg L^{-1} respectively). Concentrations of D-Cd did not exceed the dilution dependant MDL over the course of the experiment (0.005-0.01 µg L^{-1}). Concentrations of D-Cu were above the MDL (0.5 µg L^{-1}) only in week 1 (0.91 µg L^{-1}). Concentrations of D-Pb ranged from being equal to or less than the MDL (0.05 µg L^{-1}) in half of the samples to a maximum in week 3 (0.114 µg L^{-1}). Concentrations of D-Ni ranged from 52.7 µg L^{-1} to 62.7 µg L^{-1} in weeks 24 and 9 respectively. Concentrations of D-Zn were less than or equal to the MDL (3.0 µg L^{-1}) in every sample. Concentrations of DOC ranged from a minimum in week 7 (3.63 mg L^{-1}) to a maximum in week 2 (5.06 mg L^{-1}).

The SI for calcite, dolomite, and magnesite ranged from a minimum in week 3 (0.27, 1.66, and -0.24, respectively) to a maximum in week 22 (0.92, 2.96, and 0.41 respectively). The SI for gypsum was consistent through the experiment and ranged from a minimum in week 7 (-0.73) to a maximum in week 19 (-0.67).

3.5 Effluent Characterization.

3.5.1 Overview

Results of the effluent characterization are presented with those of the influent and shown in tabular and graphical form in **Appendices 9** and **10**, respectively. Parameter specific graphs plot column effluent concentrations relative to those of the influent (as a visual indicator of column performance over time). As an example, SO_4^{2-} effluent and influent concentrations are plotted together in **Figure 3.4**. The following sections present and compare the results, and frequently reference the data in the appendices. The water quality of each column is compared with influent water and analyzed for trends including maximums, minimums, and consistency. The results are analyzed in **Section 4**.

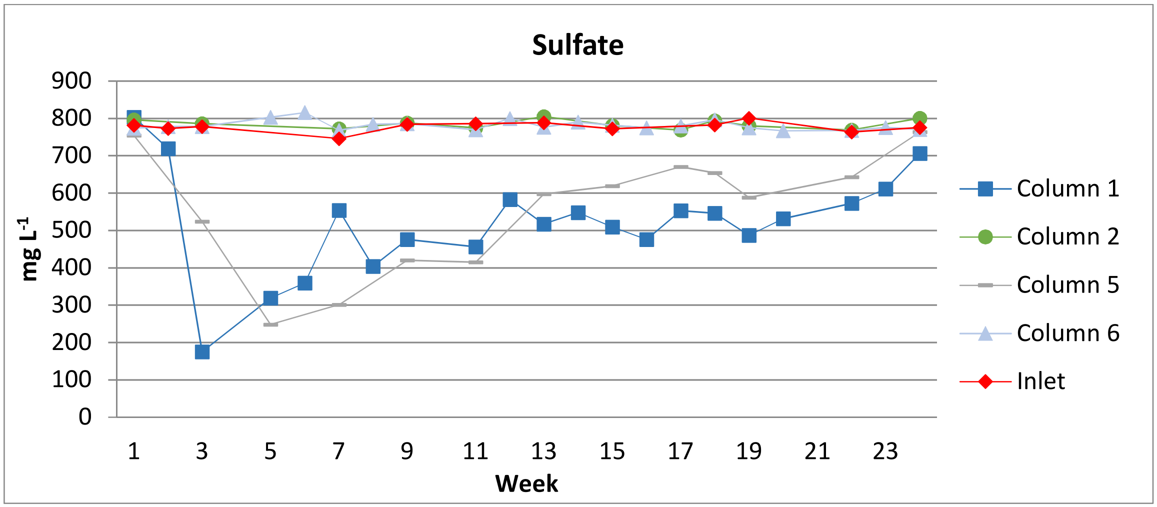


Figure 3.4: Influent and effluent SO_4^{2-} concentrations throughout the experiment.

In addition to the influent water quality parameters discussed in **Section 3.4**, the void space of each column at the beginning of the experiment is presented in **Table 3.1.** Void space ranged from 1415 cm^3 (column 1) to 1612 cm^3 (column 2).

3.5.2 Column 1 - Hay and Waste rock

3.5.2.1 Major Ions and pH

Effluent alkalinity concentrations were greater than those of the influent for the duration of the experiment. Values spiked sharply in week 2 (3880 mg L^{-1}), a questionable data point given the pre- and proceeding values, while the mean concentration for the experiment was much lower (980 mg L^{-1}). The lowest concentration was observed in the sample from week 24 (467 mg L^{-1}).

Effluent D-Ca concentrations were greater than those of the influent in every sample of the experiment. They spiked in the first 6 weeks of the trial, with concentrations peaking in weeks 2 (542 mg L^{-1}) and 6 (633 mg L^{-1}) and exhibited a minimum in week 16 (201 mg L^{-1}). The mean concentration in the 1st quarter of the experiment was 128% higher than that of the 3rd quarter (518 mg L^{-1} and 227 mg L^{-1}, respectively).

Effluent D-Mg concentrations fluctuated with alternating periods above and below the influent levels. Maximum and minimum concentrations were observed in weeks 5 and 13 (135 mg L^{-1} and 85.4 mg L^{-1} respectively), and the mean was 104 mg L^{-1}.

Chloride concentrations exhibited small fluctuations over the course of the experiment and ranged from 9.6 mg L^{-1} – 21 mg L^{-1}. Dilution required due to high concentrations of interference causing analytes resulted in elevated MDLs (as high as 25 mg L^{-1}). Due to this, Cl^- concentrations spiked in week 2, which may not be indicative of levels observed, but the preceding and proceeding concentrations (21 and 11 mg L^{-1}, respectively) provide an interval in which the true concentration may be contained.

Column 1 effluent pH generally increased very gradually throughout the experiment. The minimum was observed in week 6 (6.02) and the maximum in week 20

(6.86). Results were consistently less than those of the influent, by an average of 1.21 units. When results were approximated by a linear slope ($R^2 = 0.74$) the slope is as shown in **Equation (24)**.

(24) $\mathrm{pH} = 0.0298x^{*} + 6.0651$

*where x is the number of weeks elapsed

Fluoride concentrations were at or below the dilution dependant MDL (ranging from 0.2 mg L^{-1} to 1.0 mg L^{-1}) for samples collected in the first 12 weeks of the experiment, and sporadically afterwards. From week 13 onwards, samples that exceeded the MDL ranged from 0.22 mg L^{-1} to 0.31 mg L^{-1}.

3.5.2.2 Nitrogen Species

Twelve (12) of 21 column effluent sample concentrations were at or below the dilution dependant MDL for NO_3^- (0.05 mg L^{-1} – 0.10 mg L^{-1}). A spike was observed in week 24 (22.6 mg L^{-1}), which was the only result above 2.54 mg L^{-1}. All effluent results were below those of the influent.

Nitrite concentrations ranged from repeatedly being less than or equal to the dilution dependent MDL (0.01 mg L^{-1}- 0.05 mg L^{-1}) to 0.219 mg L^{-1} in week 18.

The concentration of NH_3 peaked in week 1 (8.79 mg L^{-1}), and by week 24, it did not exceed the MDL (0.005 mg L^{-1}). All results were greater than or equal to those of the influent.

3.5.2.3 Redox Chemistry

Dissolved O, reported as percent saturation, ranged from 6.5% in week 2 to 28.8% in week 19. ORP readings ranged from 63.1 mV in week 1 to -212.8 mV in week 14.

Dissolved Fe concentrations exhibited a maximum of 35.2 mg L^{-1} in week 5, and gradually decreased with time. Concentrations were elevated in the 1st quarter of the experiment, and in this period, they averaged 27.9 mg L^{-1}. In the 2nd, 3rd, and 4th quarters, the concentrations averaged 4.2 mg L^{-1}, 0.70 mg L^{-1}, and 0.27 mg L^{-1}, respectively. Effluent concentrations were above those of the influent for every sampling event.

Concentrations of D-Mn exhibited similar tendencies as those of D-Fe, and were elevated at the beginning of the experiment, peaking 1.27 mg L^{-1} in week 2. Concentrations were elevated in the 1st quarter of the experiment, and in this period, they averaged 0.979 mg L^{-1}. In the 2nd, 3rd, and 4th quarters, the concentrations averaged 0.204 mg L^{-1}, 0.084 mg L^{-1}, and 0.104 mg L^{-1}, respectively. All results were above those of the influent.

Effluent SO_4^{2-} concentrations only exceeded those of the influent in week 1, which had the highest recorded level throughout the experiment (803 mg L^{-1}). Concentrations dropped noticeably from week 1 to the columns lowest concentration in week 3 (175 mg L^{-1}). After week 3, concentrations rose almost steadily until the end of the experiment, achieving a final concentration of 706 mg L^{-1}.

Sulfide concentrations in Column 1 were greater than the MDL and those of the influent for the entire experiment but did not exhibit a noticeable pattern. The maximum and minimum concentrations were observed in weeks 18 (6.7 mg L^{-1}) and 12 (0.031 mg L^{-1}), respectively.

Concentrations of D-U were less than those of the influent for the entire experiment, and varied during the experiment: they dipped from week 1 (4.09 µg L^{-1}) to week 3 (2.29 µg L^{-1}), then rose to week 13 (15.6 µg L^{-1}), and dropped to week 22 (2.85 µg L^{-1}) before rising again in week 24 (10.7 µg L^{-1}).

Concentrations of D-Sb dropped sharply from a maximum in week 1 (51.6 µg L^{-1}) to a minimum in week 5 (2.16 µg L^{-1}). All results were greater than those of the influent.

Concentrations of D-Mo dropped from 26.9 µg L^{-1} in week 1 to a minimum in week 6 (0.77 µg L^{-1}). From week 3 to 24 concentrations did not exceed 4.99 µg L^{-1} and were on average, below those of the influent.

3.5.2.4 Selenium Species

Effluent D-Se concentrations peaked in weeks 1 and 24 (49.4 µg L^{-1} and 31.9 µg L^{-1}, respectively). Effluent concentrations were below those of the influent for every sampling event. Speciation results from Trent indicate that the majority of the D-Se found in Column 1 effluent was either $Se_{(VI)}$ or unidentified Se species. The sum of all dissolved phase Se concentrations did not show any consistency between the results reported by Trent and those reported by ALS. The percent of $Se_{(IV)}$, relative to total dissolved Se reported by Trent, ranged from a minimum in week 11 (0.29% of total Se) to a maximum in week 18 (10.21%). The relative percent of $Se_{(VI)}$ ranged from a minimum in week 18 (6.65%) to a maximum in week 11 (75.7%). The relative percent of unidentified Se species ranged from a minimum in week 24 (20.7%) to a maximum in week 18 (83.1%).

3.5.2.5 Trace Elements, DOC, and Solubility Controls

Concentrations of D-Al decreased from a maximum in week 1 (118 µg L^{-1}) to a minimum in week 24 (7.3 µg L^{-1}), and all results were greater than those of the influent.

Concentrations of D-Cd exhibited a sharp decrease from a maximum of 0.32 µg L^{-1} in week 1 to 0.037 µg L^{-1} in week 3. The results increased again to week 6 (0.10 µg L^{-1}) as a result of the dilution dependent MDL, and then fell to less than 0.0131 µg L^{-1} in the last 9 weeks of the experiment.

Concentrations of D-Cu were above the dilution dependant MDL (ranging from 0.5 µg L^{-1} to 1.0 µg L^{-1}) in weeks 1-3, 7 and 13. Week 1 had the highest concentration (4.55 µg L^{-1}) and all detectable results were greater than or equal to those of the influent.

Concentrations of D-Pb dropped from a maximum in week 1 (1.17 µg L^{-1}) to being marginally above, or less than equal to the MDL (0.05 µg L^{-1}) in the 2nd half of the period, and except for those of week 22, all results were greater than or equal to those of the influent.

Concentrations of D-Ni dropped from a maximum in week 1 (1.2 mg L^{-1}) to less than 0.1 mg L^{-1} from week 3 to the end of the experiment. All results before week 8 were greater than, and all results after were less than those of the influent.

Concentrations of D-Zn dropped sharply from a maximum in week 1 (1810 µg L^{-1}) to 25.2 µg L^{-1} in week 2, down to the MDL (3.0 µg L^{-1}) in weeks 18-20 and 22.

Dissolved organic C spiked up to 1110 mg L^{-1} in week 2 (from an initial value of 583 mg L^{-1} on week 1) and then generally decreased to a minimum observed in week 20 (4.39 mg L^{-1}). The 1st quarter average DOC concentration was 807 mg L^{-1} while that of the last quarter was 29.3 mg L^{-1}. All column 1 effluents had concentrations of DOC greater than those of the influent.

Saturation indices for calcite and dolomite were greater than 0 for the duration of the experiment and ranged from minimums in week 24 (0.12) and 1 (1.10) to maximums in week 2 (0.69) and 20 (2.13), respectively. The SI of magnesite was consistently less than 0 and ranged from a minimum in week 1 (-0.70) to a maximum in week 20 (-0.035). The SI of gypsum ranged from a minimum in week 3 (-1.07) to a maximum in week 1 (-0.45). The SI of FeS_2, pyrrhotite, and troilite fluctuated largely. Pyrrhotite and troilite SI values were -0.78, 0.46, -0.28, and -0.68, 0.56, -0.18, in weeks 1, 3 and 5, respectively, with large negative values observed in week 2 and the rest of the experiment. Siderite SI values were greater than 0 in weeks 1 through 6 and achieved a maximum in week 5 (0.19), before falling off to a minimum of -2.1 in week 22, and those of rhodochrosite fluctuated from a maximum in week 2 (-0.03) to a minimum in week 16 (-1.38). The SI of mackinawite ranged from a maximum in week 3 (0.88) to a minimum in week 15 (-1.34).

3.5.3 Column 2 - Waste Rock only

3.5.3.1 Major Ions and pH

Alkalinity concentrations ranged from a minimum of 134 mg L^{-1} in week 1 to a maximum of 1800 mg L^{-1} in week 19. This result has been considered a laboratory error, as it is more than 10 times higher than the next highest concentration, observed in week 3 (151 mg L^{-1}). As mentioned in **Section 3.2**, this data point has been removed. All effluent concentrations are greater than those of the influent.

Every week, D-Ca concentrations were greater than those of the influent by a margin ranging from 9-22 mg L^{-1} and were relatively constant throughout the experiment.

Average D-Mg concentrations in column 2 were consistently slightly less than those of the influent throughout the experiment (average of 104 mg L^{-1} and 110 mg L^{-1}, respectively). Maximum and minimum concentrations were observed in weeks 13 and 1 (113 mg L^{-1} and 92.5 mg L^{-1}, respectively).

Chloride concentrations ranged from 9.7 mg L^{-1} – 11 mg L^{-1}. Due to the dilution dependent MDL, Cl^- concentrations plots show a spike in week 19 (25 mg L^{-1}), which is not necessarily indicative of actual levels.

Column 2 effluent pH generally increased throughout the experiment but fluctuated on a sample-by-sample basis. The minimum was observed in week 3 (6.84) and the maximum in week 20 (7.98). Except for week 20, results were consistently less than those of the influent. When results were approximated by a linear slope ($R^2 = 0.15$) the slope is as shown in **Equation (25)**.

(25) $pH = 0.0129x^{*} + 7.0699$

*where x is the number of weeks elapsed

Effluent F^- concentrations decreased from week 1 (0.67 mg L^{-1}) to week 9 (0.29 mg L^{-1}), and then were less than the dilution dependent MDL until week 24 (0.23 mg L^{-1}).

3.5.3.2 Nitrogen Species

Column 2 effluent NO_3^- concentrations averaged 74.0 mg L^{-1} over the experiment, only 0.5 mg L^{-1} greater than those of the influent, and the similarity of these values is evident when inspecting the figures in **Appendix D.10**.

Nitrite concentrations were highest in week 1 (0.134 mg L^{-1}) and were only above the dilution dependent MDL (0.01 mg L^{-1}-0.05 mg L^{-1}) in the first four samples.

Ammonia concentrations ranged from a maximum in week 13 (0.0913 mg L^{-1}) to a minimum in week 24 (0.061 mg L^{-1}). Column effluent concentrations were greater than those of the influent during every sampling event (noting again that most influent values were below the MDL).

3.5.3.3 Redox Chemistry

Column 2 effluent DO, reported as percent saturation, ranged from 79.8% in week 14 to 20.0% in week 4, and was lower than the influent throughout the study. ORP readings were extremely close to those of the inlet water and ranged from -200 mV to 296 mV (in weeks 14 and 16, respectively)

No D-Fe concentrations exceeded the MDL (0.03 mg L^{-1}). Concentrations of D-Mn ranged from 0.0805 mg L^{-1} in week 1 to 0.131 mg L^{-1} in week 9. Effluent concentrations of D-Mn were greater than those of the influent during every sampling event.

Average SO_4^{2-} concentrations were marginally higher than those of the influent (786 mg L^{-1} and 777 mg L^{-1}, respectively). Concentrations fluctuated slightly throughout the study but remained relatively constant. Maximum and minimum concentrations were reported in weeks 13 and 22 (805 mg L^{-1} and 769 mg L^{-1}, respectively).

Effluent S^{2-} concentrations, like those of the influent were less than or equal to the MDL (0.02 mg L^{-1}) for every sample.

Effluent concentrations of D-U were slightly less than, but followed the week by week concentration changes observed in the those of the influent. They ranged from 15.1 µg L^{-1} to 20 µg L^{-1} in weeks 11 and 3, respectively.

Concentrations of D-Sb were relatively stable and ranged from 4.27 µg L^{-1} (max) to 3.29 µg L^{-1} (min) in weeks 3 and 24, respectively. All effluent concentrations were above those of the influent.

Concentrations of D-Mo decreased from week 1 to 24 (24.1 µg L^{-1} and 9.64 µg L^{-1}) and were 5.6 – 2.2 times greater than those of the influent, respectively.

3.5.3.4 Selenium Species

Effluent D-Se concentrations were greatest in week 1, which was 32% higher than that of the influent (137 µg L^{-1} and 104 µg L^{-1}, respectively). Effluent concentrations decreased very gradually over the duration of the experiment and dropped below those of the influent (approximately 2/3 into the study). The minimum effluent concentration was recorded in week 22 (89.5 µg L^{-1}), which was 17% below that of the influent. Speciation results indicate that the majority of the Se found in Column 2 effluent was $Se_{(VI)}$ with little or no unidentified Se and $Se_{(IV)}$ species. The relative percent of $Se_{(IV)}$ ranged from a minimum in week 4 (0.2%) to a maximum in week 24 (3.3%). The relative percent of $Se_{(VI)}$ decreased from a maximum in week 4 (100%) to a minimum in week 24 (91.0%). The relative percent of unidentified Se species ranged from a minimum in week 4 (0%) to a maximum in week 24 (5.75%).

3.5.3.5 Trace Elements, DOC, and Solubility Controls

Concentrations of D-Al were at or below the MDL (3.0 μg L^{-1}) for every week of the experiment. Concentrations of D-Cd ranged from a minimum in week 18 to a maximum in week 7 (1.18 μg L^{-1} and 1.73 μg L^{-1}, respectively), and were consistently above those of the influent. Concentrations of D-Cu were consistently above the those of the influent. Concentrations of D-Pb were consistently less than or equal to the MDL (0.05 μg L^{-1}). Concentrations of D-Ni gradually decreased from 143 μg L^{-1} in week 1 to 72.8 μg L^{-1} in week 24, and all results were greater than those of the influent. Concentrations of D-Zn generally decreased throughout the course of the experiment and exhibited a peak in week 3 of 90.9 μg L^{-1} and a minimum in week 24 of 49.8 μg L^{-1} and all results were greater than those of the influent.

Concentrations of DOC were low and ranged from 1.04 mg L^{-1} to 3.07 mg L^{-1} in weeks 13 and 1 respectively. Effluent DOC concentrations were slightly less than those of the influent during every sampling event.

The SI of calcite was below 0 in weeks 3, 11, and 15 below 0 while that of dolomite was consistently above 0. The SI of magnesite was above 0 in week 19 only, while that of rhodochrosite was always less than 0. The SI of calcite, dolomite, rhodochrosite, and magnesite ranged from minimums in week 3 (-0.18, 0.68, -1.64, and -0.77, respectively) to maximums in week 19 (1.21, 3.48, -0.23, and 0.65, respectively). The SI of gypsum was less that -0.5 for the entire experiment.

3.5.4 Column 5 – Hay, Sawdust and Waste Rock

3.5.4.1 Major Ions and pH

Effluent total alkalinity concentrations rose from 638 mg L^{-1} to a maximum of 884 mg L^{-1} in week 1 and 9, respectively, and then decreased to 370 mg L^{-1} by week 24. The average concentration in the 2nd quarter of the experiment (830 mg L^{-1}) was 76.5% greater than that of the 4th quarter (470 mg L^{-1}) and all concentrations were substantially greater than those of the influent water.

Dissolved Ca concentrations spiked at the onset of the trial, with concentrations peaking in week 3 (328 mg L^{-1}) from 312 mg L^{-1} in week 1. The concentrations gradually decreased with time, with a minimum concentration observed in week 18 (197 mg L^{-1}). The average concentration in the 1st quarter of the experiment was 54% higher than that of the 3rd (313 mg L^{-1} and 203 mg L^{-1}, respectively). Effluent concentrations exceeded those of the influent for every week of the trial, but difference between the two decreased with time.

Dissolved Mg concentrations remained relatively consistent throughout the length of the experiment, with maximum and minimum concentrations observed in weeks 18 and 7 (107 mg L^{-1} and 87.4 mg L^{-1} respectively). The average concentration over the course of the experiment was 98.2 mg L^{-1}. Concentrations of the influent exceeded those of column 5 effluent for every week of the trial.

Chloride concentrations were highest in week 1 (12 mg L^{-1}), lowest in week 7 (9.5 mg L^{-1}), and had an average of 10.2 mg L^{-1}. Concentrations were similar (within 1.0 mg L^{-1}) to those of the influent over the course of the experiment.

Column 5 effluent pH generally increased throughout the experiment. The minimum was observed in week 5 (6.27) and the maximum in week 20 (7.07). Results were consistently less than those of the influent, by an average of 0.92 units. When results were approximated by a linear slope ($R^2 = 0.73$) the slope is as shown in **Equation (26)**.

(26) $\mathrm{pH} = 0.0297x^* + 6.3227$

*where x is the number of weeks elapsed

Fluoride concentrations ranged from 0.21 mg L^{-1} to 0.44 mg L^{-1} and were occasionally less than of equal to the dilution dependant MDL.

3.5.4.2 Nitrogen Species

Effluent NO_3^- concentrations gradually increased from the dilution dependent MDL (0.05 mg L^{-1} to 0.1 mg L^{-1}) in weeks 1, 5, 7, and 11 to a maximum of 23.9 mg L^{-1} in week 24. No week had an effluent NO_3^- concentration greater than 33% of its influent level.

Nitrite concentrations ranged from a maximum of 19.7 mg L^{-1} in week 1 to a minimum of 0.021 mg L^{-1} in week 5. No concentration after week 1 exceeded 0.64 mg L^{-1}. Effluent concentrations exceeded those of the influent for every week of the trial.

Ammonia concentrations dropped off sharply from a maximum, observed in week 1 (7.44 mg L^{-1}) to 0.120 mg L^{-1} at week 5. Then concentrations tended to slowly decrease until week 24, when they were less than or equal to the MDL (0.005 mg L^{-1}). The average NH_3 concentration (0.864 mg L^{-1}) was more than 146 times higher in the first quarter of the experiment than the third (3.38 mg L^{-1} and 0.023 mg L^{-1}, respectively). Effluent NH_3 concentrations in the fourth quarter decrease further, but samples below the detection limit prevent a calculation of the average for this period.

3.5.4.3 Redox Chemistry

Effluent DO levels, reported as percent saturation, ranged from 1.5% in week 16 to 30.7% in week 14, and levels were lower than those of the influent for every sampling event. ORP readings ranged from 29.6 mV in week 1 to -244.3 mV in week 8 and were lower than those of the influent every week except 14 and 20.

Concentrations of D-Fe rose to a maximum in week 1 through 5 (3.26 mg L^{-1} and 15.7 mg L^{-1}, respectively), before dropping to less than 20% of these earlier results. From week 7 onwards the concentrations ranged from 0.058 mg L^{-1} (week 9) to 0.619 mg L^{-1} (week 15). The average concentration in the first quarter of the experiment (10.1 mg L^{-1}) was more than 32 times that of the last (0.312 mg L^{-1}). Effluent concentrations exceeded those of the influent for every week of the trial.

Dissolved Mn concentrations decreased by an order of magnitude from their maximum level in week 1 (0.887 mg L^{-1}) to their minimum in week 19 (0.0714 mg L^{-1}), then rebounded slightly to 0.0945 mg L^{-1} by week 24. The average D-Mn concentration for the 1st quarter of the experiment was more than 8 times that of the last (0.729 mg L^{-1} and 0.0836 mg L^{-1}, respectively).

Effluent SO_4^{2-} concentrations dropped noticeably from the start of the experiment (754 mg L^{-1} in week 1) to week 5, when the minimum level was observed (248 mg L^{-1}). After week 5, concentrations rose almost steadily until the end of the experiment, when they reached the maximum of 764 mg L^{-1}. The average SO_4^{2-} concentration over the course of the experiment was 554 mg L^{-1}. Concentrations of the influent exceeded those of the column 5 for every week of the trial.

Sulfide concentrations were greatest during the middle of the experiment peaking in week 9 (10.9 mg L^{-1}) increasing from below the MDL in week 1 (0.02 mg L^{-1}) and then decreasing to 0.053 mg L^{-1} by week 24. Effluent concentrations exceeded those of the influent for every week of the trial.

Concentrations of D-U were less than those of the influent for the entire experiment. They peaked in the weeks 1 and 18 (14.6 μg L^{-1} and 15.3 μg L, respectively) and exhibited a minimum in week 5 (3. 63 μg L^{-1}).

Concentrations of D-Sb were greater than those of the influent for the entire experiment. They dropped from a peak in week 1 (42.2 μg L^{-1}) to a minimum in week 5 (1.83 μg L^{-1}) and were less than or equal to 6.01 μg L^{-1} (observed in week 13), for the remainder of the experiment.

Concentrations of D-Mo dropped from a maximum observed in week 1 (57 μg L^{-1}) to a minimum in week 7 (0.753 μg L^{-1}), and then increased to 5.82 μg L^{-1} by week 24. Except for the high initial concentrations, levels were comparable to those of the influent.

3.5.4.4 Selenium Species

Effluent D-Se concentrations decreased from a maximum observed in week 1 (102 μg L^{-1}) to a minimum in week 3 (2.3 μg L^{-1}), after which all concentrations were less than or equal to 22.3 μg L^{-1}, observed in week 17. Effluent concentrations were below those of the influent for every sampling event. Speciation results indicate that each species of Se was dominant in at least one sampling event. The relative percentage of $Se_{(IV)}$ ranged from a minimum in week 11 (0.5%) to a maximum in week 24 (38.3%) when it was dominant. The relative percentage of $Se_{(VI)}$ ranged from a minimum in week 18 (4.2%) to a maximum in week 11 (71.0%) and was dominant in weeks 4 and 11. The relative percent of unidentified

Se species concentrations ranged from a minimum in week 11 (28.5%) to a maximum in week 18 (91.8%), when they were dominant.

3.5.4.5 Trace Elements, DOC, and Solubility Controls

Concentrations of D-Al were greater than the influent for every week in the experiment except 22 and decreased from a maximum in week 3 to a minimum in week 24 (44.5 µg L^{-1} and 5.4 µg L^{-1}, respectively). Concentrations of D-Cd ranged from an initial peak in week 1 to the MDL in weeks 18-24 (3.01 µg L^{-1} and 0.005 µg L^{-1}, respectively). Concentrations of D-Cu were above the MDL (0.5 µg L^{-1}) only in weeks 1 (3.22 µg L^{-1}), 3 (1.56 µg L^{-1}), and 7 (0.66 µg L^{-1}). Concentrations of D-Pb dropped from an initial high of 0.57 µg L^{-1} in week 1 to the MDL (0.05 µg L^{-1}) in week 7, which was only exceeded in week 13 (0.061 µg L^{-1}). Concentrations of D-Ni dropped from 0.918 mg L^{-1} to 0.0183 mg L^{-1} in weeks 1 and 24 respectively. Concentrations of D-Zn dropped from an initial spike of 911 µg L^{-1} in week 1 down to a range from the MDL (3.0 µg L^{-1}) to 8.3 µg L^{-1} in the remaining sampling events.

Concentrations of DOC increased from week 1-5 (165 mg L^{-1} and 397 mg L^{-1}, respectively), after which they decreased. Effluent DOC concentrations were less than 14 mg L^{-1} after week 11 and were greater than those of the influent during every sampling event.

Saturation indices for calcite and dolomite were greater than 0, while those of magnesite, rhodochrosite, and gypsum were less than 0 for the entirety of the experiment. Pyrrhotite, troilite, and mackinawite SI values ranged from a minimum in week 24 (-2.14, -2.04, and -2.01, respectively) to a maximum in week 5 (0.22, 0.33, and 0.66, respectively). The SI of siderite was greater than zero only in week 5 (0.06) and reached a minimum in week 11 (-1.91).

3.5.5 Column 6 - Sawdust and Waste Rock

3.5.5.1 Major Ions and pH

Effluent total alkalinity levels initially rose from 186 mg L^{-1} in week 1 to a maximum concentration of 280 mg L^{-1} in week 6. From week 7 onwards, effluent concentrations did not exceed 213 mg L^{-1} (seen in week 8) and decreased to 174 mg L^{-1} by week 24. The average concentration was 204 mg L^{-1} and all effluent concentrations exceeded those of the influent.

Calcium concentrations exhibited relatively little variation throughout the experiment, ranging from a minimum of 180 mg L^{-1} to a maximum to 215 mg L^{-1} in weeks 16 and 11, respectively. The effluent concentration of week 16 was lower than that of the influent. The average concentration was 203 mg L^{-1}.

Dissolved Mg concentrations also exhibited relatively little variation throughout the experiment, with a minimum and maximum observed in weeks 1 and 20 (93.5 mg L^{-1} and 117 mg L^{-1}), respectively. The average concentration over the course of the experiment was 104 mg L^{-1}.

Effluent Cl^- concentrations did not vary much from those of the influent. The effluent Cl^- concentrations were highest in week 1 (15 mg L^{-1}), then between weeks 3 and 24, they ranged from 9.8 mg L^{-1} to 11 mg L^{-1}. Much of the data set in the later half of the study fell below the MDL (10 mg L^{-1})

Column 6 effluent pH fluctuated but in general increased throughout the experiment. The minimum and maximum were observed in week 11 and 7 (6. 78 and 7.57), respectively. Results were consistently less than those of the influent, by an average of 0.53 units. When results were approximated by a linear slope ($R^2 = 0.028$) the slope is as shown in **Equation (27)**.

(27) $pH = 0.0049x^* + 7.0458$

*where x is the number of weeks elapsed

Fluoride concentrations rose to a maximum in week 2 (0.75 mg L$^{-`}$) then fell to a minimum in week 16 (0.27 mg L^{-1}).

3.5.5.2 Nitrogen Species

Nitrate concentrations averaged 55.3 mg L^{-1} over the experiment. Concentrations decreased from week 1 (56.5 mg L^{-1}) to the minimum in week 6 (42.9 mg L^{-1}) and then ranged from 54.4 mg L^{-1} to 61.2 mg L^{-1} from week 7 through 24 (the maximum). Influent NO_3^- concentrations exceeded those of the effluent for every week of the trial.

Nitrite concentrations ranged from a maximum of 2.79 mg L^{-1} in week 2 to a minimum of 0.16 mg L^{-1} in weeks 16-17 and 19-20. In weeks 15, 18 and 22, the concentrations fell below the dilution dependent MDL (0.02 mg L^{-1}).

Ammonia concentrations ranged from the maximum (0.0902 mg L^{-1}) to the minimum (0.009 mg L^{-1}), observed in weeks 1 and 6, respectively. No clear trend emerged during the experiment. The average NH_3 concentration over the experiment was 0.0449 mg L^{-1}.

3.5.5.3 Redox Chemistry

Dissolved O_2 levels, reported as percent saturation, ranged from 10.6% in week 5 to 57.6% in week 14, and levels were lower than those of the influent for every sampling event. ORP readings ranged from 104 mV in week 1 to -164 mV in week 14.

Effluent concentrations of D-Fe were equal to or less than the detection limit (0.03 mg L^{-1}) for all samples collected during the experiment. Dissolved Mn concentrations ranged from their maximum level in week 6 (267 µg L^{-1}) to their minimum in week 24 (151 µg L^{-1}). The average D-Mn concentration for the 1st quarter of the experiment was 50% greater that of the last quarter (246 µg L^{-1} and 164 µg L^{-1}, respectively).

Effluent SO_4^{2-} concentrations were relatively constant and did not vary greatly from those of the influent (with averages of 782 mg L^{-1} and 778 mg L^{-1} respectively). The minimum and maximum concentrations were observed in weeks 20 and 6 (767 mg L^{-1} and 816 mg L^{-1}), respectively.

Sulfide concentrations exceeded the MDL (0.02 mg L^{-1}) only in weeks 1 and 3 (0.021 mg L^{-1} and 0.023 mg L^{-1}, respectively).

Concentrations of D-U were similar to those of the influent for the entire experiment. They achieved a minimum and maximum in weeks 19 and 6 (17 µg L^{-1} and 22.7 µg L^{-1}, respectively).

Concentrations of D-Sb were greater than those of the influent during the length of the experiment. Except for some minor fluctuations, concentrations were relatively constant throughout the study and ranged from a minimum in week 7 (4.83 µg L^{-1}) to a maximum in week 22 (6.22 µg L^{-1}).

Effluent concentrations of D-Mo were less than those of the influent but steadily decreased during the experiment. They ranged from a maximum observed in weeks 1 and 2 (21.2 µg L^{-1}) to a minimum in week 24 (11.7 µg L^{-1}).

3.5.5.4 Selenium Species

Effluent D-Se concentrations exceeded those of the influent only in week 1 (119 µg L^{-1}) and generally decreased after that. The minimum concentration was observed in week 23 (23.2 µg L^{-1}). Speciation results indicate that $Se_{(VI)}$ and $Se_{(IV)}$ were the dominant species in 2 sampling events each: the relative percentage of $Se_{(IV)}$ increased from a minimum in week 4 (1.52%) to a maximum in week 18 (88.53%), and were dominant in weeks 18 and 24. The relative percentage of $Se_{(VI)}$ ranged from a minimum in week 18 (1.22%) to a maximum in week 1 (85.8%), and were dominant in weeks 4 and 11,

3.5.5.5 Trace Elements, DOC, and Solubility Controls

Concentrations of D-Al were at or below the MDL (5.0 µg L^{-1}) throughout the experiment except for weeks 6 through 8, peaking in week 7 (6.6 µg L^{-1}). Concentrations of D-Cd generally decreased from a maximum in week 1 to a minimum in week 23 (2.38 µg L^{-1} and 0.525 µg L^{-1}, respectively). Concentrations of D-Cu fluctuated at first, achieving a maximum of 1.37 µg L^{-1} in week 5, then dropping to less than or equal to the MDL after week 15. Concentrations of D-Pb ranged from being equal to or less than the MDL (0.05 µg L^{-1}) at both the beginning and the end of the experiment, to a maximum in week 7 (0.173 µg L^{-1}). Concentrations of D-Ni generally decreased from 233 µg L^{-1} to 89.6 µg L^{-1} in weeks 1 and 24 respectively. Concentrations of D-Zn generally decreased from 127 µg L^{-1} to 58.1 µg L^{-1} in weeks 1 and 24 respectively.

Concentrations of DOC generally decreased from week 1 to 22 (28.8 mg L^{-1} and 4.31 mg L^{-1}, respectively). Effluent DOC concentrations were greater than those of the influent during every sampling event.

The SI of dolomite, calcite, and magnesite each exceeded 0 for periods of time. Calcite, gypsum, and rhodochrosite SI's ranged from a minimum in week 16 (-0.16, -0.72, and -1.36, respectively) to a maximum in weeks 7 (0.65), 6 (-0.65), and 7 (-0.39), respectively. The SI of magnesite ranged from a minimum in week 11 (-0.69) to a maximum in week 20 (0.11), while that of dolomite was consistently above zero.

3.6 Qualitative Observations

In the 1st quarter of the experiment, continuing to a lesser extent later on, there was a significant difference in colour in the collected samples. Clear liquids were collected from influent and effluent from columns with no hay, while effluent from the hay amended columns was brown, suggesting decomposition. There was a significant amount of suspended material in the effluents from columns amended with hay, and less so from columns amended with sawdust, compared to the CMWR only column effluent, as shown in **Figure 3.5**. Filtration of these samples prior to shipment to Trent University lab for Se speciation was very difficult, and even after the 0.45 μm filtration step, the lab had significant difficulty analyzing the samples.

Figure 3.5: Week 4 water quality samples (filtered through 0.45 μm filter). Front four samples were collected, from left to right, from column 2 (CMWR only), 5 (hay, sawdust, and CMWR), 3 (hay and CMWR – results not included in thesis), and from 1 (hay and CMWR).

As previously mentioned, there was a buildup of gases in the columns amended with hay, which had a very pronounced odor when vented, recorded only as ‘very, very stinky’ (evidence of H_2S). No gas collection or analysis was made.

Section 4: Discussion

4.1 Overview

The results presented in **Section 3** have been analyzed and compared in this section, with the goal of addressing the research questions presented in **Section 1.9**, namely:

a) Which of two easily available (to the Brule Mine) organic amendments is best suited as an electron donor for promoting Se removal from Brule Mine effluent? How do the two amendments differ in their kinetics (time to onset of reducing conditions) and longevity (how appropriate redox conditions are maintained) with regard to their ability to foster conditions conducive to denitrification and Se removal within waste rock environments?

b) What are the biogeochemical mechanisms governing the speciation and behavior of Se and N in waste rock pore waters in response to these organic amendments?

c) How does the use of organic amendments and CMWR in a saturated low-flow, toe seep effluent environment affect column effluent water quality? i.e. in addition to Se and NO_3^-, will the concentration of any other parameter of environmental relevance be significantly affected by the column conditions?

These questions were addressed first by analyzing the characteristics of the amendments predicting organic decomposition and water quality. This was followed by assessing the factors indicative of organic matter decomposition in the columns. Indicators of organic decomposition provided a relative measure of the amount of electron donors, and the removal of target parameters likewise provided an indication of the consumption of electron acceptors. Parameters which are indicative of redox performance were analyzed as well.

The performance of the amendments, specifically with respect to processes governing the behaviour of Se and N are discussed in **Section 4.3**, with emphasis placed on removal mechanisms, speciation, attenuation pathways, reaction products and their long-term stability. Column effluent water quality was also examined for WQG exceedance. Lastly, results were evaluated to provide relevant information for field scale application, with special consideration given to downstream-environment protection during start up and operation of a large scale BCR.

4.2 Organic Amendment Performance

As described in **Section 3.2.4**, during the experiment, column 1 experienced a loss of organics and possible entrainment of air into the column during de-clogging activities (to restore flow in the blocked system), and this may have had an impact on the time to the onset of reducing conditions, the longevity of low redox conditions, and the magnitude of the decrease in redox levels. Thus, the anaerobic performance of column 1, amended with hay and CMWR, may have been under-represented in the results of the experiment. All columns amended with organics also lost liquid and / or organic mass during the week before the pumping of liquids began (as explained in **Section 3.2.2** and shown in **Table 3.1**).

4.2.1 Comparison of Amendment Nutrient Properties

The performance of anaerobic digestion is strongly dependent on the type and composition of the material to be digested (Murto et al., 2004), which suggests that a comparison of the organic amendments could provide insight to their performance in columns. The average C:N ratio of three sawdust samples was 890:1, while that of hay was 38.5:1. An optimal C:N ratio reported for anaerobic digestion ranges between 20:1 and 35:1 (Sialve et al., 2009). Overall, the higher C:N ratio of the sawdust as compared to the hay suggests the latter is a more labile form of organic C, and could be expected to show more rapid remineralization.

A conceptual diagram showing column 1 and influent and effluent parameters is presented in **Figure 4.1**.

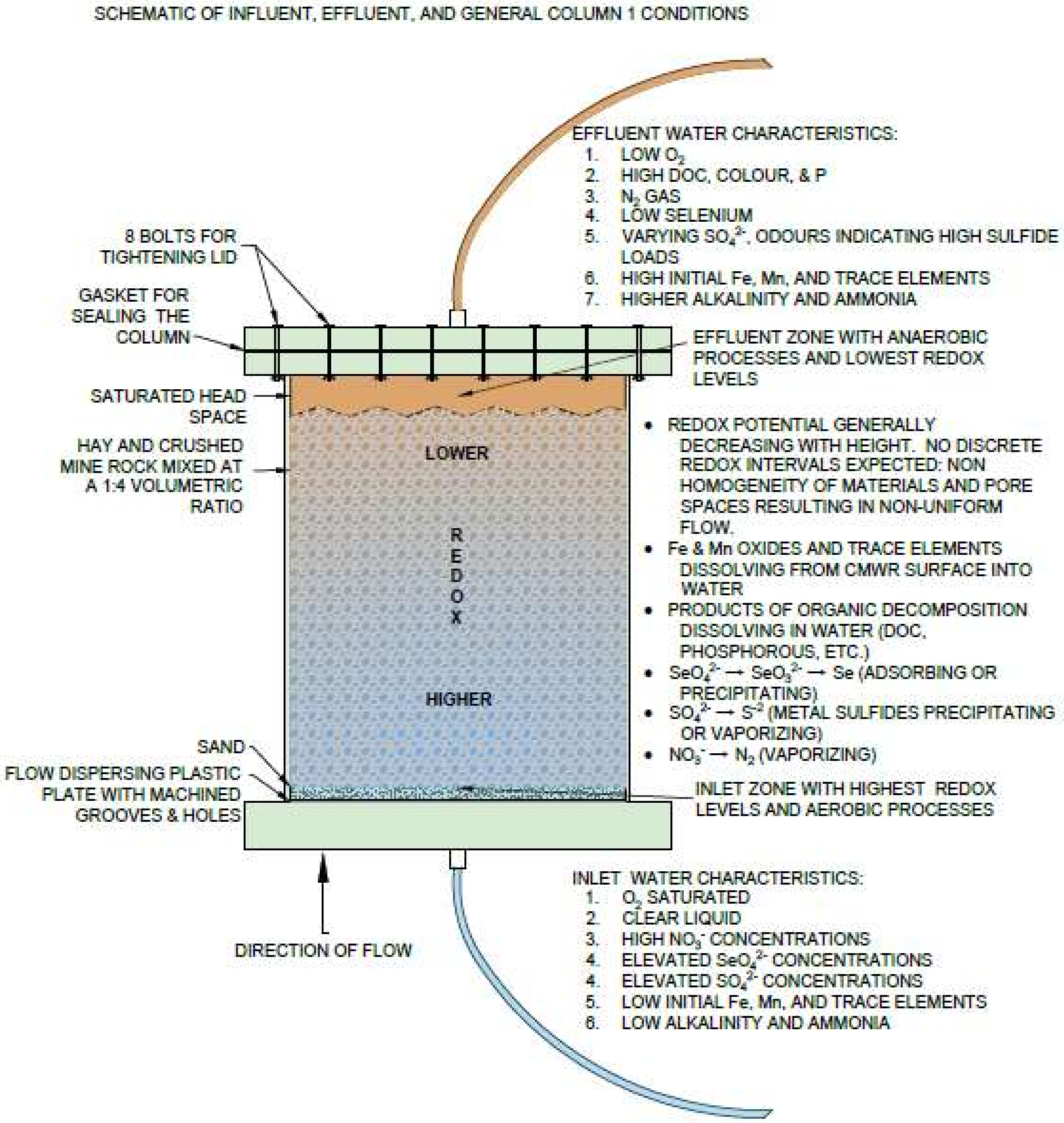


Figure 4.1: Schematic of reactions expected to have occurred within column 1

Average P concentrations in dry sawdust were less than or equal to the MDL, while those of hay were more than an order of magnitude higher (50 and 547.3 mg kg^{-1}, respectively).

Higher concentrations of P and lower C:N ratios indicate that the hay would provide a more suitable media for bacterial proliferation than the sawdust, due to the more refractory nature inferred of the sawdust materials. The sawdust may however offer benefits over longer time scales as compared to more labile forms of C.

4.2.2 Direct Products of Organic Matter Degradation

Multiple parameters support the conclusion that the hay amendment, in columns 1 and 5, provided the best organic substrate for microbial decomposition including:

1. Higher effluent concentrations of P. Influent and effluent of columns with no hay had concentrations of P less than or equal to the MDL (0.3 mg kg^{-1}). Literature suggests that nutrients in decomposing matter are governed by stoichiometric controls: N and P mineralization from plant residues may be initially immobilized from environments by decomposers until a critical concentration is achieved (Manzoni et al., 2010), after which, decomposer nutrient demand is satisfied, and excess is released. During the initial amendment chemical characterization, concentrations of P in the sawdust were less than or equal to the MDL, as were concentrations in the sawdust amended column effluent water. It is therefore likely that P concentrations did not reach the critical level for the decomposers (allowing for P release) and the lack of P was a bacterial-growth limiting factor.
2. Higher concentrations of DOC and colour. Column 1 (hay and CMWR) exhibited DOC concentrations up to 18.5 times higher than column 6 (sawdust and CMWR), and it can be assumed this number may have been higher if not for organic losses. The composition and source of DOC and colour could be attributed to sources which include:

- Soluble organics originating from the original substrate;
- Particulate material originating from the original substrate;
- Substrate material altered through microbial action; and
- Microbial biomass.

In a similar biological denitrification experiment in up flow columns using wheat straw, periods of high NO_3^- reduction were coupled with high levels of DOC, colour, and original amendment mass, suggesting higher DOC and colour levels were linked to biological activity (Aslan & Turkman, 2005).

3. The presence of elevated initial NH_3 concentrations in column 1 effluent are consistent with the onset of anaerobic conditions. Please refer to **Section 1.2** for the stoichiometry associated with the decomposition of the Redfield molecule for the reasoning supporting this assertion.

Column 1 demonstrated substantial changes in redox parameters, as measured by concentrations of parameters at the inlet and outlet. These parameters are discussed in the following sections.

4.2.3 Redox Parameters Measured in Effluents

4.2.3.1 Oxygen

Unfortunately, as described in **Section 3.2**, direct redox level measurement of the liquid with a multimeter was deemed unreliable, and the multimeter DO readings were also questionable (e.g., results greater than 170% of saturation). Notwithstanding these limitations, there were interesting trends as columns with hay amendments tended to show the most anoxic conditions, based on DO measurements. Influent and effluent average DO concentrations ranked from highest to lowest were influent (103%), column 2 (48.6%), column 6 (37.6%), column 1 (17%), and column 5 (12.1%). Out of 18 measurements, column 5 effluent DO concentrations were lower than those of column 1 twelve times, despite having twice as much hay. These results could be a manifestation of the organic losses in column 1.

4.2.3.2 Nitrogen

Nitrate removal occurred in all columns amended with organic amendments. If all results less than or equal to the detection limit are replaced with the detection limit (possibly overestimating the results) and average column effluents are considered, the following reductions of NO_3^- were achieved: column 1 - 97.8%, column 2 – 0%, column 5 – 90.8%, and column 6 – 24.7%. These numbers suggest that column 6 (CMWR and sawdust) only achieved partial NO_3^- reduction, likely reflecting the more recalcitrant nature of this organic matter source (as illustrated by high C:N ratio).

Evidence of NO_2^- in column effluents, indicating partial denitrification, is evident in columns 5 and 6 at the onset of the experiment. Nitrite presence in column 5, coupled with NO_3^- removal, could indicate that the production of this intermediary molecule is the result of insufficiently-low redox conditions (thermodynamic control) or inadequate hydraulic retention time (kinetic control). Incomplete denitrification, resulting in measurable concentrations of NO_2^-, has been reported in comparable experiments with aerobic influent (Sauthiera, et al., 1998). If column packing promoted the development of preferential flow paths, hydraulic residence time of liquids could have been greatly reduced, and this has been postulated to result in NO_2^- production due to incomplete denitrification (Sauthiera, et al., 1998). Furthermore, the rapid decrease of column 5 effluent NO_2^- concentrations between weeks 1 and 3 may be the result of the microbial population flourishing, and either a corresponding spike in demand for electron acceptors, or an increase in net immobilization.

In contrast, the presence of NO_2^- and approximately 30% NO_3^- reduction in column 6 might be indicative that demand for electron acceptors is satisfied with partial NO_3^- reduction in this column.

In **Section 1.2** and specifically in **Equations (9)** through **(12)**, the production of NH_3 was linked to anaerobic and facultative organic decomposition. Concentrations of decomposition products in hay amended columns (1 and 5), combined with comparatively lower DO levels, indicate that anaerobic conditions were likely, and these conditions are conducive to DNRA. Small increases in effluent NH_3 concentration in weeks 6 and 11, from columns 1 and 5, respectively, may be indicative of DNRA as a method of NO_3^- removal from the waters. After the NO_3^- levels fell below the detection limit for most of the experiment, there was still a supply of electron donors, and this could lead to conditions where DNRA bacteria would be more successful than denitrifying bacteria (van den Berg, et al., 2016).

Another possible mechanism for soluble N reduction in the columns is net N immobilization into microbial biomass. Mass of organisms, microbial proliferation rates, and genomic characterization of the biomass were not quantified throughout the experiment, and therefore immobilization rates are unknown. The highest periods of microbial proliferation and N immobilization would have likely occurred during or immediately after times of high DOC.

4.2.3.3 Selenium

Influent Se concentrations were relatively static over the course of the study. Column 2 effluent Se concentrations were relatively stable but dropped slightly for unknown reasons as the experiment progressed. Effluent from columns 1 and 5 showed significant reductions at the onset of the experiment. Interestingly column 6 effluent Se concentrations decreased continuously over the course of the experiment by more than 60%, and the average value was 55% lower than that of the influent. This observation is inferred to reflect the presence of mildly suboxic conditions within the sawdust-amended column, where only modest rates of Se removal may be expected. This postulate is consistent with the NO_3^- data, which also show only modest decreases in concentration through the column, indicative of minor rates of denitrification.

The percent reduction of Se concentrations in column 6 in weeks 13-24 (compared with the influent concentration) was greater than that of NO_3^-. While strict thermodynamic principles would suggest that denitrification would occur prior to Se reduction (i.e. the Gibbs free energies presented in **Table 1.1**), literature also suggests that these may occur simultaneously (Subedi, et al., 2017; Oremlund, et al., 1999). The higher proportion of Se reduction as compared to NO_3^- would also be influenced by the scale of their respective concentrations, as NO_3^- levels are multiple of orders of magnitude greater than those of Se. As noted in **Section 1**, bacteria exist with preferential affinities and inhibitions with regards to specific electron acceptors (Marietou, et al., 2009). Unfortunately, genomic analysis of the bacterial population was not performed, and as such, it is unclear if this alternate reduction sequence is an outlier or a result of a preferential reduction pathway. Also, the ORP-dependent order of reduction applies specifically to systems at thermodynamic and chemical equilibrium, conditions that may not have been present in the columns.

When reviewing the speciation of the soluble Se, columns which had the most pronounced indications of organic decomposition and anaerobic activity still showed significant proportions of $Se_{(VI)}$. This observation, coupled with the Se concentration decrease (compared to influent), indicates that while a large amount of the oxyanion concentration was reduced, dissolved molecules continued to pass through the column without being subjected to reducing conditions (or were re-oxidized during sample preparation). The columns may have possibly had specific areas of high anaerobic activity, reducing Se, while other areas may have been relatively inert, allowing the NO_3^- and SeO_4^{2-} to pass unreduced. As alluded to in **Section 4.2.3.2**, there may have been some short circuiting in the columns allowing liquid to pass through quickly (preferential flow paths may have developed). For example, this could have resulted from degrading organics plugging up the CMWR.

4.2.3.4 Iron and Manganese

Reduced Fe and Mn, which are parameters for inferring the development of suboxic conditions, exhibited relatively high concentrations in the effluent from columns 1 and 5, coinciding with high DOC and low DO concentrations. The decrease of soluble Mn and Fe concentrations in weeks 6-8 may not indicate redox levels were changing significantly; rather, the decreases in these parameters may indicate the fixed supply of these constituents (from the CMWR surfaces) had been exhausted.

Analysis of effluents from columns with no hay amendment show do not show similar initial elevations in Fe or Mn. This observation is inferred to reflect the effect of hay in promoting strongly reducing conditions, which would provide an environment for the reductive dissolution of Fe and Mn oxides from the CMWR surfaces. As evidenced by the reduction of SO_4^{2-} (presented in the next section), the redox potentials in the hay-amended columns would reduce oxidized Fe and Mn rapidly. It is less likely that the Fe and Mn enrichments in the hay-amended columns were attributed to the hay itself.

4.2.3.5 Sulfur

Compared to influent levels, a decrease in SO_4^{2-} was not observed in effluents of either column 2 or 6 . Columns 1 and 5 effluents achieved decreasing SO_4^{2-} concentrations up to week 3 (77%), and week 5 (67%), and an average reduction of 33% and 29%, respectively. Column 5 effluent S^{2-} concentrations spiked from week 5 to 9, which coincided with the decrease in Fe. This suggests another control for the effluent concentrations of Fe may have been present: co-precipitation with S^{2-} as ferrous sulfide. The low solubility of this metal sulfide will result in the loss of reactants from solution (Kiilerich, et al., 2017). Pyrrhotite and troilite had saturation indices slightly above 0 for columns 1 and 5 in weeks 3 and 5 respectively, indicating a possible S consumption mechanism in the columns.[11]

A limitation of the experiment was that it was confined to a duration of 6 months: prevalent SO_4^{2-} removal trends in hay-amended column effluents at the beginning of the experiment appeared to be ending in week 24 (refer to **Figure 4.2**). The data suggest that the production of electron donors (resulting from organic decomposition) was decreasing, indicating that the following questions are important:

1) How does the production of electrons vary over time, and at what point does the sawdust amended column become advantageous with respect to long-term reactivity?
2) At what point is the production of electrons from the hay amended columns insufficient for the continued reduction of Se oxyanions and denitrification?

---

[11] Saturation indices were above zero for other Fe and Mn compounds only when these elements exhibited concentrations above zero (mackinawite, siderite), and were otherwise negative.

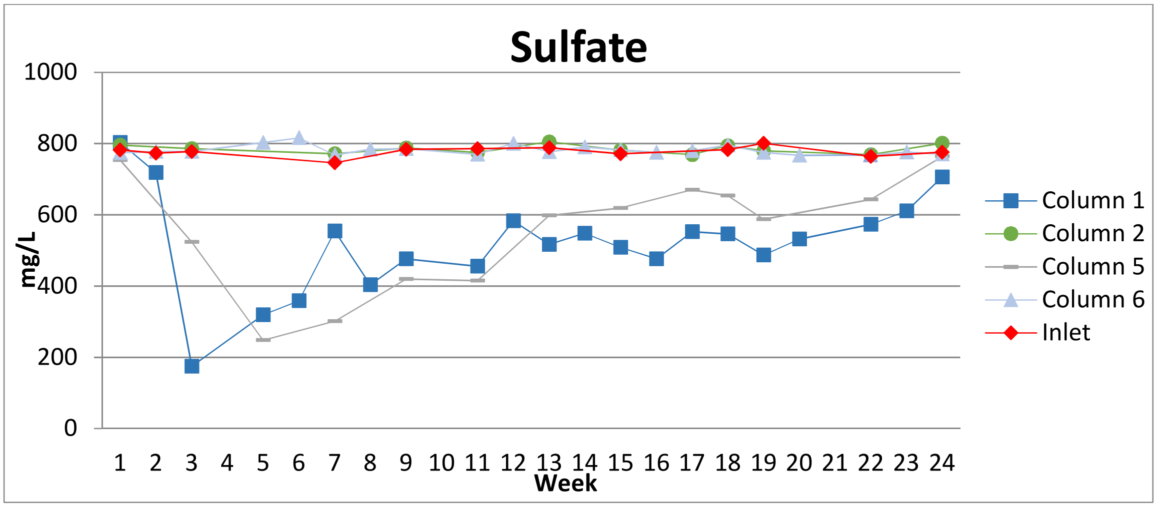


Figure 4.2: SO_4^{2-} concentrations in influent and effluents plotted as a function of time

The data does not indicate if the production of S^{2-} inhibited microbial growth in columns 1 and 5. The creation of a S^{2-} tolerant bacterial community is a desired trait for treatment of acid mine drainage or other heavy metal-contaminated streams, as these communities offer the possibility of combining the removal of selenium oxyanions with sulfidic heavy metal precipitation (Lenz, et al., 2008). The BCR at the Brule is not subject to these conditions, and large spikes in SO_4^{2-} reduction should be observed for any deleterious impacts on BCR functions (e.g., inhibition of microbial growth).

4.2.3.6 Alkalinity

When discussing indications of reducing conditions, increased alkalinity levels should be conssidered indicators of facultative or anaerobic activity (as per **Equations (9)** through **(12)** in **Section 1.2**). Alternatively, alkalinity could arise from the dissolution of soluble alkalinity (calcite) on the surface of the CMWR. Dissolution-produced alkalinity would be expected to be observed at the beginning of the trial, while alkalinity generated as a product of suboxic reactions would be commensurate with denitrification and Fe(III), Mn(IV), and SO_4^{2-} reduction. These interactions could occur simultaneously, and the production of alkalinity could be concealed by consumption as a result of oxidation reactions (those that consume alkalinity), or carbonate mineral precipitation.

To parse out the effects of calcite dissolution, effluent alkalinity concentrations from the column 2 (amended with CMWR only) were compared to those of the influent. The effluent from this column exhibited an increase in alkalinity throughout the entire experiment, ranging from 13.6% to 38.0%, suggesting a contribution from the waste rock. The persistence of elevated alkalinity in this column does not necessarily support an initial flushing event. The effluent alkalinity concentrations of organic-amended columns were greater than both the influent and the effluent from column 2, illustrating an alkalinity contribution from suboxic redox reactions. Overall however, a comprehensive interpretation of alkalinity concentrations in column effluents is hindered by the following considerations:

1. Effluent from columns amended with organics demonstrated denitrification in week 1. Parsing out effluent alkalinity increases before and after the onset of denitrification is therefore not possible. In the first half of the experiment, when the redox potential was lower (based on other indicators), effluent alkalinity concentrations in columns 1 and 5 were higher; however, no immediate increases in alkalinity were observed at the onset of SO_4^{2-} reduction.

2. Sample filtering in weeks 1 and 2 was not performed in a N_2 purged environment, and the re-introduction of O_2 may have resulted in alkalinity consumption (e.g., through Fe(II) or HS^- oxidation), skewing the results.

3. Saturation indices for both influent and effluents indicate that calcite and dolomite (carbonate minerals) were above their equilibrium saturation concentrations, possibly indicating alkalinity consumption through the formation of secondary carbonates.

4.3 Biogeochemical Processes Governing the Speciation and Behaviour of Se and NO_3^-

This section will attempt to correlate academic literature with the fluctuations of all recorded parameters to provide a conceptual understanding of the observed Se and NO_3^- removal mechanisms in the columns.

4.3.1 Reaction Pathways and Mechanisms Governing Removal

In the anaerobic environment of the columns, possible mechanisms governing the reduction of NO_3^- are primarily respiratory reduction, DNRA, and microbial assimilation. The conditions for respiratory reduction and DNRA, namely low redox potential, available NO_3^-, and labile C (Silver, et al., 2001), are prevalent in most of the columns amended with organics: column 6 effluent did not appear to have developed low redox conditions and exhibited the lowest effluent DOC concentrations.

Adsorptive losses of NO_3^- on to column amendments may have initially played a small role, but over the course of the experiment are not expected to have had a lasting effect because of the continued loading and competitive effect of other anions (e.g. SO_4^{2-}). Additionally, the amendments did not have the ideal adsorption properties (e.g. high surface area) that are found in activated C and activated sepiolite (Ozturk & Bektas, 2004)

The primary mechanisms for soluble Se removal in the columns are assimilatory reduction, dissimilatory reduction of SeO_4^{2-} to SeO_3^{2-} followed by adsorption, further reduction to elemental Se and precipitation, reduction and immobilization as organic-Se^{2-}, and reduction and immobilization as inorganic-Se^{2-} (e.g., co-precipitation with FeS_2), and biological volatilization to dimethyl Se^{2-} (Sharma, et al., 2015).

Dissimilatory reduction is expected to be the dominant mechanism of SeO_4^{2-} removal in the columns, based on indicators of organic matter decomposition and redox conditions. Adsorptive losses of SeO_4^{2-} onto FeOOH has been inversely correlated to pH (Zhang & Sparks, 1990), but at the neutral pH observed in the column effluents, this removal mechanism is not predicted to be important. Rather, the dominant repositories of reduced Se in the columns are expected to be adsorbed $Se_{(IV)}$, elemental Se, organic-Se^{2-}, and inorganic-Se^{2-}.

Removal of SeO_3^{2-} through adsorption onto soil organic matter and the oxides and oxyhydroxides of Fe, Al, and Mn is due to the large surface areas of these adsorbents, and their strong affinities for many elements and their almost universal presence in soils and sediments (Parida, et al., 1997). Balistrieri & Chao (1990) suggest that SeO_3^{2-} forms binuclear, inner-sphere complexes with amorphous Fe oxyhydroxide and monodentate, and inner-sphere complexes with MnO_2. The adsorption of SeO_3^{2} on amorphous Fe oxyhydroxides is roughly 4 times greater than MnO_2. However, given the reducing conditions in the columns, and promotion of reductive dissolution of Fe and Mn oxides, the potential for SeO_3^{2-} adsorption onto these phases is likely limited. While the organic substrates used in the study were physically pre-treated (ground up in the hammer mill), which increased the surface area significantly and likely facilitated adsorption, CMWR had a low surface area compared to more ubiquitous soil and rock materials with very fine grain sizes (e.g., sands, silts and clays). The pH of the influent and columns amended with either CMWR or sawdust and CMWR was higher than the pH of columns containing hay. This could have been a factor limiting SeO_3^{2-} adsorption in these columns, a mechanism which increases with decreasing pH (Parida, et al., 1997; Balistrieri & Chao, 1990; Naveau, et al., 2007).

Comparing Se speciation in the influent (90.4% $Se_{(VI)}$, 0.20% $Se_{(IV)}$, 9.4% unknown Se species) and effluent from column 6 (1.2% $Se_{(VI)}$, 88.5% $Se_{(IV)}$, 10.3% unknown Se species) in week 18 indicates that almost all SeO_4^{2-} was reduced. The 75% decrease in dissolved Se concentrations for this period, paired with prevailing SeO_3^{2-} concentrations suggests that Se is either

- Being mostly reduced to SeO_3^{2-}, and being partially adsorbed in the column, with a small component being reduced further and released, or,
- Being mostly reduced past SeO_3^{2-}, with the majority of the further reduced species being retained in the column.

The further reduction to elemental Se and then to Se^{2-} is supported by the higher concentrations of unknown Se species found in column 1 (83.1%) and 5 (91.8%) effluents in week 18. Without speciation of column effluents for Se^0 and Se^{-2}, the species of unidentified Se could not be verified.

By process of elimination, the abundant unidentified soluble Se species are neither $Se_{(VI)}$, nor $Se_{(IV)}$, as these forms were identified during liquid phase speciation. This leaves dissolved organo-Se, as well as possibly colloidal elemental-Se as possible phases. Indeed, Se has been reported to form 200-400 nanometer (nm) sized elemental particles that would be expected to pass through a 0.45 micron filter (Lenz, et al., 2008; Oremlund, et al., 2004), and high concentrations of dissolved organic matter (indicated by high levels of DOC) has been reported to result in prolonged suspension times, favoring transport (Buchs, et al., 2013). Contrarily, the presence of unidentified dissolved Se in the second half of the experiment suggests that Se may have been immobilized by bacteria in the earlier periods of sustained biomass growth, and the die off and subsequent decomposition of the organisms (due to declining labile C availability) released dissolved organo-Se. The presence of organo-Se compounds in sediments has been attributed more to redox conditions than substrate availability (Martin, et al., 2011), suggesting that hay amended columns, with lower redox potentials, may have produced more organo-Se. Cell lysis may have resulted in the liberation of colloidal Se^0 nanoparticles (Tomei, et al., 1995), or bacteria may have reduced SeO_3^{2-} to aqueous HSe^- (Herbel, et al., 2003) and both of these mechanisms represent pathways for the solubilization of phases not identifiend by the liquid speciation.

The decrease in the percentage of unidentified Se in week 24 effluents could have been the result of possible poor handling procedures. Incomplete N_2 purging of the collection bottles, or ambient air introduced during multiple transfers inside the N_2 filled glove bag (i.e. from collection containers to the centrifuge vials, then later via a filtering step to the shipping VCB bottles) may have introduced a small presence of O_2. In the presence of very low concentrations of DO, a quick Se^{2-} oxidation to Se^0 is expected, as the kinetics of the reaction are fast (Smith, 2014), and the elemental Se could have precipitated during transit.

Dissimilatory reduction of SeO_3^{2-} followed by the formation of nanoparticles of Se^0S^0 was observed in environmental waters with SO_4^{2-} levels of 800 mg L^{-1} using *A. brasilense*, while at lower SO_4^{2-} concentrations, only Se^0 nanoparticles were formed (Vogel, et al., 2018). The average column influent SO_4^{2-} concentration was 777 mg L^{-1}, suggesting Se^0S^0 particle formation may have occurred in the columns as well. The 400 nm size of these S-Se nanoparticles is similar to pure Se nanoparticles, and they could similarly pass through the 0.45μm filter (Vogel, et al., 2018). No information has been reported about precipitation tendencies of these spheres, so their presence is possible in both the column effluent as an unidentified species, and as attenuated solid precipitates in the columns.

The reduction of Se^0 to FeSe is favoured over HSe^- at a pH of 7 (Herbel, et al., 2003) and the retention of Se^{2-} to FeS_2 has been shown to occur via **Equation (28)** (Liu, et al., 2008). These processes could have caused a decrease in dissolved Se and Fe (in periods of high Fe reduction), and also limited the amount of unidentified Se noted in the effluents. The precipitation of FeSe would result in Fe concentration reductions in µg L^- (limited by stoichiometric relation to Se), and would not be noticeable given the mg L^- concentrations of Fe. Incorporation of Se into $FeSe_2$ is also a removal pathway (Belzile, et al., 2000). The formation reactions of these products are proposed to be similar to those of FeS_2 formation, due to the similarity of Se and S chemistry (Smith, 2014), and attenuation in the columns via this mechanism is also possible,

(28) $FeS_2 + HSe^- \rightarrow FeS + Se^0 + HS^-$

Similar to biogenic Se^0 nanoparticles, the precipitation of metal selenides can be affected by their small size (5-400 nm), and their release to the environment (and out of columns) may occur as a result of colloidal suspension (Jain, et al, 2017).

4.3.2 Attenuation Products and Long-term Stability

Reaction products of NO_3^- reduction, are either very soluble (NH_3, NO_2^-), or have sufficiently high vapour pressure that they are present primarily in gas phases. Thus, N reaction products are not expected to have precipitated out of solution and long-term stability of these products is not a concern.

The dominant removal pathways of Se in the columns is thought to be precipitation (elemental Se and organic/inorganic Se^{2-}) and adsorption (e.g., SeO_3^{2-} adsorption to mineral surfaces). Though SeO_4^{-2} was transformed from an aqueous form to an insoluble state, in the presence of an oxidizing agent, it could be re-oxidized (the re-solubilization of Se is counter productive). Fluidized bed reactor systems, which are subject to significantly more agitation than the static (unmoving) amendment column experiment performed at UNBC, require downstream liquid/solids separation systems to separate biological solids which may have sloughed off (Envirogen Technologies, 2011). This constitutes another remobilization pathway to be considered. The UNBC trial had a 0.45 μm filtration step prior to submission for metals characterization, which prevented any sloughed off biological solids from being captured in the analysis of the effluents. As a result, no information relating Se to entrained/sloughed off biomass in column effluents can be used to assess this remobilization pathway.

4.3.3 Results of Geochemical Modeling

Modeling saturation indices using PHREEQC software was inconclusive for multiple minerals. The software uses an equilibrium geochemical speciation model to predict mineral behaviour. The software was intended to model static environments which are not biologically active, and as the columns were dynamic, they were not well equilibrated. The conditions were not suitable for comparison with the model. Mineral phases containing Se were not within the range of the CoA provided in **Section 3.4.1**.

4.4 Environmental Relevance and Effect of Other Reaction Products

This study was completed to provide insight into the processes responsible for contaminant removal with BCR systems, with the long-term goal of improving the design and operations of these systems. The experiment was not designed to provide a relevant numerical prediction of BCR effluent water quality. Any conclusion drawn from the observation of specific concentrations in the column effluents is only marginally applicable to the full field scale implementation.

Unfortunately, biological oxygen demand (BOD) was not a parameter that was monitored or considered during the experiment. As discussed in **Section 3.6**, there was significant discoloration and particulate evident in the effluents in periods with high concentrations of DOC. This represents a potential pathway for oxygen depletion in downstream receiving streams. During weeks 0-8, there was a release of reduced compounds (i.e. Fe and Mn) from the water column which would also consume oxygen in the water column as they re-oxidize. Extensive precipitation of Fe and Mn oxides on stream substrates also has the potential to impact the quality of habitat for benthic invertebrates (Young, 2003).

High P, N, and DOC concentrations from decomposing hay in columns 1 and 5 indicate that while the degradation of organic material in these columns was happening at an augmented rate, downstream eutrophication potential increased as well.

4.4.1 Trace Elements

As was noted in the results sections, there was an initial brief increase in many parameters of environmental significance followed by a rapid decrease. This is likely a result of the flushing of soluble minerals and organic particles through the system.

4.4.2 Comparison of Effluent with British Columbia Water Quality Guidelines.

Influent water in the experiment already exceeded the parameter specific WQG maxima for the protection of freshwater aquatic life. Nevertheless, a table provided in **Appendix D.14** compares WQG maximums for acute toxicity to the maximum concentrations observed in column 1 effluent (MoE, 2018). Parameters with guideline exceeding levels were DO, SO_4^{-2}, D-Al, D-As, D-Co, D-Fe, D-P, D-Se, and D-Zn. Individual guidelines for DOC, colour, and pH relate to upstream (unaffected) water quality, and as such, are inconclusive in the context of this analysis. Post reactor aeration would likely remediate concerns about DO and Fe concentrations (oxidized Fe will quickly precipitate out of solution). Sulfate is below the influent levels and represents a significant amelioration in water quality. Concentrations of D-Al, D-Co, D-Fe, and D-Zn exhibited initial spikes, and are the result of the flushing of soluble or redox sensitive compounds from the amendments (no long term or continuous exceedances of these WQGs are expected). An analysis of the NO_2^- concentration in the column 1 effluents show that the Cl dependent 30-day average WQG was exceeded in weeks 18 - 20. Effluents from column 5 exceeded the 30-day and maximum NO_2^- WQG jointly in weeks 1, 9 – 11, and week 18. Lastly, the effluents from column 6 exceeded the 30-day and maximum NO_2^- WQG jointly in weeks 1-3. Nitrite is an intermediary compound produced during denitrification, and guideline exceeding concentrations at the beginning and end of the experiment can be rationalized. In the beginning, the colony of bacteria may not have been sufficiently developed, the organic decomposition rates may have been lower, and incomplete denitrification was likely a result, while at the end of the experiment, there was likely a lack of sufficient organic substrate being degraded to produce electrons required to complete the denitrification.

Column 5 effluent NO_2^- concentrations in weeks 9-11 coincide with elevated NH_3 concentrations. The NH_3 concentrations, oxidized in conjunction with the reduction of oxides of Fe and Mn, could result in NO_2^- production (Kuypers, et al., 2018).

The reduction of NO_3^- and Se concentrations was one of the primary objectives of the research. Column 1 effluents achieved an average of 97.9% and 87.8% reduction in NO_3^- and Se, resulting in an average concentration of 1.58 mg L^{1-} and 13.4 µg L^{-1}, respectively. While the average concentration of NO_3^- is below the WQG (32.8 mg L^{-1}), that of Se exceeds the WQG for the protection of freshwater species (2 µg L^{-1}) (MoE, 2018). The effluent being treated in this experiment was from a toe seep at the mine, which is a concentrated point source of these COCs. Concentration and flow data of surface or diluted flows required to make a prediction about water quality at the final effluent point, (receiving environment) are not available. The presence of unknown Se species dissolved in column effluents is problematic, due to the high comparative bioavailability of organo-Se^{2-}, and the propensity of Se to bioaccumulate.

4.5 Implications for Field Scale Application of Biological Reactors

As a precursor to any recommendations for field scale implementation based on the results of the experiment, it must be acknowledged that there were a number of limitations associated with this study. The three most significant limitations are as follows:

- There was a lack of replicate samples, and as such, the assessment of amendment performance (even if this assessment is supported by literature) cannot be statistically examined or confirmed;
- There was some inevitable operator error, due to inexperience (e.g., not handling liquid samples in N_2 purged environments in the first weeks) and scheduling constraints (experimental set up was only thoroughly inspected 2 or 3 days per week); and,
- As previously discussed, due to activities relating to removal of blockages in column 1 (this occurred numerous times) and leakage from the column during the initial wetting of amendments, a considerable amount of organic mass may have been lost. Although the mass of hay was doubled in column 1, the results of columns 1 and 5 are similar.

It is unclear whether this a result of column 1 degassing and any associated organic loss or if there were other environmental constraints limiting biomass production and organic decomposition.

4.5.1 Combined Application

Effluent SO_4^{2-} concentrations for columns amended with organics were similar at the end of the experiment, with those amended by hay demonstrating a trend of decreasing electron acceptor reduction. Column 1 effluents had higher concentrations of undesired parameters including colour, odour, possibly toxic Se^{2-}, DOC, and Fe^{2+}, and the effluent was much darker and harder to filter. Although the reductive performance of columns 1 and 5 was similar, column 5 showed less undesired parameters. These findings suggest that a combined application may have the most beneficial impact on water quality. Specifically, the application a labile C source to encourage immediate bacterial colony development, tempered with a second, more refractory organic material to sustain and maintain long term reducing conditions may achieve the lowest effluent Se concentrations over extended periods of operations. Such an application could reduce the initial loading of DOC and BOD to the receiving environment while minimizing maintenance and amendment resupply costs. The evidence at the end of the experiment suggested decreasing performance from hay (possibly a result of amendment consumption), and sawdust may provide greater longevity as an electron donor source. This is an important consideration as ideally BCRs can operate for periods of 5-10 years without having to replenish the organic amendment. In this regard, an important consideration when evaluating BCR design relates to logistics and costs associated with amendment resupply. If additional hay can be added on an annual or semi-annual basis, then the long-term ability of the amendment to achieve desired rates of reaction may be less critical. A similar upflow column study, with an organic amendment composition of 50% dry weight (dw) hay, 20% dw woodchips, and 30% dw cow manure was able to sustain SO_4^{2-} reducing conditions for 430 days (Baldwin, et al., 2015), and this result further supports the theory of a combined application.

4.5.2 Amendment Conditioning

Pretreating the organics may result in greater efficiencies in BCR operations. These efficiencies could result in sawdust being acceptable as a sole amendment, or they could result in less undesirable products in BCR effluents.

4.5.2.1 Pre-treatment to Enhance Rates of Decomposition.

The pre-treatment of wood by thermal, mechanical, acid, alkaline, oxidative, and chemical processes to generate simple sugars before methanogenesis was demonstrated Hendriks and Zeeman (2009), and such treatments may reduce the need for a secondary, alternate, C source for successful BCR operation. While the specific chemistries, economies and feasibilities of different pre-treatments are beyond the scope of this thesis, a summary of the requirements for an economic and effective pre-treatment for methanogenesis (Agbor, et al., 2011), adapted to denitrification, and Se- and S-oxyanion reduction systems are presented below. The process should:

- Have a low capital and operational cost, low energy demand and minimal handling and preconditioning requirements;
- Be effective on a wide range and loading of lignocellulosic material;
- Result in the recovery of most of the lignocellulosic components in a useable form in separate fractions; and,

- Produce no or limited amounts lignin degradation products that inhibit the growth of the target organisms for NO_3^-, Se, and SO_4^{2-} reduction.

4.5.2.2 Prewashing

To avoid having unacceptably high concentrations of soluble minerals, NO_3^-, Se, and SO_4^{2-} in the initial flow through the BCR, the CMWR should be rinsed in its original location (on an existing waste rock dump) prior to moving it. Additionally, the CMWR should only be placed in the BCR immediately before saturation to avoid further mineral weathering and oxidation on the surface of the CMWR.

4.5.3 Performance and Implementation Considerations

The following is a list of issues that should be considered before implementing a field scale bioreactor.

1. Hydrology: The field scale BCR should not be viewed as a 'passive' reactor as the diurnal, meteorological, and seasonal variations in flow through the reactor will affect performance. High throughput will result in excess loading of the system and might lead to higher ORP levels and/or poor Se attenuation. Low flow conditions would result in lower redox levels than necessary for Se attenuation (but have the benefit of reducing more SO_4^{2-}) and this could represent a waste of the organic amendment. To minimize seasonal flow variations, zones of upstream storage (e.g., pits) could be used to store water in periods of high flow and release water through the BCR in periods of low flow. In some cases (e.g., flood events), high flow conditions may be characterized by significant dilution and lower Se and NO_3^- concentrations. For these cases, a bypass should be installed to divert flows around the BCR.

2. Reduction of O_2 surface infiltration: The re-introduction of O_2 in field-based pilot-scale BCRs has been avoided with the installation of booms, mitigating wind mixing and preserving anaerobic conditions (Baldwin, et al., 2015). Freezing ambient temperatures resulting in an impermeable cover of ice and snow have also bolstered the anaerobic activities (Baldwin, et al., 2015). Reducing the resupply of O_2 by limiting permeability and advection at surface should be considered.
3. Amendment re-supply: Resupplying the BCR with organic amendments may require significant operator effort to manage BOD and eutrophication-promoting products in the effluents. For large BCRs, changes in water chemistry may be less extreme if the amendment resupply can be managed through smaller and frequent additions. A record, relating varying masses of amendment added to water quality improvements (and or deteriorations), would allow for fine tuning of future mass additions. Amendment additions could also be scheduled to coincide with the annual flow cycles, providing a higher dilution for higher levels of DOC and nutrients due to snowmelt. Baldwin, et al. (2015) suggest that an upstream surge pond be included in BCR designs into which fresh organics can be added as a re-supply method. This could be helpful, as any labile C generated during the amendment re-supply may possibly be consumed by the established biological matrix downstream.
4. As Se particles are easily transported through aqueous systems (Haygarth, 1994), and biomass sloughing or colloidal transport is a potential concern, an effluent precipitation or filtration system should be considered in the design. A membrane filter is likely not practical on an exposed BCR due to clogging and maintenance considerations, as flows and sediment loads are subject to diurnal and seasonal

influences. Proper sedimentation pond design, accounting for the size and relative density of reduced Se particles is important. Settlement tests could be performed to investigate the final Se speciation and mineral formation. While settling velocities have be calculated directly using density and size of these minerals (and Se^0 nanoparticles, including biogenic Se), the calculated results have correlated poorly to reality (Buchs, et al., 2013). Instead, settling velocities should be directly determined via observation, resulting in properly sized sedimentation ponds and avoiding the release of reduced Se products to the receiving streams (Buchs, et al., 2013). Alternatively, a downstream wetland with emergent vegetation could provide both a low-energy environment for further accumulation of small organic particles, and a continued source of organic material from which to develop stratified redox conditions close to the sediment surface (for long term storage of deposited Se) (Martin, et al., 2011). This should be investigated by any mines considering a BCR that have the topography and the size in land tenure to accommodate a wetland, though unfortunately the Brule has neither. As organo-Se compounds will be attenuated in a vegetative wetland used to supplement a BCR, an argument should be made that the effluent sampling (i.e. permit compliance) point for water quality should be after this additional unit. Effluents should be also periodically analyzed for the production of unanticipated by-products.

5. Design for plugging and accumulation: Any waste rock that is added should be competent and not subject to fracturing. This media provides surface area for bacteria to grow, but also provides a porous substrate to control hydraulic conductivity and mitigate short circuiting. Available pore space, amendment particle size, and

expected flow should be carefully considered. If the resistance to flow is too high, the height of the water column will increase, and the least resistance flowpath will be above or around the reactor. All influent and effluent infrastructure should be able to be cleaned and unplugged. In the fixed pore space of the column trial, plugging caused significant issues.

6. The volume of precipitated elemental Se, accumulated as a result of BCR activity, is relatively limited and easily managed. A comprehensive approach for reactor biomass and sludge removal at the end of the BCR life cycle should be considered before system construction. Specific consideration should be given to the final disposal of materials with significant Se accumulation. Short term draining of the BCR should be done with extreme caution, as re-oxidizing the reactor bed could result in remobilization of Se.
7. Volumes and concentrations to be treated should be analyzed considering effects on both incremental mass removal and cost. At the Brule Mine, Se is highly concentrated in specific toe seeps, and as a result, the most economical and impactful remediation strategy may be a targeted approach utilizing multiple small BCRs. While the complexity of the strategy may increase as a result of multiple reactors, the efficiency and cost savings could be significant.

Section 5: Conclusion

A saturated, anaerobic up-flow column experiment was conducted to investigate the effectiveness of two organic amendments (hay and sawdust) for promoting microbially induced reducing conditions for the attenuation of nitrate and selenium in effluent collected from a coal mine in north eastern British Columbia. The effects of the amendments were elucidated by chemical characterization of the effluents from columns containing one or both amendments mixed with mine sourced crushed rock and the analysis of the results. Hay proved to be the most suitable for promoting reducing conditions and contaminant removal (up to 98.6% and 99.9% removal for selenium and nitrate, respectively compared to influent concentrations). Decreasing performance as a function of time suggested a high organic consumption rate, and possible rapid amendment depletion, limiting the field scale applicability of the hay. Effluents from columns amended with organic material were not suitable for discharge to the receiving environments due to elevated levels of dissolved organic carbon, colour, and phosphorous, and low concentrations of oxygen, conditions which may promote eutrophication of downstream environments. A field scale application of this technology was considered, and treatment (e.g., post aeration and settlement) would be required to allow for the reduction in the concentration of any potentially harmful by-products.

References

Adams, D. J., & Pickett, T. M. (2000, Feb 11). *USA Patent No. US 6183644 B1.*

Agbor, V. B., Cicek, N., Sparling, R., Berlin, A., & Levin, D. B. (2011). Biomass Pretreatment: Fundamentals Toward Application. *Biotechnology Advances, 29*(6), 675-685.

ALS Global. (n.d.). Selenium Speciation in Water, Sediment and Food/Biota. Burnaby, BC.

Amweg, E. L., Stuart, D. L., & Weston, D. P. (2003). Comparative Bioavailability of Selenium to Aquatic Organisms after Biological Treatment of Agricultural Waste. *Aquatic Toxicology, 63*(1), 13-25.

Aslan, S., & Turkman, A. (2005, Feb). Combined Biological Removal of Nitrate and Pesticides Using Wheat Straw as Substrates. *Process Biochemistry, 40*(2), 935-943.

Baldwin, S., & Al, H. H. (2003). Selenium Uptake by a Coal Mine Wetland Sediment. *Water Quality Research Journal of Canada, 38*(3), 483-497.

Baldwin, S., Mirjafari, P., Rezahdebashi, M., Subedi, G., Taylor, J., Moger, L., McMahen, K., Frye, A. (2015). Start-Up of a Passive Remediation Bioreactor for Sulfate and Selenium Removal from Mine Tailings Water. *10th International Conference on Acid Rock Drainage & International Mine Water Association Annual COnference*, (pp. 1-11). Santiago.

Balistrieri, L. S., & Chao, T. T. (1987). Selenium Adsorption by Goethite. *Soil Science Society of America, 51*(5), 1145-1151.

Balistrieri, L. S., & Chao, T. T. (1990). Adsorption of Selenium by Amorphous Iron Oxyhydroxide and Manganese Dioxide. *Geochimica et Cosmochimica Acta, 54*(3), 739-751.

BC Ministry of Environment & Climate Change Strategy. (2018). *British Columbia Approved Water Quality Guidelines: Aquatic Life, Wildlife & Agriculture.* Summary Report, Water Protection & Sustainability Branch. Retrieved 2 15, 2018, from https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/wqgs-wqos/approved-wqgs/wqg_summary_aquaticlife_wildlife_agri.pdf

Beatty, J. M., & Russo, G. A. (2014). *Ambient Water Quality Guidelines for Selenium.* Update, British Columbia Ministry of Environment, Water Protection and Sustainability Branch Environmental Sustainability and Strategic Policy Division. Retrieved 01 25, 2018, from https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/wqgs-wqos/approved-wqgs/bc_moe_se_wqg.pdf

Belzile, N., Chen, Y.-W., & Xu, R. (2000). Early Diagenetic Behaviour of Selenium in Freshwater Sediments. *Applied Geochemistry, 15*(10), 1439-1454.

Bianchin, M., Martin, A., & Adams, J. (2012). In-Situ Immobilization of Selenium Within the Saturated Zones of Backfilled Pits at Coal-Mine Operations. *British Columbia Mine Reclamation Symposium.*

Bjerg, P. L., Rugge, K., Pedersen, J. K., & Christensen, T. H. (1995). Distribution of Redox-Sensitive Groundwater Quality Parameters Downgradient of a Landfill (Grindsted, Denmark). *Environmental Science & Technology, 29*(5), 1387-1394.

Blanchette, R. A., Nilsson, T., Daniel, G., & Abad, A. (1989). Biological Degradation of Wood. In *Archaeological Wood* (pp. 141-174). American Chemical Society.

Brunet, R. C., & Garcia-Gil, L. J. (1996). Sulfide-Induced Dissimilatory Nitrate Reduction to Ammonia in Anaerobic Freshwater Sediments. *FEMS Microbiology Ecology, 21*(2), 131-138.

Buchs, B., Evangelou, M. W., Winkel, L. H., & Lenz, M. (2013). Colloidal Properties of Nanoparticular Biogenic Selenium Govern Environmental Fate and Bioremediation Effectiveness. *Environmental Science & Technology, 47*(5), 2401-2407.

Burgin, A. J., & Hamilton, S. K. (2007). Have We Overemphasized the Role of Denitrification in Aquatic Ecosystems? A Review of Nitrate Removal Pathways. *Frontiers in Ecology and the Environment, 5*(2), 89-96.

Cabello, P., Roldan, D. M., & Moreno-Vivian, C. (2004). Nitrate Reduction and the Nitrogen Cycle in Archaea. *Microbiology, 150*(11), 3527-3546.

Calkins, W. H. (1993). *The Chemistry of Sulfur in Coal A Historical Perspective.* Retrieved Jan 31, 2016, from Argonne National Laboratory: https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/Volumes/Vol38-2.pdf

Calkins, W. H. (1994). The Chemical Forms of Sulfur in Coal: A Review. *Fuel, 73*(4), 475-484.

Camargo, J. A., Alonso, A., & Salamanca, A. (2005). Nitrate Toxicity to Aquatic Animals; A Review with New Data for Freshwater Invertebrates. *Chemosphere, 58*(9), 1255-1267.

Camargo, J., & Ward, J. (1992). Short-Term Toxicity of Sodium Nitrate ($NaNO_3$) to Non-Target Freshwater Invertebrates. *Chemosphere, 24*(1), 23-28.

CH2M Hill. (2010). *Review of Available Technologies for the Removal of Selenium from Water.* North American Metals Council.

CH2M Hill. (2013). *Technical Addendum: Review of Available Technologies for the Removal of Selenium from Water. North American Metals Council White Paper Report Addendum.*

Clark, M. (Ed.). (2013). British Columbia Field Sampling Manual. *Water, Air and Climate Change Branch, Ministry of Water, Land and Air Protection*, 312. Victoria, BC, Canada: Province of British Columbia. Retrieved 01 25, 2018, from https://www2.gov.bc.ca/gov/content/environment/research-monitoring-reporting/monitoring/sampling-methods-quality-assurance/bc-field-sampling-manual

Couture, R.-M., Gobeil, C., & Tessier, A. (2010). Arsenic, Iron, and Sulfur Co-Diagenesis in Lake Sediments. *Geochimica et Cosmochimica Acta, 74*(4), 1238-1255.

Dannenberg, S., Kroder, M., Dilling, W., & Cypionka, H. (1992). Oxidation of H_2, Organic Compounds and Inorganic Sulfur Compounds Coupled to Reduction of 0_2 or Nitrate by Sulfate-Reducing Bacteria. *Archives of Microbiology, 158*(2), 93-99.

de Souza, M. P., Chu, D., Zhao, M., Zayed, A. M., Ruzin, S. E., Schichnes, D., & Terry, N. (1999). Rhizosphere Bacteria Enhance Selenium Accumulation and Volatilization by Indian Mustard. *Plant Physiology, 119*(2), 565-573.

de Souza, M. P., Pilon-Smits, E. A., Lytle, C. M., Hwang, S., Tai, J., Honma, T. S., Yeh, L., Terry, N. (1998). Rate-Limiting Steps in Selenium Assimilation and Volatilization by Indian Mustard. *Plant Physiology, 117*(4), 1487-1494.

Diehl, S. F., Goldhaber, M. B., Koenig, A. E., Lowers, H. A., & Ruppert, L. F. (2012). Distribution of Arsenic, Selenium, and Other Trace Elements in High Pyrite Appalachian Coals: Evidence for Multiple Episodes of Pyrite Formation. *International Journal of Coal Geology, 94*, 238-249.

Dreher, G. B., & Finkelman, R. B. (1992). Selenium Mobilization in a Surface Coal Mine, Powder River Basin, Wyoming, USA. *Environmental Geology and Water Sciences, 19*(3), 155-167.

Dungan, R. S., & Frankenberger, W. T. (1999). Microbial Transformations of Selenium and the Bioremediation of Seleniferous Environments. *Bioremediation Journal, 3*(3), 171-188.

Electric Power Research Institute. (1991). *Use of Batch and Column Methodologies to Assess Utility Waste Leaching and Subsurface Chemical Attentuation.* Richland, Washington: Battelle, Pacific Northwest Laboratories.

Enriquez, S., Duarte, C. M., & Sand-Jensen, K. (1993). Patterns in Decomposition Rates Among Photosynthetic Organisms: The Importance of Detritus C :N :P Content. *Oecologia, 94*(4), 457-471.

Envirogen Technologies. (2011). *Treatment of Selenium-Containing Coal Mining Wastewater with Fluidized Bed Reactor Technology.* Envirogen Technologies.

Eswayah, A. S., Smith, T., & Gardiner, P. H. (2016). Microbial Transformations of Selenium Species of Relevance to Bioremediation. *Applied and Environmental Microbiology, 82*(16), 4848-4859.

Ferguson, K. D., & Leask, S. M. (1988). *The Export of Nutrients from Surface Coal Mines.* Enviroment Canada, Conservation and Protection, Environmental Protection, Pacific and Yukon Division, Vancouver. Retrieved 01 25, 2018, from http://www.rosemonteis.us/files/references/ferguson-leask-1988.pdf

Frankenberger, W. T., & Arshad, M. (2001). Bioremediation of Selenium-Contaminated Sediments and Water. *Biofactors, 14*(1-4), 241-254.

Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., & Dauphin, P. (1979). Early Oxidation of Organic Matter in Pelagic Sediments of the Eastern Equatorial Atlantic: Suboxic Diagenesis. *Geochimica et Cosmochimica Acta, 43*, 1075-1090.

Fujita, M., Ike, M., Kashiwa, M., Hashimoto, R., & Soda, S. (2002). Laboratory-Scale Continuous Reactor for Soluble Selenium Removal Using Selenate-Reducing Bacterium, *Bacillus* sp. SF-1. *Biotechnology and Bioengineering, 80*(7), 755-761.

Green, F. B., Lundquist, T. J., Quinn, N., Zarate, M. A., Zubieta, I. X., & Oswald, W. J. (2003). Selenium and Nitrate Removal From Agricultural Drainage Using the AIWPS® Technology. *Water Science and Technology, 48*(2), 229-305.

Gusek, J. J. (2002). Sulfate-Reducing Bioreactor Design and Operating Issues: Is This the Passive Treatment Technology for Your Mine Drainage? *National Association of Abandoned Mine Land Programs*, (pp. 1-14). Park City.

Hageman, S. P., van der Weijden, R. D., Weijma, J., & Buisman, C. J. (2013). Microbiological Selenate to Selenite Conversion for Selenium Removal. *Water Research, 47*(7), 2118-2128.

Hamilton, S. J. (2004). Review of Selenium Toxicity in the Aquatic Food Chain. *Science of the Total Environment, 326*(1-3), 1-31.

Hansen, D., Duda, P. J., Zayed, A., & Terry, N. (1998). Selenium Removal by Constructed Wetlands: Role of Biological Volatilization. *Environmental Science and Technology, 32*(5), 591-597.

Hartikainen, H. (2005). Biogeochemistry of Selenium and its Impact on Food Chain Quality and Human Health. *Journal of Trace Elements in Medicine and Biology, 18*(4), 309-318.

Haygarth, P. M. (1994). Global Importance and Global Cycling of Selenium. In W. T. Frankenberger, & S. Benson (Eds.), *Selenium in the Environment* (pp. 1-27). CRC Press.

Hem, J. D., & Cropper, W. H. (1962). *Chemistry of Iron in Natural Water.* United States Department of the Interior. Washington: United States Government Printing Office. Retrieved 01 25, 2018, from https://pubs.usgs.gov/wsp/1459a/report.pdf

Hendriks, A., & Zeeman, G. (2009). Pretreatments to Enhance the Digestibility of Lignocellulosic Biomass. *Bioresource Technology, 100*(1), 10-18.

Hendry, J. M., Biswas, A., Essilfie-Dughan, J., Chen, N., Day, S. J., & Barbour, S. L. (2015). Reservoirs of Selenium in Coal Waste Rock: Elk Valley, British Columbia, Canada. *Environmental Science & Technology, 49*(13), 8228-8236.

Herbel, M. J., Blum, J. S., & Oremlund, R. S. (2003). Reduction of Elemental Selenium to Selenide: Experiments with Anoxic Sediments and Bacteria that Respire Se-Oxyanions. *Geomicrobiology Journal, 20*(6), 587-602.

Herbert, R. B., Benner, S. G., & Blowes, D. W. (2000). Solid Phase Iron-Sulfur Geochemistry of a Reactive Barrier for Treatment of Mine Drainage. *Applied Geochemistry, 15*(9), 1331-1343.

Hochbaum, D. S., & Chen, A. (2000). Performance Analysis and Best Implementations of Old and New Algorithms for the Open - Pit Mining Problem. *Operations Research, 48*(6), 894-914.

Horwath, W. R. (2015). Carbon Cycling: the Dynamics and Formation of Organic Matter. In E. Paul (Ed.), *Soil Microbiology, Ecology and Biochemistry* (4th ed., pp. 339-382). San Diego, CA, USA: Academic Press, an imprint of Elsevier.

Hulshof, A. H., Blowes, D. W., & Gould, D. (2006). Evaluation of In Situ Layers for Treatment of Acid Mine Drainage: A Field Comparison. *Water Research, 40*(9), 1816-1826.

Hulshof, A. H., Blowes, D. W., Ptacek, C. J., & Gould, W. D. (2003). Microbial and Nutrient Investigations Into the Use of In Situ Layers for Treatment of Tailings Effluent. *Environmental Science & Technology, 37*(21), 5027-5033.

Jain, R., Dominic , D., Jordan, N., Rene, E. R., Weiss, S., van Hullebusch, E. D., Hubner, R., Lens, P. L. (2016). Preferential Adsorption of Cu in a Multi-Metal Mixture Onto Biogenic Elemental Selenium. *Chemical Engineering Journal, 284*, 917-925.

Jain, R., van Hullebusch, E. D., Lenz, M., & Farges, F. (2017). Understanding Selenium Biogeochemistry in Engineered Ecosystems: Transformation and Analytical Methods. In E. van Hullebusch (Ed.), *Bioremediation of Selenium Contaminated Wastewater* (pp. 33-56). Springer.

Johnson, J., Oelkers, E., & Helgeson, H. (1992). SUPCRT92 - A Software Package for Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous Species, and Reactions from 1 to 5000 bar and 0 to 1000°C. *Computers & Geosciences, 18*(7), 899-947.

Jong, T., & Parry, D. L. (2003). Removal of Sulfate and Heavy Metals by Sulfate Reducing Bacteria in Short-Term Bench Scale Upflow Anaerobic Packed Bed Reactor Runs. *Water Research, 37*(14), 3379-3389.

Kennedy, C., Day, S., MacGregor, D., & Pumphrey, J. (2012). Selenium Leaching from Coal Waste Rock in the Elk Valley, B.C. *9th International Conference on Acid Rock Drainage*, (pp. 1690-1702).

Kiilerich, B., Van de Ven, W., Nielson, A. H., & Vollertsen, J. (2017). Sulfide Precipitation in Wastewater at Short Timescales. *Water, 9*(9), 670.

Knossow, N., Blonder, B., Eckert, W., Turchyn, A. V., Antler, G., & Kamyshny, A. (2015). Annual Sulfur Cycle in a Warm Monomictic Lake with Sub-Millimolar Sulfate Concentrations. *Geotechincal Transactions, 16*(7), 1-24.

Kristensen, E., Ahmed, S. I., & Devol, A. H. (1995). Aerobic and Anaerobic Decomposition of Organic Matter in Marine Sediment: Which is Fastest? *Limnology and Oceanography, 40*(8), 1430-1437.

Kulp, T. R., & Pratt, L. M. (2004). Speciation and Weathering of Selenium in Upper Cretaceous Chalk and Shale from South Dakota and Wyoming, USA. *Geochimica et Cosmochimica Acta, 65*(18), 3687-3701.

Kuypers, M. M., Marchant, H. K., & Kartal, B. (2018). The Microbial Nitrogen-Cycling Network. *Nature Reviews, Microbiology, 16*(5), 263-276.

Lakin, H. W. (1973). Selenium in Our Environment. In E. Kothny, *Trace Elements in the Environment* (pp. 96-111). American Chemical Society.

Lemly, D. A. (1998). Pathology of Selenium Poisoning in Fish. In W. T. Frankenberger, & R. A. Engberg (Eds.), *Environmental Chemistry of Selenium* (pp. 281-295). New York: Marcel Dekker, Inc.

Lemly, D. A. (1999). Selenium Impacts on Fish: An Insidious Time Bomb. *Human and Ecological Risk Assessment, 5*(6), 1139-1151.

Lemly, D. A., Finger , S. E., & Nelson, M. K. (1993). Sources and Impacts of Irrigation Drainwater Contaminants in Arid Wetlands. *Environmental Toxicology and Chemistry, 12*(12), 2265-2279.

Lenz, M., Van Hullebusch, E., Hommes , G., Corvini, P. F., & Lens, P. N. (2008). Selenate Removal in Methanogenic and Sulfate-Reducing Upflow Anaerobic Sludge Bed Reactors. *Water Research, 42*(8-9), 2184-2194.

Lewis, A. E. (2010). Review of Metal Sulphide Precipitation. *Hydrometallurgy, 104*(2), 222-234.

Lewis, J., & Sjostrom, J. (2010). Optimizing the Experimental Design of Soil Columns in Saturated and Unsaturated Transport Experiments. *Journal of Contaminant Hydrology, 115*(1-4), 1-13.

Lin, Z.-q., & Terry, N. (2003). Selenium Removal by Constructed Wetlands: Quantitative Importance of Biological Volatilization in the Treatment of Selenium-Laden Agricultural Drainage Water. *Environmental Science and Technology, 37*(3), 606-615.

Lindsay, M. B., Blowes, D. W., Condon, P. D., & Ptacek, C. J. (2009). Managing Pore-Water Quality in Mine Tailings by Inducing Microbial Sulfate Reduction. *Environmental Science & Technology, 43*(18), 7086-7091.

Lindsay, M. B., Blowes, D. W., Ptacek, C. J., & Condon, P. D. (2011). Transport and Attenuation of Metal(loid)s in Mine Tailings Amended with Organic Carbon: Column Experiments. *Journal of Contaminant Hydrology, 125*(1-4), 26-38.

Liu, X., Fattahi, M., & Grambow, B. (2008). Selenide Retention Onto Pyrite Under Reducing Conditions. *Radiochimica Acta, 96*(8), 473-479.

Losi, M. E., & Frankenberger, W. T. (1997). Reduction of Selenium Oxyanions by *Enterobacter cloacae* SLD1a-1: Isolation and Growth of the Bacterium and its Expulsion of Selenium Particles. *Applied and Environmental Microbiology, 63*(8), 3079-3084.

Lovley, D. R. (1995). Bioremediation of Organic and Metal Contaminants with Dissimilatory Metal Reduction. *Journal of Industrial Microbiology, 14*(2), 85-91.

Luek, A., Brock, C., Rowan, D. K., & Rasmussen, J. B. (2014). A Simplified Anaerobic Bioreactor for the Treatment of Selenium-Laden Discharges from Non-acidic, End-Pit Lakes. *Mine Water Environment, 33*(4), 295-306.

Luo, Q., Tsukamoto, T. K., Zamzow, K. I., & Miller, G. C. (2008). Arsenic, Selenium, and Sulfate Removal Using an Ethanol-Enhanced Sulfate-Reducing Bioreactor. *Mine Water and the Environment, 27*(2), 100-108.

Lussier, C., Veiga, V., & Baldwin, S. (2003). The Geochemistry of Selenium Associated with Coal Waste in the Elk River Valley, Canada. *Environmental Geology, 44*, 905-913.

Luther III, G. W., Giblin, A. E., & Varsolona, R. (1985). Polarographic Analysis of Sulfur Species in Marine Porewaters. *Limnology and Oceanography, 60*(4), 727-736.

Manzoni, S., Trofymow, J. A., Jackson, R. B., & Porporato, A. (2010). Stoichiometric Controls on Carbon, Nitrogen, and Phosphorus Dynamics in Decomposing Litter. *Ecological Monographs, 80*(1), 89-106.

Marietou, A., Griffiths, L., & Cole, J. (2009). Preferential Reduction of the Thermodynamically Less Favorable Electron Acceptor, Sulfate, by a Nitrate-Reducing Strain of the Sulfate-Reducing Bacterium *Desulfovibrio desulfuricans* 27774. *Journal of Bacteriology, 191*(3), 882-889.

Martin, A. J., Goldblatt, R., & Stockwell, J. (2013). *Passive Attenuation of Selenium in a Coal Mine Flooded Pit.* North American Metals Council – Selenium Working Group Meeting.

Martin, A. J., Jones, R., & Buckwalter-Davis, M. (2009). Passive and Semi-Passive Treatment Alternatives for the Bioremediation of Selenium from Mine Waters. *British Columbia Technical and Research Committee on Reclamation.* Cranbrook.

Martin, A. J., Simpson, S., Fawcett, S., Wiramanaden, C. I., Pickering, I. J., Belzile, N., Chen, Y.-W., London, J., Wallschlager, D. (2011). Biogechemical Mechanisms of Selenium Exchange between Water and Sediments in Two Contrasting Lentic Environments. *Environmental Science & Technology, 45*(7), 2605-2612.

Masscheleyn, P., Delaune, R. D., & Patrick, W. H. (1990). Transformations of Selenium as Affected by Sediment Oxidation-Reduction Potential and pH. *Environmental Science and Technology, 24*(1), 91-96.

Meays, C., & Nordin, R. (2013). *Ambient Water Quality Guidelines For Sulphate - Technical Appendix Update.* Water Protection & Sustainability Branch, Environmental Sustainability and Strategic Policy Division, BC Ministry of Environment. Retrieved 01 25, 2018, from https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/wqgs-wqos/approved-wqgs/bc_moe_wqg_sulphate.pdf

Mioska, M. J. (2012). *A Column Experiment for Groundwater Remediation Post-Mine Closure at the Wolverine Mine, Yukon.* Victoria: Royal Roads University, Unpublished M.Sc Thesis.

Molson, J. W., Fala, O., Aubertin, M., & Bussiere, B. (2005). Numerical Simulations of Pyrite Oxidation and Acid Mine Drainage in Unsaturated Waste Rock Piles. *Journal of Contaminant Hydrology, 78*(4), 343-371.

Morin, K. A., & Hutt, N. M. (2009). *Mine-Water Leaching of Nitrogen Species from Explosive Residues.* Minesite Drainage Assessment Group, Surrey, BC.

Murphy, A. P. (1988). Removal of Selenate from Water by Chemical Reduction. *Industrial & Engineering Chemistry Research, 27*(1), 187-191.

Murto, M., Bjornsson, L., & Mattiasson, B. (2004, Feb). Impact of Food Industrial Waste on Anaerobic Co-Digestion of Sewage Sludge and Pig Manure. *Journal of Environmental Management, 70*(2), 101-107.

Muscatello, J. R., & Janz, D. M. (2009). Selenium Accumulation in Aquatic Biota Downstream of a Uranium Mining and Milling Operation. *Science of The Total Environment, 407*(4), 1318-1325.

Naveau, A., Monteil-Rivera, F., Guillon, E., & Dumonceau, J. (2007). Interactions of Aqueous Selenium (-II) and (IV) with Metallic Sulfide Surfaces. *Environmental Science & Technology, 41*(15), 5376-5382.

Nealson, K. H., & Meyers, C. (1992). Microbial Reduction of Manganese and Iron: New Approaches to Carbon Cycling. *Applied and Environmental Microbiology, 58*(2), 439-443.

Neculita, C.-M., Zagury, G. J., & Bussiere, B. (2007). Passive Treatment of Acid Mine Drainage in Bioreactors Using Sulfate-Reducing Bacteria: Critical Review and Research Needs. *Journal of Environmental Quality, 36*(1), 1-16.

Nerenberg, N., & Rittman, B. E. (2004). Hydrogen Based, Hollow-Fiber Membrane Biofilm Reactor for Reduction of Perchlorate and Other Oxidized Contaminants. *Water Science and Technology, 49*(11), 223-230.

Newman, D. K., Ahmann, D., & Morel, F. M. (1998). A Brief Review of Microbial Arsenate Respiration. *Geomicrobiology Journal, 15*(4), 225-268.

Nordin, R. N., Pommen, L. W., & Meays, C. L. (2009). *Water Quality Guidelines for Nitrogen (Nitrate, Nitrite, and Ammonia).* Water Stewardship Division, Ministry of Environment, Province of British Columbia. Retrieved 01 25, 2018, from https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/wqgs-wqos/approved-wqgs/nitrogen-overview.pdf

Nordstrom, D. K. (1982). Aqueous Pyrite Oxidation and the Consequent Formation of Secondary Iron Minerals. In D. M. Kral (Ed.), *Acid Sulfate Weathering* (pp. 37-56). Madison, Wisconsin, USA: Soil Science Society of America.

Opara, A., Peoples, M. J., Adams, D. J., & Martin, A. J. (2014, November). Electro-Biochemical Reactor (EBR) Technology for Selenium Removal from British Columbia's Coal-Mining Waste Waters. *Minerals & Metallurgical Processing, 31*(4), 209-214.

Oremlund, R. S., Blum, J. S., Bindi, A. B., Dowdle, P. R., Herbel, M., & Stolz, J. F. (1999). Simultaneous Reduction of Nitrate and Selenate by Cell Suspensions of Selenium-Respiring Bacteria . *Applied and Environmental Microbiology, 65*(10), 4385-4392.

Oremlund, R. S., Herbel, M. J., Blum, J. S., Langley, S., Beveridge, T. S., Ajayan, P. M., Sutto, T., Ellis, A. V., Curran, S. (2004). Structural and Spectral Features of Selenium Nanospheres Produced by Se-Respiring Bacteria. *Applied and Environmental Microbiology, 70*(1), 52-60.

Orica. (2015). *ANFO - Safety Data Sheet.* Orica. Retrieved 2 25, 2018, from Orica: http://msds.orica.com/pdf/shess-en-cds-010-000022013201.pdf

Otte, S., Kuenen, J. G., Nielson, L. P., Paerl, H. W., Zopfi, J., Schulz, H. N., Teske, A., Strottman, B., Gallardo, V. A., Jorgensen, B. B. (1999). Nitrogen, Carbon, and Sulfur Metabolism in Natural *Thioploca* Samples. *Applied and Environmental Microbiology, 65*(7), 3148-3157.

Ozturk, N., & Bektas, E. T. (2004). Nitrate Removal From Aqueous Solution by Adsorption Onto Various Materials. *Journal of Hazardous Materials, 112*(1-2), 155-162.

Pahler, J., Walker, R., Rutkowski, T., & Gusek, J. (2007). *Passive Removal of Selenium from Gravel Pit Seepage Using Selenium Reducing Bioreactors.* Golder Associates Inc. Lakewood: Golder Associates Inc. Retrieved 01 25, 2018, from https://www.researchgate.net/publication/237604607_passive_removal_of_selenium_from_gravel_pit_seepage_using_selenium_reducing_bioreactors1

Parida, K. M., Gorai, B., Das, N. N., & Rao, S. B. (1997). Studies on Ferric Oxide Hydroxides: III. Adsorption of Selenite (SeO_3^{2-}) on Different Forms of Iron Oxyhydroxides. *Journal of Colloid and Interface Science, 185*(2), 355-362.

Parkhurst, D. L., & Appelo, C. (n.d.). *User's Guide to PHREEQC (Version 2)-A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations.* Retrieved 6 19, 2017, from https://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/html/final.html

Peak, D. (2006). Adsorption Mechanisms of Selenium Oxyanions at the Aluminum Oxide/Water Interface. *Journal of Colloid and Interface Science, 303*(2), 337-345.

PetraScience Consultants Inc. (2005). *Characterization of Waste Rock Samples, Petrography and Rietveld XRD Analysis.* Vancouver: PetraScience Consultants Inc.

Pommen, L. (1983). *The Effect on Water Quality of Explosive Use in Surface Mining.* British Columbia Ministry of Environment, Water Management Branch, Victoria. Retrieved 01 25, 2018, from https://www.for.gov.bc.ca/hfd/library/documents/bib53789.pdf

Robertson, L. A., & Kuenen, J. G. (1984). Aerobic Denitrification: A Controversy Revived. *Archives of Microbiology, 139*, 351-354.

Ryan, B. D., & Ledda, A. (1997). A Review of Sulphur in Coal: With Specific Reference to the Telkwa Deposit, North-Western British Columbia. *Geological Fieldwork*, 22.

Santos, S., Ungureanu, G., Boaventura, R., & Botelho, C. (2015). Selenium Contaminated Waters: An Overview of Analytical Methods, Treatment Options and Recent Advances in Sorption Methods. *Science of the Total Environment, 521*, 246-260.

Sauthiera, N., Grasmicka, A., & Blanchetonb, J. (1998). Biological Denitrification Applied to a Marine Closed Aquaculture System. *Water Research, 32*(6), 1932-1938.

Schlesinger, W. H., & Bernhardt, E. S. (2013). *Biogeochemistry : An Analysis of Global Change* (3rd ed.). Boston: Academic Press - an Imprint of Elsevier.

Schmidt, O. (2006). *Wood and Tree Fungi, Biology, Damage, Protection, and Use.* Springer-Verlag Berlin Heidelberg.

Schumaker, B., Shines, K. C., Burton, J. V., & Papp, M. L. (1989). *A Comparison of Soil Sample Homogenization Techniques.* U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas. Retrieved 01 25, 2018, from https://www.researchgate.net/profile/Brian_Schumacher/publication/248696175_Comparison_of_Soil_Sample_Homogenization_Techniques/links/5408715d0cf2bba34c28c8f6/Comparison-of-Soil-Sample-Homogenization-Techniques.pdf

Seby, F., Potin-Gautier, M., Giffaut, E., & Donard, O. (2001). A Critical Review of Thermodynamic Data for Selenium Species at 25°C. *Chemical Geology, 171*(3-4), 173-194.

Sharma, V. K., McDonald, T. J., Sohn, M., Anquandah, A. K., Pettine, M., & Zboril, R. (2015). Biogeochemistry of Selenium. A review. *Environmental Chemistry Letters, 13*(1), 49-58.

Sialve, B., Bernet, N., & Bernard, O. (2009). Anaerobic Digestion of Microalgae as a Necessary Step to Make Microalgal Biodiesel Sustainable. *Biotechnology Advances, 27*(4), 409-416.

Siddique, T., Arocena, J. M., Thring, R. W., & Zhang, Y. (2007). Bacterial Reduction of Selenium in Coal Mine Tailings Pond Sediment. *Journal of Environmental Quality, 36*(3), 621-627.

Siddique, T., Okeke, B. C., Zhang, Y., Arshad, M., Han, S. K., & Frankenberger, W. T. (2005). Bacterial Diversity in Selenium Reduction of Agricultural Drainage Water Amended with Rice Straw. *Journal of Environmental Quality, 34*(1), 217-226.

Silver, W. L., Herman, D. J., & Firestone, M. K. (2001). Dissimilatory Nitrate Reduction to Ammonium in Upland Tropical Forest Soils. *Ecology, 82*(9), 2410-2416.

Simonton, S., Dimsha, M., Thomson, B., Barton, L. L., & Cathey, G. (2000). Long-Term Stability of Metals Immobilized by Microbial Reduction. *Proceedings of the 2000 Conference on Hazardous Waste Research*, (pp. 394-403). Denver.

Smith, M. (2014). *Analysis and Reactions of Aqueous Selenide and Other Reduced Inorganic Selenium Compounds Under Anoxic Conditions.* Unpublished M.Sc Thesis.

Soomo, A., & Gardner, W. S. (2002). Dissimilatory Nitrate Reduction to Ammonium (DNRA) as a Nitrogen Link, Versus Denitrification as a Sink in a Shallow Estuary (Laguna Madre/Baffin Bay, Texas). *Marine Ecology Progress Series, 237*, 41-50.

Spears, D. A., Manzanares-Papayanopoulos, L. I., & Booth, C. A. (1999). The Distribution and Origin of Trace Elements in a UK Coal; the Importance of Pyrite. *Fuel, 78*(14), 1671-1677.

Spencer, D. W., & Brewer, P. G. (1971). Vertical Advection Diffusion and Redox Potential as Controls on the Distribution of Manganese and Other Trace Metals Dissolved in Water of the Black Sea. *Journal of Geophysical Research, 76*(24), 5877-5892.

Steinberg, N. A., Blum, J. S., Hochstein, L., & Oremlund, R. A. (1992). Nitrate Is a Preferred Electron Acceptor for Growth of Freshwater Selenate-Respiring Bacteria. *Applied and Environmental Microbiology, 58*(1), 426-428.

Stolz, J. F., & Oremland, R. S. (1999). Bacterial Respiration of Arsenic and Selenium. *FEMS Microbiology Reviews, 23*(5), 615-627.

Subedi, G., Taylor, J., Hatam, I., & Baldwin, S. A. (2017). Simultaneous Selenate Reduction and Denitrification by a Consortium of Enriched Mine Site Bacteria. *Chemosphere, 183*, 536-545.

Tachi, Y., Shibutani, T., Sato, H., & Yui, M. (1998). Sorption and Diffusion Behavior of Selenium in Tuff. *Journal of Contaminant Hydrology, 35*(1-3), 77-89.

Takeno, N. (2005). *Atlas of Eh-pH diagrams, Intercomparison of thermodynamic databases, Geological Survey of Japan Open File Report No.419.* National Institute of Advanced Industrial Science and Technology.

Tan, L. C., Nancharaiah, Y. V., van Hullebusch, E. D., & Lens, P. N. (2016). Selenium: Environmental Significance, Pollution, and Biological Treatment Technologies. *Biotechnology Advances, 34*(5), 886-907.

Taylor, S. R. (1964). Abundance of Chemical Elements in the Continental Crust: A New Table. *Geochimica et Cosmochimica, 28*(8), 1273-1285.

Terry, N., Carlson, C., Raab, T. K., & Zayed, A. M. (1992). Rates of Selenium Volatilization Among Crop Species. *Journal of Environmental Quality, 21*(3), 341-344.

Tiwary, R. K. (2001). Environmental Impact of Coal Mining on Water Regime and Its Management. *Water, Air, and Soil Pollution, 132*(1-2), 185-199.

Tomei, F. A., Barton, L. L., Lemanski, C. L., Zocco, T. G., Fink, N. H., & Sillerud, L. O. (1995). Selenium Metabolism in *Desulfovibrio desulfuricans*. *Journal of Industrial Microbiology, 14*(3-4), 329-336.

United States Environmental Protection Agency. (1993). *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources, Appendix C.2.* Retrieved 01 25, 2018, from https://www3.epa.gov/ttn/chief/ap42/appendix/app-c2.pdf

United States Environmental Protection Agency. (2000). *Assigning Values to Non-Detected/Non-Quantified Pesticide Residues in Human Health Food Exposure Assessments.* Washington: Office of Pesticide Programs. Retrieved 01 25, 2018, from https://archive.epa.gov/pesticides/trac/web/pdf/trac3b012.pdf

United States Environmental Protection Agency. (2006). *Data Quality Assessment: Statistical Methods for Practitioners.* Washington: Office of Enviroonmental Information. Retrieved November 30, 2016, from https://nepis.epa.gov/Exe/ZyNET.exe/900B0D00.txt?ZyActionD=ZyDocument&Client=EPA&Index=2006%20Thru%202010&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&UseQField=&IntQFieldOp=0&ExtQFiel

URS Corporation. (2003). *Final Draft Report - Passive and Semi-Active Treatment of Acid Rock Drainage from Metal Mines - State of the Practice.* Portland: URS Corporation. Retrieved 5 12, 2014, from http://www.epa.gov/region1/superfund/sites/elizmine/43547.pdf van den Berg, E. M., Boleij, M., Kuenen, J. G., Kleerebezem, R., & van Loosdrecht, M. C. (2016). DNRA and Denitrification Coexist over a Broad Range of Acetate/N-NO_3^- Ratios, in a Chemostat Enrichment Culture. *Frontiers in Microbiology, 7*, 1842.

van der Wal, A., de Boer, W., Smant, W., & van Veen, J. A. (2007). Initial Decay of Woody Fragments in Soil is Influenced by Size, Vertical Position, Nitrogen Availability and Soil Origin. *Plant and Soil, 301*(1-2), 189-201.

Van Der Weijden, C. H. (1992). Early Diagenesis and Marine Pore Water. In G. V. Chilingarian, & K. H. Wold (Eds.), *Diagenesis, III, Volume 47* (1 ed.). Elsevier Science.

Vitousek, P. M., Aber, J. D., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., Schlesinger, W. H., Tilman, D. G. (1997). Human Alteration of the Global Nitrogen Cycle: Sources and Consequences. *Ecological Applications, 7*(3), 737-750.

Vogel, M., Fischer, S., Maffert, A., Hubner, R., Scheinost, A. C., Franzen, C., & Steudtner, R. (2018). Biotransformation and Detoxification of Selenite by Microbial Biogenesis of Selenium-Sulfur Nanoparticles. *Journal of Hazardous Materials, 344*, 749-757.

Walter Energy. (2015). *2014 Annual Water Quality Report - Brule Mine.* Walter Energy.

Weber, K. A., Urrutia, M. M., Churchill, P. F., Kukkadapu, R. K., & Roden, E. E. (2006). Anaerobic Redox Cycling of Iron by Freshwater Sediment Microorganisms. *Environmental Microbiology, 8*(1), 100-113.

Wedepohl, K. H. (1995). The Composition of the Continental Crust. *Geochimica et Cosmochimica Acta,, 59*(7), 1217-1232.

Wellen, C. C., Shatilla, N. J., & Carey, S. K. (2015). Regional Scale Selenium Loading Associated with Surface Coal Mining, Elk Valley, British Columbia, Canada. *Science of The Total Environment, 532*(1), 791-802.

Western Canadian Coal. (2006). *Application for an Environmental Assessment Certficate.*

Will, B. (2012, 5). *Teck Plans a Line Creek Water Treatment Facility*. Retrieved 3 26, 2016, from Canadian Mining & Energy: http://www.miningandexploration.ca/britishcolumbia/article/west_line_creek_water_treatment_facility/

Winkel, L. H., Johnson, C. A., Lenz, M., Grundl, T., Leupin, O. X., Amini, M., & Charlet, L. (2012). Environmental Selenium Research: From Microscopic Processes to Global Understanding. *Environmental Science & Technology, 46*, 571-579.

World Health Organization. (2004). *Sulfate in Drinking-Water.* World Health Organization. Retrieved 01 25, 2018, from http://www.who.int/water_sanitation_health/dwq/chemicals/sulfate.pdf

Wu, L. (2004). Review of 15 Years of Research on Ecotoxicology and Remediation of Land Contaminated by Agricultural Drainage Sediment Rich in Selenium. *Ecotoxicology and Environmental Safety, 57*(3), 257-269.

Young, L. M. (2003). *Evaluation of the Effect of Water Quality Degradation and Iron Oxide Precipitation on the Benthic Macroinvertebrate Community Downstream of F.E. Walter Reservoir.* Pennsylvania Fish and Boat Commission.

Zhang, P., & Sparks, D. L. (1990). Kinetics of Selenate and Selenite Adsorption/Desorption at the Goethite/Water Interface. *Environmental Science & Technology, 24*(12), 1848-1856.

Zheng, S., Su, L., Wang, L., Yao, R., Wang, D., Deng, Y., Wang, D., Wang, G., Rensing, C. (2014). Selenite Reduction by the Obligate Aerobic Bacterium Comamonas testosteroni S44 Isolated From a Metal-Contaminated Soil. *BioMed Central Microbiology, 14*(204), 1-13. Retrieved from Biomedcental Microbiology.

Appendix A.

The E_h-pH diagrams for N, Se, and S are displayed in this appendix. The diagrams are the result of thermodynamic modelling, and have been produced by the National Institute of Advanced Industrial Science and Technology (Takeno, 2005) referencing the default database "thermo.dat" based on LLNL (Lawrence Livermore National Lab.) data 0.3245r46, bundled with commercially available software GWB (Geochemist's Workbench) written by C. M. Bethke, Illinois University.

When comparing the diagrams for N, Se, or S resulting from the use of other databases, there is a general agreement with the LLNL database of the dominant species. One database (SUPCRT: SUPCRT92 (Johnson et al., 1992) applied with 98 update distributed by Everette Shock from his website on the Internet) does not show the presence of elemental Se as a stable phase. This diagram is not included.

Please note that the inability to secure permission for the use of the images from the author has resulted in their removal from the thesis. Please find E_h-pH diagrams for N, Se, and S on pages 153, 229, and 219, respectively in Takeno (2005).

Appendix B – Photographs

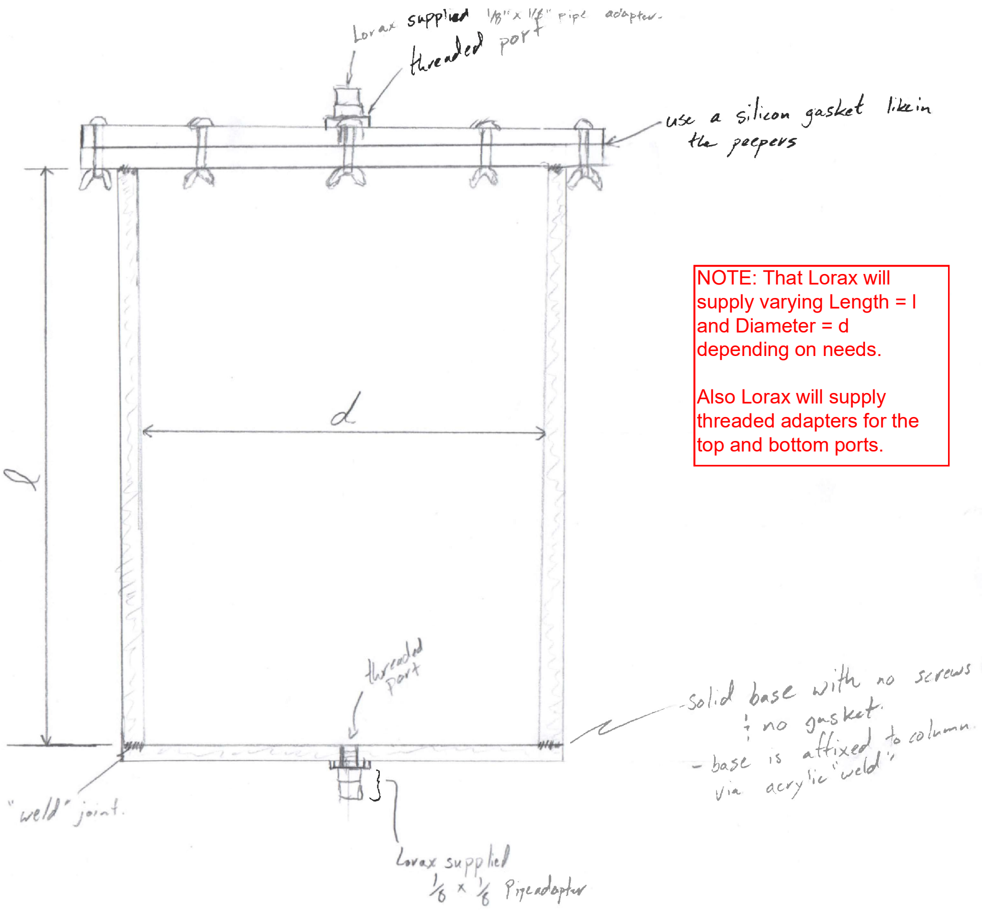
1. ANFO emulsion trails on the ground at a mine
2. Luer lock image
3. Sand layer at the base of a column

Descriptions of images, starting in the upper right and proceeding clockwise)

1. ANFO emulsion trails between blast holes on a blasting pattern at the Brule Mine
2. 4-way valves (stopcock with male Luer lock connections)
3. 1 cm thick layer of partially saturated Ottawa Sand overlain by organic amendment mixed with CMWR (photo taken while filling the columns with mine water).

Appendix C – Specifications

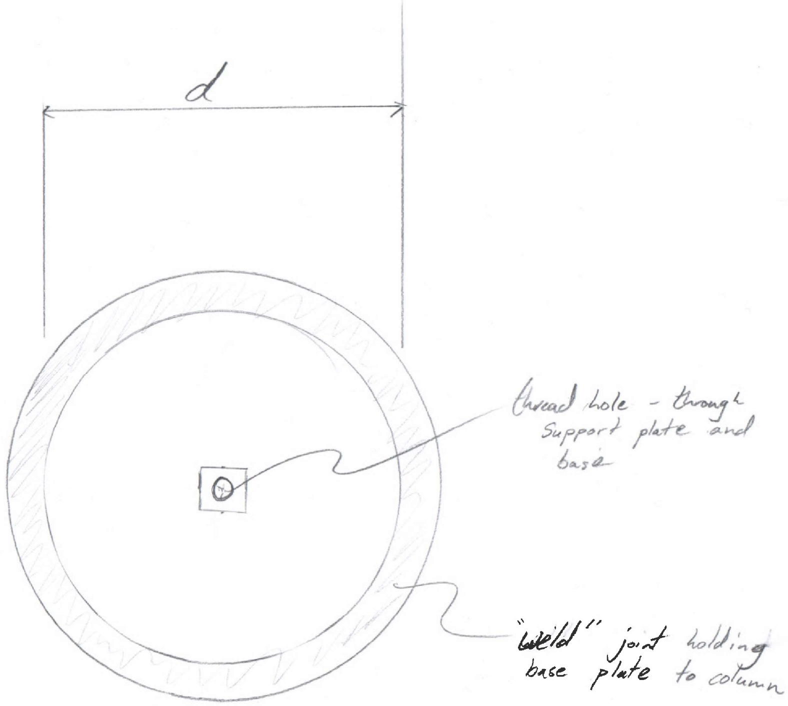
1. Lorax Supplied Column Specification
2. National Institute of Standards and Technology – Pump Calibration
3. Methods Used by ALS
4. ALS Sample Preservation Instructions



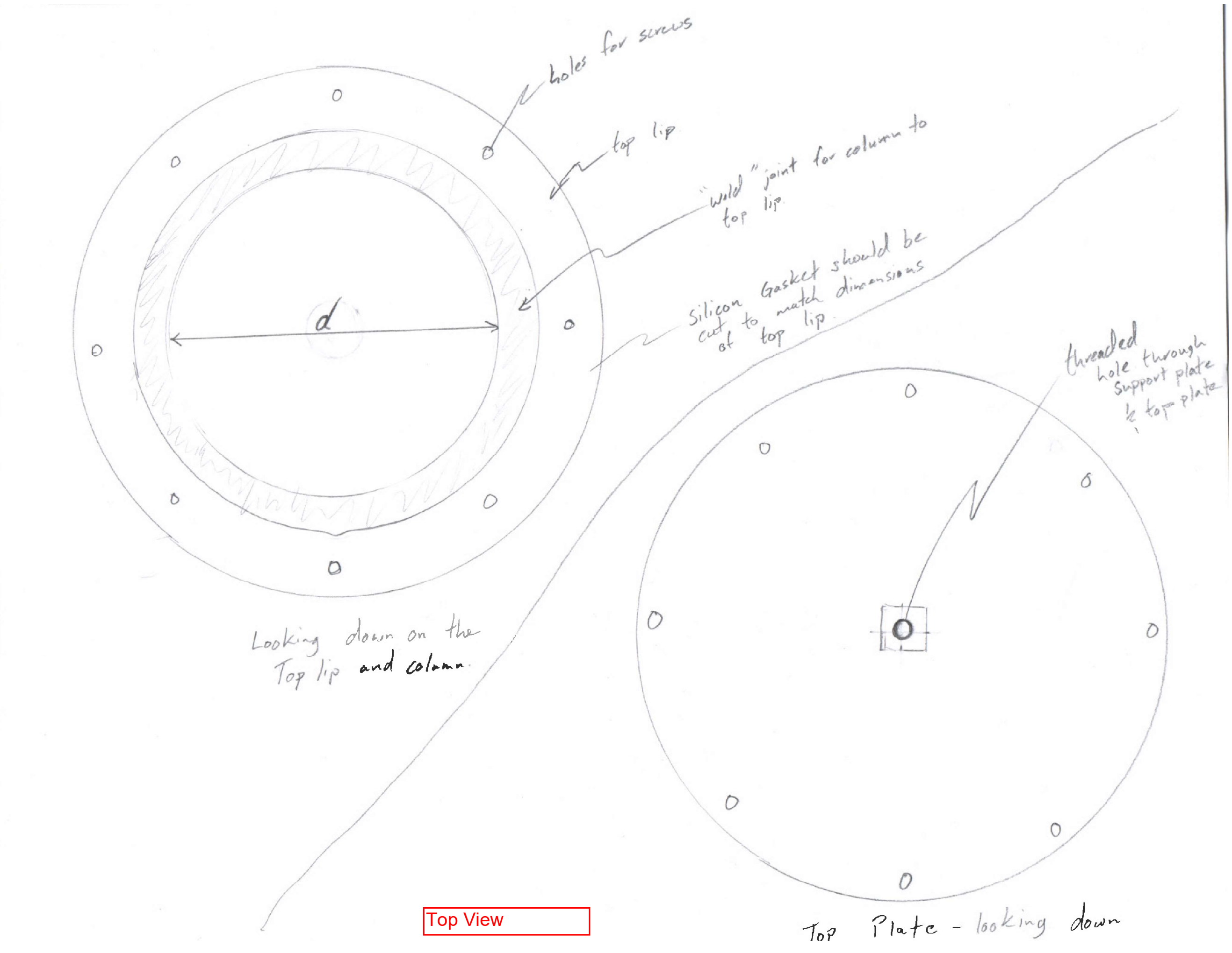
NOTE: That Lorax will supply varying Length = l and Diameter = d depending on needs.

Also Lorax will supply threaded adapters for the top and bottom ports.

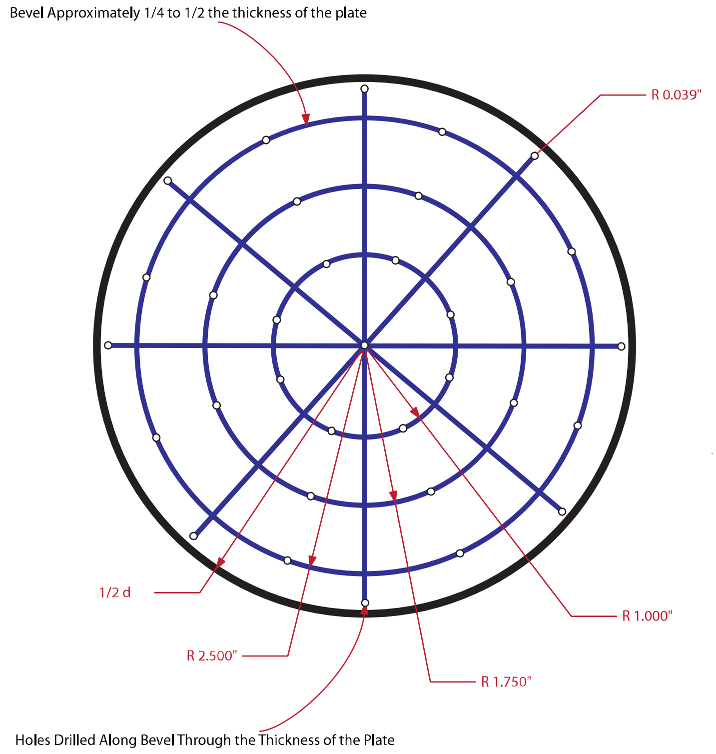
Side View



Bottom View



Top View



1/8" Thick Plexi-plate That Is Approximately 1/16 " smaller than the diameter

INNOCAL®
INNOVATIVE CALIBRATION SOLUTIONS
625 East Bunker Court
Vernon Hills, Illinois 60061
PH: 866-466-6225
Fax: 847-327-2993
www.innocalsolutions.com

NIST Traceable Calibration Report

REPORT NUMBER
667296

Reference Number: **577843**
PO Number: **531070**

Univ of Northern British Columbia
3333 University Way
Prince George, BC V2N 4Z9 Canada

Manufacturer:	Ismatec	**Calibration Date:**	10/16/2014
Model Number:	C.P.78001-12	**Calibration Due Date:**	10/16/2015
Description:	Pump, 8 Channel 8 Roller	**Condition As Found:**	Initial Calibration
Asset Number:	CP150850	**Condition As Left:**	In Tolerance, No adjustment
Serial Number:	610293-1		
Procedure:	DS Cole-Parmer 78001-12		

Remarks:
NIST-traceable calibration performed on the unit referenced above in accordance with customer requirements, published specifications and the lab's standard operating procedures. No adjustments were made to the unit.

Standards Utilized

Asset No.	Manufacturer	Model No.	Description	Cal. Date	Due Date
CP50123	Hewlett-Packard	53131A-010-030	Electronic, Universal Counter	09/04/2014	09/04/2015

Calibration Data

FUNCTION TESTED	Nominal Value	As Found	Out of Tol	As Left	Out of Tol	CALIBRATION TOLERANCE
20% Max Speed	9.0 rpm	9.0		Same		8.6 to 9.4 rpm [EMU 0.058 rpm][TUR 7.8:1]
40% Max Speed	18.0 rpm	17.8		Same		17.1 to 18.9 rpm [EMU 0.058 rpm][TUR 16:1]
60% Max Speed	27.0 rpm	26.6		Same		25.7 to 28.3 rpm [EMU 0.058 rpm][TUR 23:1]
80% Max Speed	36.0 rpm	35.5		Same		34.2 to 37.8 rpm [EMU 0.058 rpm][TUR 31:1]
100% Max Speed	45.0 rpm	44.5		Same		42.8 to 47.2 rpm [EMU 0.058 rpm][TUR 39:1]

Temperature: 22° C
Humidity: 49% RH
Rpt. No.: 667296

Calibration Performed By:				**Quality Reviewer:**	
Hazen, Jack A	306	Metrologist	847-327-5306	Szplit, Tony	10/16/2014
Name	ID #	Title	Phone	Name	Date

This report may not be reproduced, except in full, without written permission of Innocal. The results stated in this report relate only to the items tested or calibrated. Measurements reported herein are traceable to SI units via national standards maintained by NIST and were performed in compliance with MIL-STD-45662A, ANSI/NCSL Z540-1-1994, 10CFR50, Appendix B, ISO 9002-94, and ISO 17025:2005. Guard Banding, if reported on this certificate, is applied at a Z-factor of 30% for test points with a test uncertainty ratio (TUR) below 4:1. The estimated measurement uncertainty (EMU), if reported on this certificate, is being reported at a confidence level of 95% or K=2 unless otherwise noted in the remarks section.

Cole-Parmer® Delivering Solutions You Trust — Davis Instruments — DIGI-SENSE THE STANDARD IN PRECISION MEASUREMENT — OAKTON® INSTRUMENTS

Appendix C.3 - Parameters and Methods

Matrix	**Parameter**	**Method**
Water	TOC, DOC	American Public Health Association 5310B
	Ammonia	Journal of Environmental Monitoring, 2005, 7, 37 - 42, The Royal Society of Chemistry
	Nutrients/Anions	Environmental Protection Agency 300.1 (modified)
	Total Metals	Environmental Protection Agency 200.2/6020A (modified) and Environmental Protection Agency SW-846 3005A/6010B
	Dissolved metals	Environmental Protection Agency 200.2/6020A (modified) and Environmental Protection Agency SW-846 3005A/6010B
	Sulphide	American Public Health Association 4500-S2 Sulphide
	Alkalinity	American Public Health Association 2320 Alkalinity or Environmental Protection Agency 310.2
CMWR	Patricle Size - Sieve and Pipette Detailed	Burt, R. (2009). Soil Survey Field and Laboratory Methods Manual. Soil Survey Investigations Report No. 5. Method 3.2.1.2.2.
	Sulfide/sulfur	ALS Specialty Assay Procedure - Leco Sulphur Analyzer, Gravimetric
	Total inorganic carbon	ALS Specialty Assay Procedure - Carbonate Carbon in Solid Samples by CO_2 Coulometry
	Sobek ABA analysis	Sobek Method – Method Code OA-VOL08
		Modified Sobek Method – Method Code OA-VOL08m
		Siderite-Corrected Sobek Method – Method Code OA-VOL08s
		Mine Environment Neutral Drainage 2009 Method – Method Code OA-VOL08mn
		Paste pH – Method Code OA-ELE07
	ICP-MS Metals Analysis With Finish and Aqua Regia Digest	Aqua Regia Digestion (GEO-AR01)
		Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)
Organics	Moisture	American Society for Testing and Materials D2974-00 Method A
	Leachable Anions and Nutrients	American Society for Testing and Materials 4110 IC and Environmental Protection Agency 300.1
	Total N by Leco	Soil Science Society of America (1996) P. 973-974
	Available Ammonium	Canadian Society of Soil Science (1993) 4.2/COMM SOIL SCI 19(6)
	Metals	Environmental Protection Agency 200.2/6020A (mod)
	Total C	Method is assumed to be LECO, but cannot be confirmed

Bottle Order Request

6/1/2015 4:52 PM

Bottle Order #:	BR132932	**Company:**	Brule Coal Partnership
Lab:	VANCOUVER	**Client Contact:**	Nicholas Dumaresq
Account #:	WCC350	**Address:**	Box 508
Order Created By:	Kaitlyn Gardner		
Expected Date:	11/24/2014 12:00 AM		Chetwynd, BC, V0C 1J0
Order Priority:	Regular		
Ship/Pickup Via:	Pick Up by Client	**Phone Number:**	250-788-3619
Waybill Number:	ready 1 pallettx11coolers	**Fax Number:**	--
Prepared Date:	11/24/2014 11:02 AM		
Prepared By:	Stuart Mclean	**Client Job Number:**	ND-RESEARCH PROJECT Q48064

Checked By: Date ____________ Initials ________

Comments:

	Qty	Item (Analysis)	Container	Colour	Preservative	Instructions #
☐	25	General-Anions (BC)	125mL HDPE Bottle			3
☐	23	Metals (BC)	125mL HDPE (VCB) Bottle	Blue	1.5 mL 1:3 HNO3	23,13, 3,39
☐	7	NH3	250mL Amber Glass Bottle	Purple	1 mL 1:1 H2SO4	3,11
☐	25	Sulfide (BC)	125mL HDPE Bottle	Orange	1-2 mL Zn Acetate/1 mL 6N NaOH	3,14,15,22
☐	6	TOC	250mL Amber Glass Bottle	Purple	1 mL 1:1 H2SO4	3,11

**Please note the "Instructions #" above for the sample containers and items shipped to you.
Find the corresponding number below and follow the instructions/guidelines.**

Instructions #	Guideline
3	Keep cool (4oC).
11	Sulfuric acid (H2SO4): oxidizer/corrosive-in case of contact with skin, rinse affected area with excess cold water.
13	Nitric acid (HNO3): highly toxic/corrosive- in case of contact with skin, rinse affected area with excess cold water.
14	Sodium Hydroxide (NaOH): corrosive/toxic-in case of contact with skin, rinse affected area with excess cold water.
15	Zinc acetate (ZnC4H6O4): toxic-in case of contact with skin, rinse affected area several times with cold water.
22	Add the zinc acetate (reagent #1 - red cap) to an almost full bottle, cap and shake, then add the sodium hydroxide (reagent#2 - blue cap) and shake.
23	Dissolved Metals: filter in the field, then acidify. Total Metals: acidify in the field without filtering, further digested in the laboratory.
39	Add the contents of the blue (nitric acid) vial to the 125 or 250 mL plastic (HDPE) bottle after the sample has been added.

Appendix D – Results

1. QAQC – Results Summarized
2. QAQC – Duplicate Analysis
3. QAQC – Blank Analysis
4. QAQC – Reference Analysis
5. CMWR Particle Size Analysis
6. CMWR Chemical Characterization
7. Hay Chemical Characterization
8. Sawdust Chemical Characterization
9. Influent and Effluent Analysis – Tabulated Presentation
10. Influent and Effluent Analysis – Graphical Presentation

<u>Field Parameters</u>

i. pH
ii. Dissolved Oxygen
iii. ORP

<u>Anions</u>

iv. Hardness (as $CaCO_3$)
v. Total Alkalinity (as $CaCO_3$)
vi. Ammonia (as N)
vii. Bromide
viii. Chloride
ix. Fluoride
x. Nitrate (as N)
xi. Nitrite (as N)
xii. Sulfate
xiii. Sulfide (as S)

xiv. Dissolved Organic Carbon

<u>Dissolved Metals</u>

xv. Aluminum
xvi. Antimony
xvii. Arsenic
xviii. Barium
xix. Beryllium
xx. Bismuth
xxi. Boron
xxii. Cadmium
xxiii. Calcium
xxiv. Chromium
xxv. Cobalt
xxvi. Copper
xxvii. Iron

    xxviii. Lead
    xxix. Lithium
    xxx. Magnesium
    xxxi. Manganese
    xxxii. Molybdenum
    xxxiii. Nickel
    xxxiv. Phosphorous
    xxxv. Potassium
    xxxvi. Selenium
    xxxvii. Silicon
    xxxviii. Silver
    xxxix. Sodium
    xl. Strontium
    xli. Thallium
    xlii. Tin
    xliii. Titanium
    xliv. Uranium
    xlv. Vanadium
    xlvi. Zinc
11. Liquid Phase Selenium Speciation – Tabulated Presentation
12. Liquid Phase Selenium Speciation – Graphical Presentation
13. PHREEQC Modelled Saturation Indices for Minerals of Interest
14. Comparison of Column 1 Effluent and British Columbia Water Quality Guidelines

Appendix D.1 - Quality Analysis and Quality Control (QAQC) Results Summarized

D.1.1 Field (independent of ALS)

D.1.1.1 Overview

The CoA for duplicate field sample QAQC results is based on those proposed in the BC Field Sampling Manual (Clark, 2003) which notes that if either measurement is greater or equal to five times the MDL, RPD greater than 20% indicate a possible problem, and greater than 50% indicate a definite problem (Clark, 2003). This issue is most likely arising from contamination or lack of sample representativeness. For values within five times the MDL, results of duplicate RPD analysis are not useful predictors of data quality. The CoA for the blank sample QAQC is that no measured parameter value should exceed the MDL. The CoA for the reference sample QAQC is that the RPD between the obtained value and expected value is less than 20%, again with the qualification that the results need to be greater than 500% of the MDL for this analysis to be relevant.

D.1.1.2 Duplicate

Sample and duplicate analysis results are presented in tabular form in **Appendix D.2**, with those that exceed the CoA highlighted. These exceedances and the associated RPD values are displayed in **Table D.1**.

Table D.1: Duplicate sample results exceeding the RPD CoA (20%).

Week	RPD (%)	Parameter
5	50.00	T-NH_3 (as N)
13	34.00	D-Co
	45.20	D-Mo
15	21.30	T-Alkalinity (as $CaCO_3$)
	21.30	D-Bo
	53.40	D-Se
19	46.40	D-As
22	110.13	NO_3^- (as N)
	22.40	NO_2^- (as N)

D.1.1.3 Blank

Blank analysis results are presented in tabular form in **Appendix D.3**, with those that exceed the CoA highlighted. Concentrations of parameters exceeding the CoA are presented in **Table D.2.**

D.1.1.4 Reference Samples

Results of analysis of reference samples are presented in tabular form in **Appendix D.4**, with those that exceed the CoA highlighted. These exceedances and the associated RPD values are displayed in **Table D.3**

Table D.2: Blank sample results exceeding the method detection limits.

Week	Value (in mg L^{-1})	Parameter
3	0.0154	NO_3^-
	3.36	DOC
5	0.0058	NO_3^-
	0.000131	D-Ba
	0.00278	D-Cu
	0.000053	D-Mn
	0.101	D-Si
7	0.0057	T-NH_3
	0.0276	NO_3^-
	0.000103	D-Pb
9	0.0059	NO_3^-
	0.000176	D-Ba
	0.052	D-Ca
	0.000245	D-Mo
	0.00032	D-Sr
13	2.7	T-Alkalinity (as $CaCO_3$)
	0.105	D-Si
15	0.0052	T-NH_3
17	2.6	T-Alkalinity (as $CaCO_3$)
	0.008	NO_3^-
	0.059	DOC

D.1.2 Lab

ALS performed their own internal QAQC program, which included laboratory control samples, internal method blanks, matrix spikes, and no results were outside their limits of acceptability.

Table D.3: Reference Samples Exceeding the RPD CoA (20%).

Parameter	Week	RPD (%)
D-Al	11	36.5
	13	26.5
	15	36.6
	17	45.8
	18	38.1
	19	57.8
	22	62.2
	24	74.2
D-Pb	11	20.3
D-Mo	11	20.3
D-Se	22	23.0
D-Tl	11	23.5
	13	20.8
D-U	11	24.2

QAQC - Duplicate Analysis

🟨 total concentration! not dissolved
🟩 RPD > 20%
🟥 RPD > 50%
🟦 Result < 5x MDL

Results that are acceptable or not calculated due to a lack of suitable data are labelled 'N/A'

Samples	Date		Physical Tests	Anions and Nutrients									Organic Carbon	Dissolved Metals									
		Week	Hardness (as CaCO3)	Alkalinity, Total (as CaCO3)	Ammonia, Total (as N)	Bromide (Br)	Chloride (Cl)	Fluoride (F)	Nitrate (as N)	Nitrite (as N)	Sulfate (SO4)	Sulfide as S	Dissolved Organic Carbon	Aluminum (Al)-Dissolved	Antimony (Sb)-Dissolved	Arsenic (As)-Dissolved	Barium (Ba)-Dissolved	Beryllium (Be)-Dissolved	Bismuth (Bi)-Dissolved	Boron (B)-Dissolved	Cadmium (Cd)-Dissolved	Calcium (Ca)-Dissolved	Chromium (Cr)-Dissolved
Inlet	10-Feb-15	1	931	118	0.0069	1	11	0.4	73.6	0.02	782	0.02	-	0.003	0.00188	0.00016	0.0266	0.0001	0.0005	0.119	0.00001	189	0.0001
14 (Duplicate)	10-Feb-15	1	930	116	-	1	11	0.4	73.5	0.02	781	-	-	0.003	0.00184	0.00015	0.0269	0.0001	0.0005	0.119	0.00001	190	0.0001
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.50	2.0	0.0050	1.0	10	0.40	0.10	0.020	6.0	0.020	-	0.0030	0.00010	0.00010	0.000050	0.00010	0.00050	0.010	0.000010	0.050	0.00010
3	24-Feb-15	3	-	984	9.24	1	14	0.4	0.14	0.02	604	-	810	0.358	0.0151	0.0105	0.113	0.0002	0.001	0.452	0.00152	445	0.00685
9	24-Feb-15	3	-	965	9.06	1	14	0.4	0.12	0.02	604	-	779	0.299	0.0151	0.0110	0.134	0.0002	0.001	0.442	0.00160	439	0.00683
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			-	1.0	0.25	1.0	10	0.40	0.10	0.020	6.0	-	50	0.0060	0.00020	0.00020	0.00010	0.00020	0.0010	0.020	0.000020	0.050	0.00020
4	11-Mar-15	5	880	293	0.132	0.5	10.2	0.40	28.5	0.352	776	0.02	15.0	0.003	0.00578	0.00101	0.0191	0.0001	0.0005	0.237	0.00166	203	0.0001
10	11-Mar-15	5	889	298	0.220	0.5	10.1	0.39	28.0	0.310	774	-	14.9	0.003	0.00646	0.00107	0.0193	0.0001	0.0005	0.256	0.00170	202	0.0001
Duplicate RPD			N/A	N/A	50.00	10.15	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.50	2.0	0.013	0.50	5.0	0.20	0.050	0.010	3.0	0.020	1.0	0.0030	0.00010	0.00010	0.000050	0.00010	0.00050	0.010	0.000010	0.050	0.00010
2	25-MAR-15	7	903	145	0.0747	<0.50	9.7	0.31	72.7	0.014	772	-	2.71	<0.0030	0.00426	0.00020	0.0164	<0.00010	<0.00050	0.202	0.00173	192	<0.00010
8	25-MAR-15	7	891	142	0.0805	<0.50	9.5	0.30	70.8	0.016	752	-	2.65	0.0268	0.00408	0.00023	0.0163	<0.00010	<0.00050	0.201	0.00164	190	<0.00010
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.50	1.0	0.0050	0.50	5.0	0.20	0.050	0.010	3.0	-	0.50	0.0030	0.00010	0.00010	0.000050	0.00010	0.00050	0.010	0.000010	0.050	0.00010
6	08-APR-15	9	927	211	0.0321	<0.50	10.3	0.36	54.4	0.099	786	-	9.39	<0.0030	0.00524	0.00081	0.0197	<0.00010	<0.000050	0.230	0.00136	208	<0.00010
12	08-APR-15	9	933	209	0.0296	<0.50	10.3	0.35	54.1	0.102	783	-	10.3	<0.0030	0.00522	0.00081	0.0196	<0.00010	<0.000050	0.235	0.00136	208	<0.00010
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.50	2.0	0.0050	0.50	5.0	0.20	0.050	0.010	3.0	-	0.50	0.0030	0.00010	0.00010	0.000050	0.00010	0.000050	0.010	0.0000050	0.050	0.00010
6	22-APR-15	11	967	197	0.0536	<1.0	10	<0.40	56.6	0.042	770	-	7.16	<0.0030	0.00487	0.00070	0.0187	<0.00010	<0.000050	0.164	0.00137	215	<0.00010
12	22-APR-15	11	961	196	0.0502	<1.0	10	<0.40	57.7	0.042	789	-	7.24	<0.0030	0.00509	0.00068	0.0183	<0.00010	<0.000050	0.165	0.00131	215	<0.00010
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.50	2.0	0.0050	1.0	10	0.40	0.10	0.020	6.0	-	0.50	0.0030	0.00010	0.00010	0.000050	0.00010	0.000050	0.010	0.0000050	0.050	0.00010
3	05-MAY-15	13	992	1010	1.37	<0.50	9.9	0.37	<0.050	<0.010	329	29.3	74.2	0.0222	0.00621	0.0137	0.317	<0.00010	<0.000050	0.136	0.0000204	229	0.00154
9	05-MAY-15	13	939	870	1.28	<0.50	10.0	0.36	3.51	0.065	295	-	76.2	0.0227	0.00625	0.0131	0.330	<0.00010	<0.000050	0.119	0.0000373	209	0.00161
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	58.58	4.08	N/A
Specific MDL for Sample			0.50	20	0.025	0.50	5.0	0.20	0.050	0.010	3.0	4.0	5.0	0.0030	0.00010	0.00010	0.000050	0.00010	0.000050	0.010	0.00	0.050	0.00010
3	20-MAY-15	15	947	826	1.53	<1.0	<10	<0.40	3.79	0.139	229	31.6	105	0.0243	0.00612	0.0155	0.345	<0.00010	<0.000050	0.143	0.0000179	212	0.00177
9	20-MAY-15	15	953	667	1.68	<1.0	<10	<0.40	3.86	0.150	230	-	107	0.0246	0.00624	0.0149	0.350	<0.00010	<0.000050	0.177	0.0000259	216	0.00173
Duplicate RPD			N/A	21.30	667.00	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	14.30	21.25	36.53	3.58	N/A
Specific MDL for Sample			0.50	1.0	0.050	1.0	10	0.40	0.10	0.020	6.0	4.0	5.0	0.0030	0.00010	0.00010	0.000050	0.00010	0.000050	0.010	0.0000050	0.050	0.00010
3	02-JUN-15	17	939	778	3.22	<0.50	10.0	0.33	8.61	2.17	439	31	59	0.0156	0.00564	0.0128	0.258	<0.00010	<0.000050	0.139	0.0000138	210	0.00109
9	02-JUN-15	17	920	713	3.06	<0.50	9.9	0.33	8.45	2.15	436	-	58	0.0146	0.00551	0.0126	0.258	<0.00010	<0.000050	0.136	0.0000125	206	0.00099
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.50	20	0.050	0.50	5.0	0.20	0.050	0.010	3.0	10	10	0.0030	0.00010	0.00010	0.000050	0.00010	0.000050	0.010	0.0000050	0.050	0.00010
4	17-Jun-2015	19	923	217	0.206	<0.50	9.9	0.31	46.6	0.581	770	<0.020	4.26	<0.0030	0.00496	0.00154	0.0203	<0.00010	<0.000050	0.169	0.000694	199	<0.00010
10	17-Jun-2015	19	903	215	0.212	<0.50	10.4	0.29	48.5	0.662	802		4.68	<0.0030	0.00488	0.00096	0.0205	<0.00010	<0.000050	0.165	0.000695	200	<0.00010
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	46.40	9.60	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.50	1.0	0.0050	0.050	0.50	0.020	0.0050	0.0010	0.30	0.020	0.50	0.0030	0.00010	0.00010	0.000050	0.00010	0.000050	0.010	0.0000050	0.050	0.00010
1	7-Jul-2015	22	1060	666	0.0686	<0.25	9.6	0.31	0.652	0.0679	573	5.5	33.3	0.0186	0.00233	0.00912	0.381	<0.00010	<0.000050	0.147	0.0000092	254	0.00142
7	7-Jul-2015	22	1050	704	0.0607	<1.0	<10	<0.40	2.25	0.085	581	N/A	32.7	0.0195	0.00247	0.00937	0.400	<0.00010	<0.000050	0.144	<0.0000050	249	0.00141
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	130.40	110.13	22.37	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.50	1.0	0.0050	0.050	0.50	0.020	0.0050	0.0010	0.30	0.020	0.50	0.0030	0.00010	0.00010	0.000050	0.00010	0.000050	0.010	0.0000050	0.050	0.00010
1	22-Jul-2015	24	1010	467	<0.0050	<0.50	10.0	<0.20	22.6	0.117	706	0.206	FIELD	0.0073	0.00444	0.00566	0.111	<0.00010	<0.000050	0.138	<0.0000050	238	0.00042
7	22-Jul-2015	24	1000	438	<0.0050	<0.50	9.9	<0.20	22.4	0.116	701	0.178	FIELD	0.0060	0.00449	0.00572	0.111	<0.00010	<0.000050	0.136	<0.0000050	235	0.00038
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.50	1.0	0.0050	0.050	0.50	0.020	0.0050	0.0010	0.30	0.020		0.0030	0.00010	0.00010	0.000050	0.00010	0.000050	0.010	0.0000050	0.050	0.00010

🟨 total concentration! not dissolved
🟩 RPD > 20%
🟥 RPD > 50%
🟦 Result < 5x MDL

Results that are acceptable or not calculated due to a lack of suitable data are labelled 'N/A'

Dissolved Metals

		Week	Cobalt (Co)-Dissolved	Copper (Cu)-Dissolved	Iron (Fe)-Dissolved	Lead (Pb)-Dissolved	Lithium (Li)-Dissolved	Magnesium (Mg)-Dissolved	Manganese (Mn)-Dissolved	Molybdenum (Mo)-Dissolved	Nickel (Ni)-Dissolved	Phosphorus (P)-Dissolved	Potassium (K)-Dissolved	Selenium (Se)-Dissolved	Silicon (Si)-Dissolved	Silver (Ag)-Dissolved	Sodium (Na)-Dissolved	Strontium (Sr)-Dissolved	Thallium (Tl)-Dissolved	Tin (Sn)-Dissolved	Titanium (Ti)-Dissolved	Uranium (U)-Dissolved	Vanadium (V)-Dissolved	Zinc (Zn)-Dissolved
Inlet	10-Feb-15	1	0.0001	0.00091	0.03	0.000075	0.186	111	0.000097	0.00432	0.0583	0.3	4.3	0.104	2.46	0.00001	101	0.339	0.000024	0.0001	0.012	0.0202	0.001	0.003
14 (Duplicate)	10-Feb-15	1	0.0001	0.00092	0.03	0.000082	0.191	111	0.000085	0.00426	0.0588	0.3	4.2	0.104	2.46	0.00001	101	0.351	0.000023	0.0001	0.012	0.0201	0.001	0.003
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00010	0.00050	0.030	0.000050	0.00050	0.10	0.000050	0.000050	0.00050	0.30	2.0	0.00010	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.0010	0.0030
3	24-Feb-15	3	0.209	0.0075	26.3	0.00148	0.214	87.7	1.19	0.0152	1.33	3.36	107	0.00374	19.8	0.000032	104	0.784	0.000077	0.00046	0.042	0.00236	0.0221	0.223
9	24-Feb-15	3	0.206	0.0078	25.9	0.00162	0.211	86.6	1.20	0.0148	1.31	3.35	105	0.00382	19.2	0.000052	101	0.751	0.000084	0.00050	0.040	0.00236	0.0226	0.224
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	47.62	1.60	less than 5 x MDL		N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00020	0.0010	0.030	0.00010	0.0010	0.10	0.00010	0.00010	0.0010	0.30	2.0	0.00020	0.050	0.000020			0.000020	0.00020	0.010	0.000020	0.0020	0.0060
4	11-Mar-15	5	0.0372	0.00063	0.03	0.000143	0.193	90.6	0.252	0.0227	0.186	0.3	6.1	0.0286	2.91	0.00001	104	0.326	0.000081	0.0001	0.012	0.0232	0.0028	0.115
10	11-Mar-15	5	0.0376	0.00075	0.03	0.000153	0.206	93.2	0.256	0.0246	0.189	0.3	6.3	0.0292	2.90	0.00001	105	0.353	0.000089	0.0001	0.012	0.0257	0.0028	0.116
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00010	0.00050	0.030	0.000050	0.00050	0.10	0.000050	0.000050	0.00050	0.30	2.0	0.00010	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.0010	0.0030
2	25-MAR-15	7	0.0206	0.00153	<0.030	<0.000050	0.227	103	0.128	0.0150	0.125	<0.30	5.0	0.111	2.36	<0.000010	105	0.353	0.000085	<0.00010	<0.010	0.0189	<0.0010	0.0830
8	25-MAR-15	7	0.0202	0.00168	<0.030	<0.000050	0.225	101	0.129	0.0153	0.122	<0.30	4.9	0.107	2.28	<0.000010	103	0.350	0.000088	<0.00010	<0.010	0.0183	<0.0010	0.0805
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00010	0.00050	0.030	0.000050	0.00050	0.10	0.000050	0.000050	0.00050	0.30	2.0	0.00010	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.0010	0.0030
6	08-APR-15	9	0.0327	0.00066	<0.030	0.000078	0.241	99.0	0.258	0.0173	0.177	<0.30	4.9	0.0512	2.57	<0.000010	97.9	0.341	0.000068	<0.00010	0.016	0.0199	0.00101	0.102
12	08-APR-15	9	0.0320	0.00058	<0.030	0.000087	0.243	100	0.256	0.0171	0.174	<0.30	4.9	0.0507	2.56	<0.000010	98.1	0.335	0.000065	<0.00010	0.016	0.0200	0.00103	0.101
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00010	0.00050	0.030	0.000050	0.0010	0.10	0.00010	0.000050	0.00050	0.30	2.0	0.000050	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.00050	0.0030
6	22-APR-15	11	0.0223	0.00067	<0.030	<0.000050	0.187	104	0.184	0.0145	0.134	<0.30	5.1	0.0456	2.56	<0.000010	102	0.349	0.000064	<0.00010	0.014	0.0180	0.00057	0.0834
12	22-APR-15	11	0.0220	0.00065	<0.030	<0.000050	0.192	103	0.183	0.0149	0.133	<0.30	5.4	0.0456	2.60	<0.000010	105	0.353	0.000069	<0.00010	0.014	0.0181	0.00056	0.0822
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00010	0.00050	0.030	0.000050	0.0010	0.10	0.00010	0.000050	0.00050	0.30	2.0	0.000050	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.00050	0.0030
3	05-MAY-15	13	0.00066	<0.00050	0.419	<0.000050	0.175	102	0.102	0.00154	0.0189	1.62	18.1	0.00997	16.6	<0.000010	102	0.378	<0.000010	<0.00010	0.013	0.00606	0.00739	<0.0030
9	05-MAY-15	13	0.00093	<0.00050	0.132	0.000060	0.149	101	0.0967	0.00244	0.0202	1.65	16.8	0.00973	15.5	<0.000010	94.5	0.390	<0.000010	<0.00010	<0.010	0.00619	0.00755	<0.0030
Duplicate RPD			33.96	6.60	104.17	4.40	N/A	N/A	N/A	45.23	30.80	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00010	0.00050	0.030	0.000050	0.0010	0.10	0.00010	0.000050	0.00050	0.30	2.0	0.000050	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.00050	0.0030
3	20-MAY-15	15	0.00081	<0.00050	0.064	<0.000050	0.190	102	0.0797	0.00194	0.0238	1.65	15.5	0.0116	15.5	<0.000010	98.5	0.373	<0.000010	<0.00010	0.015	0.00516	0.00881	<0.0030
9	20-MAY-15	15	0.00077	<0.00050	0.067	0.000065	0.221	101	0.0816	0.00198	0.0240	1.70	15.9	0.00671	15.9	<0.000010	102	0.380	<0.000010	<0.00010	0.014	0.00514	0.00872	<0.0030
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	53.41	134.20	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00010	0.00050	0.030	0.000050	0.0010	0.10	0.00010	0.000050	0.00050	0.30	2.0	0.000050	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.00050	0.0030
3	02-JUN-15	17	0.00084	<0.00050	0.120	<0.000050	0.209	101	0.0684	0.00208	0.0231	0.99	12.6	0.0112	11.6	<0.000010	98.3	0.386	<0.000010	<0.00010	<0.010	0.00759	0.00591	<0.0030
9	02-JUN-15	17	0.00080	<0.00050	0.122	<0.000050	0.205	98.2	0.0666	0.00204	0.0218	1.00	12.5	0.0109	11.5	<0.000010	99.6	0.382	<0.000010	<0.00010	<0.010	0.00769	0.00566	<0.0030
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00010	0.00050	0.030	0.000050	0.0010	0.10	0.00010	0.000050	0.00050	0.30	2.0	0.000050	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.00050	0.0030
4	17-Jun-2015	19	0.0170	<0.00050	<0.030	<0.000050	0.192	104	0.145	0.0130	0.0972	<0.30	5.0	0.0455	2.58	<0.000010	98.4	0.322	0.000077	<0.00010	<0.010	0.0175	0.00113	0.0629
10	17-Jun-2015	19	0.0163	<0.00050	<0.030	<0.000050	0.186	98.2	0.140	0.0128	0.0932	<0.30	5.1	0.0450	2.63	<0.000010	99.0	0.318	0.000078	<0.00010	<0.010	0.0173	0.00105	0.0613
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00010	0.00050	0.030	0.000050	0.0010	0.10	0.00010	0.000050	0.00050	0.30	2.0	0.000050	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.00050	0.0030
1	7-Jul-2015	22	0.00039	<0.00050	0.055	<0.000050	0.202	103	0.107	0.000818	0.00829	<0.30	12.4	0.0177	12.7	<0.000010	104	0.432	<0.000010	<0.00010	<0.010	0.00285	0.00478	<0.0030
7	7-Jul-2015	22	0.00041	<0.00050	0.050	<0.000050	0.205	103	0.111	0.000867	0.00833	<0.30	12.0	0.0171	12.5	<0.000010	102	0.439	<0.000010	<0.00010	<0.010	0.00295	0.00501	<0.0030
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00010	0.00050	0.030	0.000050	0.0010	0.10	0.00010	0.000050	0.00050	0.30	2.0	0.000050	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.00050	0.0030
1	22-Jul-2015	24	0.00076	<0.00050	0.835	0.000057	0.205	102	0.115	0.00295	0.0103	<0.30	6.9	0.0319	6.45	<0.000010	97.4	0.419	<0.000010	<0.00010	<0.010	0.0107	0.00204	0.0032
7	22-Jul-2015	24	0.00077	<0.00050	0.821	<0.000050	0.199	101	0.116	0.00300	0.0103	<0.30	6.7	0.0344	6.39	<0.000010	95.7	0.417	<0.000010	<0.00010	<0.010	0.0104	0.00201	<0.0030
Duplicate RPD			N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Specific MDL for Sample			0.00010	0.00050	0.030	0.000050	0.0010	0.10	0.00010	0.000050	0.00050	0.30	2.0	0.000050	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.00050	0.0030

🟩 QAQC CoA exceeded

Date	Week	Physical Tests	Anions and Nutrients									Organic Carbon
		Hardness (as CaCO3)	Alkalinity, Total (as CaCO3)	Ammonia, Total (as N)	Bromide (Br)	Chloride (Cl)	Fluoride (F)	Nitrate (as N)	Nitrite (as N)	Sulfate (SO4)	Sulfide as S	Dissolved Organic Carbon
17-Feb-15	2	0.5	2	0.005	0.05	0.5	0.02	0.005	0.001	0.3	0.02	0.5
24-Feb-15	3	0.5	2	0.005	0.05	0.5	0.02	0.0154	0.001	0.3	0.02	3.36
11-Mar-15	5	0.5	2	0.005	0.05	0.5	0.02	0.0058	0.001	0.3	0.02	0.5
25-MAR-15	7	0.5	1	0.0057	0.05	0.5	0.02	0.0276	0.001	0.3	0.02	0.5
08-APR-15	9	0.5	2	0.005	0.05	0.5	0.02	0.0059	0.001	0.3	0.02	0.5
22-APR-15	11	0.5	2	0.005	0.05	0.5	0.02	0.005	0.001	0.3	0.02	0.5
05-MAY-15	13	0.5	2.7	0.005	0.05	0.5	0.02	0.05	0.001	0.3	0.02	0.5
20-MAY-15	15	0.5	2	0.0052	0.05	0.5	0.02	0.005	0.001	0.3	0.02	0.5
02-JUN-15	17	0.5	2.6	0.005	0.05	0.5	0.02	0.0080	0.001	0.3	0.02	0.59
08-JUN-15	18	0.5	2	0.005	0.05	0.5	0.02	0.005	0.001	0.3	0.02	0.5
23-Jun-15	20	0.5	2	0.005	0.05	0.5	0.02	0.005	0.001	0.3	0.02	0.5
7-Jul-2015	22	0.5	2	0.005	0.05	0.5	0.02	0.005	0.001	0.3	0.02	0.5
22-Jul-2015	24	0.5	1	0.005	0.05	0.5	0.02	0.005	0.001	0.3	0.02	N/A

Date	Week	Dissolved Metals Continued									
		Copper (Cu)-Dissolved	Iron (Fe)-Dissolved	Lead (Pb)-Dissolved	Lithium (Li)-Dissolved	Magnesium (Mg)-Dissolved	Manganese (Mn)-Dissolved	Molybdenum (Mo)-Dissolved	Nickel (Ni)-Dissolved	Phosphorus (P)-Dissolved	Potassium (K)-Dissolved
17-Feb-15	2	0.0005	0.03	0.00005	0.0005	0.1	0.00005	0.00005	0.0005	0.3	2
24-Feb-15	3	0.0005	0.03	0.00005	0.0005	0.1	0.00005	0.00005	0.0005	0.3	2
11-Mar-15	5	0.00278	0.03	0.00005	0.0005	0.1	0.000053	0.00005	0.0005	0.3	2
25-MAR-15	7	0.0005	0.03	0.000103	0.0005	0.1	0.00005	0.00005	0.0005	0.3	2
08-APR-15	9	0.0005	0.03	0.00005	0.001	0.1	0.0001	0.000245	0.0005	0.3	2
22-APR-15	11	0.0005	0.03	0.00005	0.001	0.1	0.0001	0.00005	0.0005	0.3	2
05-MAY-15	13	0.0005	0.03	0.00005	0.001	0.1	0.0001	0.00005	0.0005	0.3	2
20-MAY-15	15	0.0005	0.03	0.00005	0.001	0.1	0.0001	0.00005	0.0005	0.3	2
02-JUN-15	17	0.0005	0.03	0.00005	0.001	0.1	0.0001	0.00005	0.0005	0.3	2
08-JUN-15	18	0.0005	0.03	0.00005	0.001	0.1	0.0001	0.00005	0.0005	0.3	2
23-Jun-15	20	0.0005	0.03	0.00005	0.001	0.1	0.0001	0.00005	0.0005	0.3	2
7-Jul-2015	22	0.0005	0.03	0.00005	0.001	0.1	0.0001	0.00005	0.0005	0.3	2
22-Jul-2015	24	0.0005	0.03	0.00005	0.001	0.1	0.0001	0.00005	0.0005	0.3	2

🟩 QAQC CoA exceeded

Date	Week	Dissolved Metals										
		Aluminum (Al)-Dissolved	Antimony (Sb)-Dissolved	Arsenic (As)-Dissolved	Barium (Ba)-Dissolved	Beryllium (Be)-Dissolved	Bismuth (Bi)-Dissolved	Boron (B)-Dissolved	Cadmium (Cd)-Dissolved	Calcium (Ca)-Dissolved	Chromium (Cr)-Dissolved	Cobalt (Co)-Dissolved
17-Feb-15	2	0.003	0.0001	0.0001	0.00005	0.0001	0.0005	0.01	0.00001	0.05	0.0001	0.0001
24-Feb-15	3	0.003	0.0001	0.0001	0.00005	0.0001	0.0005	0.01	0.00001	0.05	0.0001	0.0001
11-Mar-15	5	0.003	0.0001	0.0001	0.000131	0.0001	0.0005	0.01	0.00001	0.05	0.0001	0.0001
25-MAR-15	7	0.003	0.0001	0.0001	0.00005	0.0001	0.0005	0.01	0.00001	0.05	0.0001	0.0001
08-APR-15	9	0.003	0.0001	0.0001	0.000176	0.0001	0.00005	0.01	0.000005	0.052	0.0001	0.0001
22-APR-15	11	0.003	0.0001	0.0001	0.00005	0.0001	0.00005	0.01	0.000005	0.05	0.0001	0.0001
05-MAY-15	13	0.003	0.0001	0.0001	0.00005	0.0001	0.00005	0.01	0.000005	0.05	0.0001	0.0001
20-MAY-15	15	0.003	0.0001	0.0001	0.00005	0.0001	0.00005	0.01	0.000005	0.05	0.0001	0.0001
02-JUN-15	17	0.003	0.0001	0.0001	0.00005	0.0001	0.00005	0.01	0.000005	0.05	0.0001	0.0001
08-JUN-15	18	0.003	0.0001	0.0001	0.00005	0.0001	0.00005	0.01	0.000005	0.05	0.0001	0.0001
23-Jun-15	20	0.003	0.0001	0.0001	0.00005	0.0001	0.00005	0.01	0.000005	0.05	0.0001	0.0001
7-Jul-2015	22	0.003	0.0001	0.0001	0.00005	0.0001	0.00005	0.01	0.000005	0.05	0.0001	0.0001
22-Jul-2015	24	0.003	0.0001	0.0001	0.00005	0.0001	0.00005	0.01	0.000005	0.05	0.0001	0.0001

Date	Week	Dissolved Metals Continued										
		Selenium (Se)-Dissolved	Silicon (Si)-Dissolved	Silver (Ag)-Dissolved	Sodium (Na)-Dissolved	Strontium (Sr)-Dissolved	Thallium (Tl)-Dissolved	Tin (Sn)-Dissolved	Titanium (Ti)-Dissolved	Uranium (U)-Dissolved	Vanadium (V)-Dissolved	Zinc (Zn)-Dissolved
17-Feb-15	2	0.0001	0.05	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.001	0.003
24-Feb-15	3	0.0001	0.05	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.001	0.003
11-Mar-15	5	0.0001	0.101	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.001	0.003
25-MAR-15	7	0.0001	0.05	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.001	0.003
08-APR-15	9	0.00005	0.05	0.00001	2	0.00032	0.00001	0.0001	0.01	0.00001	0.0005	0.003
22-APR-15	11	0.00005	0.05	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.0005	0.003
05-MAY-15	13	0.00005	0.105	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.0005	0.003
20-MAY-15	15	0.00005	0.05	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.0005	0.003
02-JUN-15	17	0.00005	0.05	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.0005	0.003
08-JUN-15	18	0.00005	0.05	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.0005	0.003
23-Jun-15	20	0.00005	0.05	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.0005	0.003
7-Jul-2015	22	0.00005	0.05	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.0005	0.003
22-Jul-2015	24	0.00005	0.05	0.00001	2	0.0002	0.00001	0.0001	0.01	0.00001	0.0005	0.003

Appendix D.4

QAQC - Reference Analysis

🟦 Result < 5x MDL	🟩 20% RPD exceeded	🟥 50% RPF exceeded	

			Dissolved Metals															
Samples	Date	Week	Aluminum (Al)-Dissolved	Antimony (Sb)-Dissolved	Arsenic (As)-Dissolved	Barium (Ba)-Dissolved	Beryllium (Be)-Dissolved	Bismuth (Bi)-Dissolved	Boron (B)-Dissolved	Cadmium (Cd)-Dissolved	Calcium (Ca)-Dissolved	Chromium (Cr)-Dissolved	Cobalt (Co)-Dissolved	Copper (Cu)-Dissolved	Iron (Fe)-Dissolved	Lead (Pb)-Dissolved	Lithium (Li)-Dissolved	Magnesium (Mg)-Dissolved
Reference	17-Feb-15	2	0.058	0.0428	0.0460	0.0428	0.0444	<0.005	0.1	0.0444	0.05	0.0429	0.0432	0.0425	0.049	0.0418	<0.0050	0.1
Reference	24-Feb-15	3	0.0564	0.0556	0.0476	0.0465	0.0449	<0.00025	0.053	0.0472	0.061	0.0449	0.0442	0.0448	0.053	0.0450	<0.0025	0.1
Reference	11-Mar-15	5	0.0510	0.0462	0.0443	0.0444	0.0456	<0.00025	0.058	0.0471	0.05	0.0425	0.0426	0.0426	0.051	0.0439	<0.0025	0.1
Reference	25-MAR-15	7	0.0577	0.0477	0.0468	0.0456	0.0438	<0.00025	0.061	0.0477	0.05	0.0439	0.0434	0.0443	0.054	0.0428	<0.0050	0.1
Reference	08-APR-15	9	0.0609	0.0505	0.0470	0.0450	0.0444	<0.00025	0.068	0.0493	0.077	0.0433	0.0450	0.0444	0.054	0.0440	<0.0050	0.1
Reference	22-APR-15	11	0.0723	0.0471	0.0464	0.0438	0.0439	<0.00025	0.077	0.0466	0.057	0.0424	0.0440	0.0444	0.049	0.0408	<0.0050	0.1
Reference	06-May-15	13	0.0653	0.0469	0.0450	0.0434	0.0476	<0.00025	0.080	0.0474	0.050	0.0431	0.0432	0.0435	0.048	0.0422	<0.0050	0.1
Reference	20-MAY-15	15	0.0724	0.0486	0.0463	0.0457	0.0443	<0.00025	0.082	0.0481	0.054	0.0445	0.0436	0.0458	0.051	0.0443	<0.0050	0.1
Reference	02-JUN-15	17	0.0797	0.0490	0.0460	0.0458	0.0448	<0.00025	0.089	0.0459	0.056	0.0438	0.0431	0.0430	0.054	0.0452	<0.0050	<0.10
Reference	08-JUN-15	18	0.0735	0.0496	0.0447	0.0455	0.0445	<0.00025	0.095	0.0488	0.058	0.0429	0.0430	0.0447	0.053	0.0453	<0.0050	<0.10
Reference	17-Jun-2015	19	0.0906	0.0484	0.0441	0.0450	0.0428	<0.00025	0.103	0.0460	0.061	0.0429	0.0435	0.0447	0.051	0.0435	<0.0050	<0.10
Reference	7-Jul-2015	22	0.0951	0.0476	0.0472	0.0464	0.0461	<0.00025	0.140	0.0466	0.056	0.0420	0.0423	0.0434	0.053	0.0435	<0.0050	<0.10
Reference	22-Jul-2015	24	0.109	0.0481	0.0474	0.0474	0.0461	<0.00025	0.190	0.0478	0.056	0.0434	0.0465	0.0473	0.055	0.0455	<0.0050	<0.10
Detection Limit			0.0030	0.00010	0.00010	0.000050	0.00010	0.000050	0.050	0.0000050	0.050	0.00010	0.00010	0.00050	0.030	0.000050	0.0010	0.10
Goal			0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
RPD between value and Goal																		
Reference	17-Feb-15	2	14.8%	15.5%	8.3%	15.5%	11.9%	N/A	66.7%	11.9%	0.0%	15.3%	14.6%	16.2%	2.0%	17.9%	N/A	N/A
Reference	24-Feb-15	3	12.0%	10.6%	4.9%	7.3%	10.7%	N/A	5.8%	5.8%	19.8%	10.7%	12.3%	11.0%	5.8%	10.5%	N/A	N/A
Reference	11-Mar-15	5	2.0%	7.9%	12.1%	11.9%	9.2%	N/A	14.8%	6.0%	0.0%	16.2%	16.0%	16.0%	2.0%	13.0%	N/A	N/A
Reference	25-MAR-15	7	14.3%	4.7%	6.6%	9.2%	13.2%	N/A	19.8%	4.7%	0.0%	13.0%	14.1%	12.1%	7.7%	15.5%	N/A	N/A
Reference	08-APR-15	9	19.7%	1.0%	6.2%	10.5%	11.9%	N/A	30.5%	1.4%	42.5%	14.4%	10.5%	11.9%	7.7%	12.8%	N/A	N/A
Reference	22-APR-15	11	36.5%	6.0%	7.5%	13.2%	13.0%	N/A	42.5%	7.0%	13.1%	16.5%	12.8%	11.9%	2.0%	20.3%	N/A	N/A
Reference	06-May-15	13	26.5%	6.4%	10.5%	14.1%	4.9%	N/A	46.2%	5.3%	0.0%	14.8%	14.6%	13.9%	4.1%	16.9%	N/A	N/A
Reference	20-MAY-15	15	36.6%	2.8%	7.7%	9.0%	12.1%	N/A	48.5%	3.9%	7.7%	11.6%	13.7%	8.8%	2.0%	12.1%	N/A	N/A
Reference	02-JUN-15	17	45.8%	2.0%	8.3%	8.8%	11.0%	N/A	56.1%	8.6%	11.3%	13.2%	14.8%	15.1%	7.7%	10.1%	N/A	N/A
Reference	08-JUN-15	18	38.1%	0.8%	11.2%	9.4%	11.6%	N/A	62.1%	2.4%	14.8%	15.3%	15.1%	11.2%	5.8%	9.9%	N/A	N/A
Reference	17-Jun-2015	19	57.8%	3.3%	12.5%	10.5%	15.5%	N/A	69.3%	8.3%	19.8%	15.3%	13.9%	11.2%	2.0%	13.9%	N/A	N/A
Reference	7-Jul-2015	22	62.2%	4.9%	5.8%	7.5%	8.1%	N/A	94.7%	7.0%	11.3%	17.4%	16.7%	14.1%	5.8%	13.9%	N/A	N/A
Reference	22-Jul-2015	24	74.2%	3.9%	5.3%	5.3%	8.1%	N/A	116.7%	4.5%	11.3%	14.1%	7.3%	5.5%	9.5%	9.4%	N/A	N/A
Max			74.2%	15.5%	12.5%	15.5%	15.5%	0.0%	116.7%	11.9%	42.5%	17.4%	16.7%	16.2%	9.5%	20.3%	0.0%	0.0%

			Dissolved Metals															
Samples	Date	Week	Manganese (Mn)-Dissolved	Molybdenum (Mo)-Dissolved	Nickel (Ni)-Dissolved	Phosphorus (P)-Dissolved	Potassium (K)-Dissolved	Selenium (Se)-Dissolved	Silicon (Si)-Dissolved	Silver (Ag)-Dissolved	Sodium (Na)-Dissolved	Strontium (Sr)-Dissolved	Thallium (Tl)-Dissolved	Tin (Sn)-Dissolved	Titanium (Ti)-Dissolved	Uranium (U)-Dissolved	Vanadium (V)-Dissolved	Zinc (Zn)-Dissolved
Reference	17-Feb-15	2	0.0449	0.0408	0.0434	<0.30	<2.0	0.0424	0.224	0.0435	<2.0	0.0425	0.0421	0.0438	0.048	0.0421	0.044	0.044
Reference	24-Feb-15	3	0.0457	0.0419	0.0443	<0.30	<2.0	0.0420	0.268	0.0547	<2.0	0.0428	0.0446	0.0494	0.051	0.0441	0.0445	0.0495
Reference	11-Mar-15	5	0.0421	0.0415	0.0437	<0.30	<2.0	0.0425	0.312	0.0461	<2.0	0.0419	0.0438	0.0448	0.047	0.0420	0.0431	0.0417
Reference	25-MAR-15	7	0.0450	0.0424	0.0449	<0.30	<2.0	0.0411	0.429	0.0493	<2.0	0.0431	0.0425	0.0475	0.050	0.0421	0.0437	0.0423
Reference	08-APR-15	9	0.0465	0.0444	0.0462	<0.30	<2.0	0.0467	0.544	0.0508	<2.0	0.0451	0.0440	0.0497	0.052	0.0430	0.0443	0.0446
Reference	22-APR-15	11	0.0448	0.0408	0.0448	<0.30	<2.0	0.0444	0.643	0.0436	<2.0	0.0424	0.0395	0.0467	0.049	0.0392	0.0439	0.0458
Reference	06-May-15	13	0.0431	0.0417	0.0434	<0.30	<2.0	0.0445	0.784	0.0469	<2.0	0.0412	0.0406	0.0469	0.049	0.0414	0.0436	0.0427
Reference	20-MAY-15	15	0.0439	0.0437	0.0453	<0.30	<2.0	0.0430	0.937	0.0490	<2.0	0.0437	0.0435	0.0482	0.049	0.0442	0.0451	0.0452
Reference	02-JUN-15	17	0.0458	0.0430	0.0433	<0.30	<2.0	0.0418	1.09	0.0509	<2.0	0.0441	0.0447	0.0460	0.050	0.0456	0.0438	0.0444
Reference	08-JUN-15	18	0.0424	0.0441	0.0440	<0.30	<2.0	0.0423	1.16	0.0498	<2.0	0.0443	0.0447	0.0482	0.050	0.0450	0.0435	0.0423
Reference	17-Jun-2015	19	0.0442	0.0415	0.0431	<0.30	<2.0	0.0425	1.29	0.0509	<2.0	0.0422	0.0436	0.0467	0.050	0.0424	0.0426	0.0444
Reference	7-Jul-2015	22	0.0432	0.0416	0.0420	<0.30	<2.0	0.0397	1.69	0.0483	<2.0	0.0424	0.0437	0.0464	0.049	0.0437	0.0423	0.0437
Reference	22-Jul-2015	24	0.0449	0.0452	0.0465	<0.30	<2.0	0.0467	2.04	0.0484	<2.0	0.0446	0.0453	0.0487	0.051	0.0430	0.0461	0.0460
Detection Limit			0.00010	0.000050	0.00050	0.30	2.0	0.000050	0.050	0.000010	2.0	0.00020	0.000010	0.00010	0.010	0.000010	0.00050	0.0030
Goal			0.05	0.05	0.05	0.05	0.05	0.05	0.050	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
RPD between value and Goal																		
Reference	17-Feb-15	2	10.7%	20.3%	14.1%	N/A	N/A	16.5%	127.0%	13.9%	N/A	16.2%	17.2%	13.2%	4.1%	17.2%	12.8%	12.8%
Reference	24-Feb-15	3	9.0%	17.6%	12.1%	N/A	N/A	17.4%	137.1%	9.0%	N/A	15.5%	11.4%	1.2%	2.0%	12.5%	11.6%	1.0%
Reference	11-Mar-15	5	17.2%	18.6%	13.4%	N/A	N/A	16.2%	144.8%	8.1%	N/A	17.6%	13.2%	11.0%	6.2%	17.4%	14.8%	18.1%
Reference	25-MAR-15	7	10.5%	16.5%	10.7%	N/A	N/A	19.5%	158.2%	1.4%	N/A	14.8%	16.2%	5.1%	0.0%	17.2%	13.4%	16.7%
Reference	08-APR-15	9	7.3%	11.9%	7.9%	N/A	N/A	6.8%	166.3%	1.6%	N/A	10.3%	12.8%	0.6%	3.9%	15.1%	12.1%	11.4%
Reference	22-APR-15	11	11.0%	20.3%	11.0%	N/A	N/A	11.9%	171.1%	13.7%	N/A	16.5%	23.5%	6.8%	2.0%	24.2%	13.0%	8.8%
Reference	06-May-15	13	14.8%	18.1%	14.1%	N/A	N/A	11.6%	176.0%	6.4%	N/A	19.3%	20.8%	6.4%	2.0%	18.8%	13.7%	15.7%
Reference	20-MAY-15	15	13.0%	13.4%	9.9%	N/A	N/A	15.1%	179.7%	2.0%	N/A	13.4%	13.9%	3.7%	2.0%	12.3%	10.3%	10.1%
Reference	02-JUN-15	17	8.8%	15.1%	14.4%	N/A	N/A	17.9%	182.5%	1.8%	N/A	12.5%	11.2%	8.3%	0.0%	9.2%	13.2%	11.9%
Reference	08-JUN-15	18	16.5%	12.5%	12.8%	N/A	N/A	16.7%	183.5%	0.4%	N/A	12.1%	11.2%	3.7%	0.0%	10.5%	13.9%	16.7%
Reference	17-Jun-2015	19	12.3%	18.6%	14.8%	N/A	N/A	16.2%	185.1%	1.8%	N/A	16.9%	13.7%	6.8%	0.0%	16.5%	16.0%	11.9%
Reference	7-Jul-2015	22	14.6%	18.3%	17.4%	N/A	N/A	23.0%	188.5%	3.5%	N/A	16.5%	13.4%	7.5%	2.0%	13.4%	16.7%	13.4%
Reference	22-Jul-2015	24	10.7%	10.1%	7.3%	N/A	N/A	6.8%	190.4%	3.3%	N/A	11.4%	9.9%	2.6%	2.0%	15.1%	8.1%	8.3%
Max			17.2%	20.3%	17.4%	0.0%	0.0%	23.0%	190.4%	13.9%	0.0%	19.3%	23.5%	13.2%	6.2%	24.2%	16.7%	18.1%

Appendix D.5 Crushed Mine Waste Rock Particle Size Analysis

Client Sample ID			SAMPLE 1	SAMPLE 2	SAMPLE 3	
Date Sampled			29-Jul-2015	29-Jul-2015	29-Jul-2015	
Parameter	Lowest Detection Limit	Units	Soil	Soil	Soil	Average
% Gravel (>2mm)	0.10	%	57.8	50.8	57.1	55.2
% Sand (2.00mm - 1.00mm)	0.10	%	14.7	14.6	13.7	14.3
% Sand (1.00mm - 0.50mm)	0.10	%	8.61	11.0	9.84	9.8
% Sand (0.50mm - 0.25mm)	0.10	%	5.55	7.10	5.83	6.2
% Sand (0.25mm - 0.125mm)	0.10	%	3.10	4.01	3.31	3.5
% Sand (0.125mm - 0.063mm)	0.10	%	2.05	2.56	2.00	2.2
% Silt (0.063mm - 0.0312mm)	0.10	%	2.16	2.76	2.11	2.3
% Silt (0.0312mm - 0.004mm)	0.10	%	3.68	4.39	3.76	3.9
% Clay (<4um)	0.10	%	2.38	2.80	2.36	2.5

Appendix D.6 Crushed Mine Waste Rock Chemical Characterization

			SAMPLE 1	SAMPLE 2	SAMPLE 3
			23-Jul-2015	23-Jul-2015	23-Jul-2015
Parameter	Lowest Detection Limit	Units	Soil	Soil	Soil
Physical Tests (Soil)					
Moisture	0.25	%	<0.25	<0.25	<0.25
pH	0.10	Unity	8.1	8.1	8.2
Acid Soluble Sulphate Sulphu	0.010	%	<0.01	0.01	<0.01
Organic / Inorganic Carbon (Soil)					
Carbon (C)	0.050	%	0.88	0.77	0.79
Acid Base Accounting (Soil)					
FIZZ RATING	1.0	Unity	2	2	2
MPA	0.30	tCaCO3/1Kt	6.3	8.8	7.5
Neutralization Potential (NP)	1.0	tCaCO3/1Kt	57	57	55
NNP	1.0	tCaCO3/1Kt	51	48	48
Ratio (NP/MPA)	0.010	Unity	9.12	6.51	7.33
Total Metals (Soil)					
Aluminum (Al)	0.010	%	0.8	0.77	0.7
Antimony (Sb)	0.050	ppm	0.78	0.98	0.89
Arsenic (As)	0.10	ppm	5.8	7.1	6.2
Barium (Ba)	10	ppm	570	620	610
Beryllium (Be)	0.050	ppm	0.96	0.9	0.87
Bismuth (Bi)	0.010	ppm	0.17	0.17	0.17
Boron (B)	10	ppm	10	10	10
Cadmium (Cd)	0.010	ppm	2.06	2.64	2.35
Calcium (Ca)	0.010	%	2.12	1.94	1.98
Cerium (Ce)	0.020	ppm	14.75	14.95	14.2
Cesium (Cs)	0.050	ppm	1.15	1.09	1.04
Chromium (Cr)	1.0	ppm	18	18	17
Cobalt (Co)	0.10	ppm	6	7.5	6.8
Copper (Cu)	0.20	ppm	21.1	23.9	21.6
Gallium (Ga)	0.050	ppm	2.21	2.35	1.96
Germanium (Ge)	0.050	ppm	0.11	0.1	0.1
Gold (Au)	0.20	ppm	0.2	0.2	0.2
Hafnium (Hf)	0.020	ppm	0.06	0.06	0.06
Indium (In)	0.0050	ppm	0.035	0.04	0.035
Iron (Fe)	0.010	%	1.64	1.47	1.47
Lanthanum (La)	0.20	ppm	9.1	9.2	8.7
Lead (Pb)	0.20	ppm	11.5	12.8	12
Lithium (Li)	0.10	ppm	8.2	7.8	7.1
Magnesium (Mg)	0.010	%	0.27	0.26	0.25
Manganese (Mn)	5.0	ppm	128	115	115
Mercury (Hg)	0.010	ppm	0.1	0.13	0.12
Molybdenum (Mo)	0.050	ppm	2.18	2.89	2.69
Nickel (Ni)	0.20	ppm	33.7	43.6	37.8
Niobium (Nb)	0.050	ppm	0.05	0.05	0.05
Phosphorus (P)	10	ppm	830	790	790
Potassium (K)	0.010	%	0.26	0.25	0.22
Rhenium (Re)	0.0010	ppm	0.006	0.005	0.005
Rubidium (Rb)	0.10	ppm	19.1	18.6	17
Scandium (Sc)	0.10	ppm	4.7	4.7	4.5
Selenium (Se)	0.20	ppm	2.9	2.9	2.7
Silver (Ag)	0.010	ppm	0.34	0.39	0.4
Sodium (Na)	0.010	%	0.05	0.04	0.04
Strontium (Sr)	0.20	ppm	96.5	93.8	90.9
Sulfur (S)	0.010	%	0.1	0.15	0.12
Tantalum (Ta)	0.010	ppm	0.01	0.01	0.01
Tellurium (Te)	0.010	ppm	0.04	0.05	0.04
Thallium (Tl)	0.020	ppm	0.03	0.03	0.03
Thorium (Th)	0.20	ppm	3.9	4	3.8
Tin (Sn)	0.20	ppm	0.6	0.7	0.6
Titanium (Ti)	0.0050	%	0.005	0.005	0.005
Tungsten (W)	0.050	ppm	0.05	0.05	0.05
Uranium (U)	0.050	ppm	1.73	1.9	1.79
Vanadium (V)	1.0	ppm	76	88	86
Yttrium (Y)	0.050	ppm	12.8	13.2	12.1
Zinc (Zn)	2.0	ppm	171	199	178
Zirconium (Zr)	0.50	ppm	2.5	2.5	2.4
Permanent Gases (Soil)					
Carbon Dioxide (CO2)	0.20	%	3.2	2.8	2.9

Appendix D.7 Hay Chemical Characterization

Sample ID	SAMPLE 1 - HAY	SAMPLE 2 - HAY	SAMPLE 3 - HAY
Date Sampled	07-SEP-14	07-SEP-14	07-SEP-14
Matrix	Soil	Soil	Soil
Physical Tests			
Moisture	11.2	13.7	13.3
Leachable Anions & Nutrients			
Bromide (Br)	<25	<25	<25
Chloride (Cl)	2160	2420	640
Nitrate (as N)	4.3	150	10.6
Nitrite (as N)	<0.50	<0.50	<0.50
Sulfate (SO4)	1600	2490	<500
Anions and Nutrients			
Total Nitrogen by LECO	1.22	1.19	1.04
Organic / Inorganic Carbon			
Total Organic Carbon	43.7	44.9	44.2
Plant Available Nutrients			
Available Ammonium-N	41.7	130	75.1
Metals			
Aluminum (Al)	<50	51	<50
Antimony (Sb)	<0.10	<0.10	<0.10
Arsenic (As)	0.066	0.060	<0.050
Barium (Ba)	62.0	54.9	49.3
Beryllium (Be)	<0.20	<0.20	<0.20
Bismuth (Bi)	<0.20	<0.20	<0.20
Cadmium (Cd)	0.179	0.131	0.107
Calcium (Ca)	5310	5030	4510
Chromium (Cr)	<0.50	<0.50	<0.50
Cobalt (Co)	<0.10	<0.10	<0.10
Copper (Cu)	3.38	2.72	2.88
Iron (Fe)	84	147	74
Lead (Pb)	<0.50	<0.50	<0.50
Lithium (Li)	<5.0	<5.0	<5.0
Magnesium (Mg)	966	985	893
Manganese (Mn)	11.3	18.1	19.0
Molybdenum (Mo)	1.37	1.15	2.64
Nickel (Ni)	<0.50	0.54	0.57
Phosphorus (P)	582	502	558
Potassium (K)	11300	7780	9650
Selenium (Se)	0.20	<0.20	<0.20
Silver (Ag)	<0.10	<0.10	<0.10
Sodium (Na)	<100	<100	<100
Strontium (Sr)	20.4	13.0	15.5
Sulfur (S)-Total	1900	1500	1600
Thallium (Tl)	<0.050	<0.050	<0.050
Tin (Sn)	<2.0	<2.0	<2.0
Titanium (Ti)	<1.0	<1.0	<1.0
Uranium (U)	<0.050	<0.050	<0.050
Vanadium (V)	0.36	0.47	0.33
Zinc (Zn)	14.1	15.3	16.0

Appendix D.8 Sawdust Chemical Characterization

Sample ID	SAMPLE 1-SAWDUST	SAMPLE 2-SAWDUST	SAMPLE 3-SAWDUST
Date Sampled	07-SEP-14	07-SEP-14	07-SEP-14
Matrix	Soil	Soil	Soil
Physical Tests			
Moisture	17.2	16.4	17.8
Leachable Anions & Nutrients			
Bromide (Br)	<5.0	<5.0	<5.0
Chloride (Cl)	<50	<50	<50
Nitrate (as N)	<0.50	<0.50	<0.50
Nitrite (as N)	<0.10	<0.10	<0.10
Sulfate (SO4)	<100	<100	<100
Anions and Nutrients			
Total Nitrogen by LECO	0.062	0.051	0.048
Organic / Inorganic Carbon			
Total Organic Carbon	47.5	47.8	48.0
Metals			
Aluminum (Al)	<50	<50	<50
Antimony (Sb)	<0.10	<0.10	<0.10
Arsenic (As)	<0.050	<0.050	<0.050
Barium (Ba)	17.3	16.7	17.4
Beryllium (Be)	<0.20	<0.20	<0.20
Bismuth (Bi)	<0.20	<0.20	<0.20
Cadmium (Cd)	0.102	0.095	0.100
Calcium (Ca)	753	687	699
Chromium (Cr)	<0.50	<0.50	<0.50
Cobalt (Co)	0.22	<0.10	<0.10
Copper (Cu)	2.38	1.97	2.54
Iron (Fe)	73	<50	<50
Lead (Pb)	<0.50	<0.50	<0.50
Lithium (Li)	<5.0	<5.0	<5.0
Magnesium (Mg)	117	104	100
Manganese (Mn)	34.4	32.5	33.5
Molybdenum (Mo)	<0.50	<0.50	<0.50
Nickel (Ni)	<0.50	<0.50	<0.50
Phosphorus (P)	<50	<50	<50
Potassium (K)	350	310	290
Selenium (Se)	<0.20	<0.20	<0.20
Silver (Ag)	<0.10	<0.10	<0.10
Sodium (Na)	<100	<100	<100
Strontium (Sr)	2.05	2.05	1.95
Sulfur (S)-Total	2000	1500	1300
Thallium (Tl)	<0.050	<0.050	<0.050
Tin (Sn)	<2.0	<2.0	<2.0
Titanium (Ti)	2.2	1.3	<1.0
Uranium (U)	<0.050	<0.050	<0.050
Vanadium (V)	<0.20	<0.20	<0.20
Zinc (Zn)	10.2	9.1	9.7

Appendix D.9 Tabulated Water Results - Dissolved Oxygen

Date	Week	Column 1	Column 2	Column 5	Column 6	Inlet
11-Feb-15	**1**	17.10	28.40	9.20	21.80	57.70
17-Feb-15	**2**	6.50	32.70	20.80	25.10	
24-Feb-15	**3**					
1-Mar-15	**4**	7.47	20.00	13.10	28.50	66.50
10-Mar-15	**5**	10.80		6.20	10.60	
17-Mar-15	**6**	9.90	44.30	21.00	23.40	
24-Mar-15	**7**	15.60	31.10	14.10	35.30	58.90
31-Mar-15	**8**	19.90	37.86	5.53	41.68	80.90
No Data	**9**	26.90	40.70	5.70	38.50	79.60
14-Apr-15	**10**					
21-Apr-15	**11**	25.50	58.10	10.60	37.90	118.00
No Data	**12**					
6-May-15	**13**	15.80	52.20	13.00	47.30	130.90
12-May-15	**14**	7.50	79.80	30.70	57.60	172.30
20-May-15	**15**	16.30	67.53	6.00	46.10	106.25
25-May-15	**16**	19.80	74.20	1.50	40.30	132.00
02-Jun-15	**17**	9.40	32.10	12.30	25.70	71.10
No Data	**18**					
16-Jun-15	**19**	28.80	63.40	17.40	41.05	115.40
23-Jun-15	**20**					
No Data	**21**					
07-Jul-15	**22**	17.23	69.80	17.30	56.30	136.50
15-Jul-15	**23**	24.60	47.00	7.31	55.20	121.30
21-Jul-15	**24**	26.70	46.70	5.40	44.80	100.83

All values are presented in units % Oxygen saturation

Appendix D.9

Tabulated Water Results - ORP

Date	Week	Column 1	Column 2	Column 5	Column 6	Inlet
11-Feb-15	**1**	63	15	30	104	107
17-Feb-15	**2**	-155	39	-7	10	58
24-Feb-15	**3**	-73	50	-132	45	28
1-Mar-15	**4**	-118	33	-86	35	22
10-Mar-15	**5**	-71		-100	-2	
No Data	**6**					
No Data	**7**					
31-Mar-15	**8**	-107	44	-244	-30	34
8-Apr-15	**9**	-138	24	-155	51	4
14-Apr-15	**10**	-168	26	-189	36	1
21-Apr-15	**11**	-37	81	-201	59	72
No Data	**12**					
No Data	**13**					
12-May-15	**14**	-213	-200	-15	-164	-122
20-May-15	**15**	-140	33	-58	45	288
25-May-15	**16**	-82	296	-66	38	41
02-Jun-15	**17**	-59	-37	9	23	57
No Data	**18**					
16-Jun-15	**19**	-105	20	-114	6	18
23-Jun-15	**20**	-6		21	-7	20
No Data	**21**					
07-Jul-15	**22**	-66		-13	71	102
15-Jul-15	**23**	7	8	7	7	8
21-Jul-15	**24**	7	7	7	7	8

All values are presented in units of mV

Appendix D.9 Tabulated Water Results - pH

Date	Week	Column 1	Column 2	Column 5	Column 6	Inlet
11-Feb-15	**1**	6.19	7.17	6.42	7.06	7.62
17-Feb-15	**2**	6.11	7.22	6.30	7.07	7.61
24-Feb-15	**3**	6.13	6.84	6.31	6.92	7.42
1-Mar-15	**4**	6.08	7.07	6.32	7.18	7.16
10-Mar-15	**5**	6.04		6.27	6.95	
17-Mar-15	**6**	6.02	7.33	6.45	6.99	7.73
24-Mar-15	**7**	6.35	7.19	6.62	7.57	7.66
31-Mar-15	**8**	6.41	7.24	6.77	7.27	7.61
No Data	**9**					
14-Apr-15	**10**	6.54	7.51	6.85	7.24	7.82
21-Apr-15	**11**	6.46	7.00	6.67	6.78	7.66
No Data	**12**					
6-May-15	**13**	6.67	7.15	6.78	7.04	7.71
12-May-15	**14**	6.45	6.96	6.58	6.97	7.44
20-May-15	**15**	6.40	7.02	6.83	6.95	7.59
25-May-15	**16**	6.51	7.21	6.86	6.83	7.61
02-Jun-15	**17**	6.67	7.28	6.90	7.01	7.88
No Data	**18**					
16-Jun-15	**19**	6.56	7.28	6.83	7.09	7.59
23-Jun-15	**20**	6.86	7.98	7.07	7.53	7.81
No Data	**21**					
07-Jul-15	**22**	6.61	7.18	6.97	7.27	8.14
15-Jul-15	**23**	6.81	7.56	7.02	7.36	7.99
21-Jul-15	**24**	6.59	7.19	6.75	7.01	7.67

All values are presented in units of pH

	Date	Week	Hardness (as CaCO3)	Alkalinity Total (as CaCO3)	Ammonia, Total (as N)	Bromide (Br)	Chloride (Cl)	Fluoride (F)	Nitrate (as N)	Nitrite (as N)
Inlet	**10-Feb-15**	**1**	931	118	0.0069	**1**	11.0	**0.4**	73.6	**0.02**
Inlet	**17-Feb-15**	**2**	948	121	**0.005**	**1**	12.0	**0.4**	72.7	**0.02**
Inlet	**24-Feb-15**	**3**	930	121	**0.005**	**1**	10.5	**0.2**	73.2	0.011
Inlet	**2-Mar-15**	**4**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**11-Mar-15**	**5**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**17-Mar-15**	**6**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**24-Mar-15**	**7**	895	108	**0.005**	**0.5**	9.5	**0.2**	70.9	**0.01**
Inlet	**31-Mar-15**	**8**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**7-Apr-15**	**9**	910	116	0.0063	**0.5**	10.2	**0.2**	74.1	**0.01**
Inlet	**14-Apr-15**	**10**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**22-Apr-15**	**11**	#N/A	118	**0.005**	**1**	10.0	**0.4**	74.1	**0.02**
Inlet	**29-Apr-15**	**12**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**6-May-15**	**13**	934	118	**0.005**	**0.5**	10.2	**0.2**	74.7	0.010
Inlet	**12-May-15**	**14**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**19-May-15**	**15**	920	113	**0.005**	**1**	10.0	**0.4**	73.4	**0.02**
Inlet	**26-May-15**	**16**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**2-Jun-15**	**17**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**8-Jun-15**	**18**	912	114	**0.005**	**0.5**	10.3	**0.2**	74.0	**0.01**
Inlet	**17-Jun-15**	**19**	932	110	**0.005**	**0.5**	10.4	**0.2**	75.6	**0.01**
Inlet	**23-Jun-15**	**20**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**30-Jun-15**	**21**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**7-Jul-15**	**22**	918	111	**0.005**	**1**	10.0	**0.4**	72.4	**0.02**
Inlet	**14-Jul-15**	**23**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**22-Jul-15**	**24**	908	97.8	**0.005**	**0.5**	10.0	**0.2**	73.4	**0.01**
Column 1	**10-Feb-15**	**1**	1530	869	8.79	**1**	21.0	**0.4**	**0.1**	**0.02**
Column 1	**17-Feb-15**	**2**	1810	3880	5.47	**2.5**	**25.0**	**1**	0.26	**0.05**
Column 1	**24-Feb-15**	**3**	1410	1040	0.258	**1**	11.0	**0.4**	0.16	**0.02**
Column 1	**2-Mar-15**	**4**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	**11-Mar-15**	**5**	1950	1310	0.72	**1**	**10.0**	**0.4**	2.54	0.070
Column 1	**17-Mar-15**	**6**	2040	1410	1.61	**1**	**10.0**	**0.4**	2.47	0.038
Column 1	**24-Mar-15**	**7**	1220	768	1.03	**1**	**10.0**	**0.4**	**0.1**	0.026
Column 1	**31-Mar-15**	**8**	1400	981	0.991	**1**	**10.0**	**0.4**	**0.1**	**0.02**
Column 1	**7-Apr-15**	**9**	1230	995	0.715	**0.5**	10.1	**0.2**	0.05	**0.01**
Column 1	**14-Apr-15**	**10**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	**22-Apr-15**	**11**	1090	861	0.0544	**1**	**10.0**	**0.4**	**0.1**	**0.02**
Column 1	**29-Apr-15**	**12**	964	770	0.0085	**1**	**10.0**	**0.4**	**0.1**	**0.02**
Column 1	**6-May-15**	**13**	932	554	0.0168	**0.5**	10.2	0.26	**0.05**	**0.01**
Column 1	**12-May-15**	**14**	996	787	0.0189	**0.5**	10.4	0.30	**0.05**	**0.01**
Column 1	**19-May-15**	**15**	1010	839	0.0102	**1**	**10.0**	**0.4**	**0.1**	**0.02**
Column 1	**26-May-15**	**16**	#N/A	641	0.0153	**0.5**	**10.0**	**0.26**	**0.05**	0.030
Column 1	**2-Jun-15**	**17**	908	880	0.0107	**0.5**	**10.0**	**0.28**	**0.05**	0.022
Column 1	**8-Jun-15**	**18**	971	767	0.0643	**0.5**	10.1	0.26	1.61	0.219
Column 1	**17-Jun-15**	**19**	974	728	0.0093	**0.5**	**10.0**	0.27	0.05	0.046
Column 1	**23-Jun-15**	**20**	1010	692	0.0690	**0.5**	9.9	0.22	0.490	0.176
Column 1	**30-Jun-15**	**21**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	**7-Jul-15**	**22**	1060	666	0.0686	**0.25**	9.6	0.31	0.652	0.0679
Column 1	**14-Jul-15**	**23**	1040	674	0.0107	**0.5**	10.2	0.28	1.60	0.013
Column 1	**22-Jul-15**	**24**	1010	467	**0.005**	0.5	**10.0**	**0.2**	22.6	0.117
Column 2	**10-Feb-15**	**1**	907	134	0.0845	**1**	11.0	0.67	74.5	0.134
Column 2	**17-Feb-15**	**2**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**24-Feb-15**	**3**	926	151	0.0806	**0.5**	10.9	0.51	73.7	0.097
Column 2	**2-Mar-15**	**4**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**11-Mar-15**	**5**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**17-Mar-15**	**6**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**24-Mar-15**	**7**	903	145	0.0747	**0.5**	9.7	0.31	72.7	0.014
Column 2	**31-Mar-15**	**8**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**7-Apr-15**	**9**	951	147	0.0786	**0.5**	10.2	0.29	74.2	0.011
Column 2	**14-Apr-15**	**10**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**22-Apr-15**	**11**	953	149	0.0712	**1**	**10.0**	**0.4**	73.0	**0.02**

Speciation samples collected	No sample collected	Results discarded due to irregularities	**Bold Values are less than or equal to the MDL**
More than 15% of results are less than or equal to the MDL, no mean calculated		0-15% of values are less than or equal to the MDL, 0.5 x MDL used as replacement value in mean calculation	

	Date	Week	Hardness (as CaCO3)	Alkalinity Total (as CaCO3)	Ammonia, Total (as N)	Bromide (Br)	Chloride (Cl)	Fluoride (F)	Nitrate (as N)	Nitrite (as N)
Column 2	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	6-May-15	13	965	145	0.0913	**1**	**10.0**	**0.4**	75.6	**0.02**
Column 2	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	19-May-15	15	959	141	0.0843	**1**	**10.0**	**0.4**	73.8	**0.02**
Column 2	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	2-Jun-15	17	938	143	0.0827	**0.5**	9.9	0.22	72.8	**0.01**
Column 2	8-Jun-15	18	944	147	0.0746	**1**	11.0	**0.4**	74.8	**0.02**
Column 2	17-Jun-15	19	928	#N/A	0.0715	**2.5**	**25.0**	**1**	74.3	**0.05**
Column 2	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	7-Jul-15	22	955	147	0.0714	**1**	**10.0**	**0.4**	72.7	**0.02**
Column 2	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	22-Jul-15	24	939	135	0.0610	**0.5**	10.3	0.23	75.2	**0.01**
Column 5	10-Feb-15	1	1150	638	7.44	**1**	12.0	0.44	**0.1**	19.7
Column 5	17-Feb-15	2	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	24-Feb-15	3	1190	783	2.57	**0.5**	10.8	0.29	0.14	0.075
Column 5	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	11-Mar-15	5	1120	873	0.120	**1**	**10.0**	**0.4**	**0.1**	0.021
Column 5	17-Mar-15	6	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	24-Mar-15	7	940	771	0.225	**0.5**	9.5	0.21	**0.05**	0.026
Column 5	31-Mar-15	8	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	7-Apr-15	9	969	884	0.288	**0.5**	9.9	0.22	11.9	0.438
Column 5	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	22-Apr-15	11	976	834	0.485	**1**	**10.0**	**0.4**	**0.1**	0.642
Column 5	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	6-May-15	13	939	663	0.0189	**0.5**	10.2	0.36	9.52	0.155
Column 5	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	19-May-15	15	941	624	0.0084	**1**	**10.0**	**0.4**	7.68	0.044
Column 5	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	2-Jun-15	17	918	468	0.0058	**0.5**	9.8	0.30	14.8	0.028
Column 5	8-Jun-15	18	932	495	0.0589	**0.5**	10.2	0.32	6.59	0.359
Column 5	17-Jun-15	19	938	463	0.0069	**0.5**	9.8	0.29	5.18	0.055
Column 5	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	7-Jul-15	22	960	577	0.0063	**1**	**10.0**	**0.4**	7.79	0.031
Column 5	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	22-Jul-15	24	967	370	**0.005**	**0.5**	10.2	0.23	23.9	0.029
Column 6	10-Feb-15	1	907	186	0.0902	**1**	15.0	0.68	56.5	2.18
Column 6	17-Feb-15	2	943	213	0.0798	**1**	14.0	0.75	50.1	2.79
Column 6	24-Feb-15	3	932	220	0.0479	**1**	10.6	0.53	48.9	1.44
Column 6	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	11-Mar-15	5	894	252	0.0128	**1**	11.0	**0.4**	46.3	0.162
Column 6	17-Mar-15	6	939	280	0.0090	**0.5**	10.5	0.39	42.9	0.099
Column 6	24-Mar-15	7	921	201	0.0195	**0.5**	9.8	0.37	56.2	0.057
Column 6	31-Mar-15	8	972	213	0.0374	**0.5**	10.3	0.32	55.1	0.090
Column 6	7-Apr-15	9	927	211	0.0321	**0.5**	10.3	0.36	54.4	0.099
Column 6	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	22-Apr-15	11	967	197	0.0536	**1**	**10.0**	**0.4**	56.6	0.042
Column 6	29-Apr-15	12	942	194	0.0398	**1**	**10.0**	**0.4**	57.8	0.086
Column 6	6-May-15	13	953	196	0.0424	**0.5**	10.2	0.29	58.9	0.055
Column 6	12-May-15	14	933	199	0.0414	**0.5**	10.4	0.34	58.0	0.039
Column 6	19-May-15	15	959	193	0.0419	**1**	**10.0**	**0.4**	58.6	**0.02**
Column 6	26-May-15	16	#N/A	183	0.0504	**0.5**	**10.0**	0.27	60.9	0.016
Column 6	2-Jun-15	17	894	192	0.0466	**0.5**	**10.0**	0.29	60.2	0.016
Column 6	8-Jun-15	18	930	202	0.0485	**1**	**10.0**	**0.4**	58.3	**0.02**
Column 6	17-Jun-15	19	940	186	0.0412	**0.5**	**10.0**	0.31	56.4	0.016
Column 6	23-Jun-15	20	979	199	0.0338	**0.5**	9.9	0.31	54.7	0.016
Column 6	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	7-Jul-15	22	944	199	0.0656	**1**	**10.0**	**0.4**	54.8	**0.02**
Column 6	14-Jul-15	23	940	192	0.0682	**0.5**	10.1	0.31	54.9	0.027
Column 6	22-Jul-15	24	947	174	0.0410	**0.5**	**10.0**	0.27	61.2	0.064

Speciation samples collected

No sample collected

Results discarded due to irregularities

Bold Values are less than or equal to the MDL

More than 15% of results are less than or equal to the MDL, no mean calculated

0-15% of values are less than or equal to the MDL, 0.5 x MDL used as replacement value in mean calculation

	Date	Week	Sulfate (SO4)	Sulfide (as S)	Dissolved Organic Carbon	Aluminum (Al)-Dissolved	Antimony (Sb)-Dissolved	Arsenic (As)-Dissolved	Barium (Ba)-Dissolved	Beryllium (Be)-Dissolved
Inlet	10-Feb-15	1	782	**0.02**	#N/A	**0.003**	0.00188	0.00016	0.0266	**0.0001**
Inlet	17-Feb-15	2	773	**0.02**	5.06	**0.003**	0.00192	0.00018	0.0262	**0.0001**
Inlet	24-Feb-15	3	778	**0.02**	3.74	**0.003**	0.00196	0.00018	0.0269	**0.0001**
Inlet	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	11-Mar-15	5	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	17-Mar-15	6	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	24-Mar-15	7	746	**0.02**	3.63	**0.003**	0.00198	0.00017	0.0267	**0.0001**
Inlet	31-Mar-15	8	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	7-Apr-15	9	784	**0.02**	4.14	0.0132	0.00186	0.00016	0.0284	**0.0001**
Inlet	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	22-Apr-15	11	786	**0.02**	4.00	**0.003**	0.00189	0.00015	0.0265	**0.0001**
Inlet	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	6-May-15	13	789	**0.02**	3.83	**0.003**	0.00191	0.00016	0.0267	**0.0001**
Inlet	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	19-May-15	15	772	**0.02**	4.33	**0.003**	0.00187	0.00017	0.0247	**0.0001**
Inlet	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	2-Jun-15	17	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	8-Jun-15	18	783	**0.02**	4.36	**0.003**	0.00184	0.00016	0.0269	**0.0001**
Inlet	17-Jun-15	19	801	**0.02**	4.55	**0.003**	0.00172	0.00016	0.0283	**0.0001**
Inlet	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	7-Jul-15	22	764	**0.02**	3.82	0.0111	0.00185	0.00018	0.0269	**0.0001**
Inlet	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	22-Jul-15	24	776	**0.02**	#N/A	**0.003**	0.00189	0.00017	0.0282	**0.0001**
Column 1	10-Feb-15	1	803	0.189	583	0.118	0.0516	0.0548	0.0845	**0.0002**
Column 1	17-Feb-15	2	719	0.218	1110	0.0929	0.00577	0.00391	0.0818	**0.0002**
Column 1	24-Feb-15	3	175	4.28	629	0.0670	0.00273	0.00325	0.473	**0.0002**
Column 1	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	11-Mar-15	5	319	0.81	886	0.0345	0.00216	0.00673	2.14	**0.0005**
Column 1	17-Mar-15	6	359	2.05	825	0.0383	0.00219	0.00858	0.957	**0.001**
Column 1	24-Mar-15	7	554	0.62	237	0.0143	0.00356	0.00668	0.183	**0.0002**
Column 1	31-Mar-15	8	404	1.58	381	0.0247	0.00250	0.00712	0.497	**0.0002**
Column 1	7-Apr-15	9	476	0.82	219	0.0175	0.00367	0.00763	0.535	**0.0002**
Column 1	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	22-Apr-15	11	456	1.09	112	0.0155	0.00426	0.00866	0.552	**0.0001**
Column 1	29-Apr-15	12	583	0.031	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	6-May-15	13	517	0.26	29.1	0.0103	0.00474	0.00793	0.415	**0.0001**
Column 1	12-May-15	14	548	0.173	38.9	0.0140	0.00523	0.00865	0.405	**0.0001**
Column 1	19-May-15	15	509	0.215	39.1	0.0147	0.00369	0.00790	0.368	**0.0001**
Column 1	26-May-15	16	476	1.01	48.3	0.0174	0.00293	0.00955	0.304	**0.0001**
Column 1	2-Jun-15	17	553	0.57	33.6	0.0155	0.00340	0.0106	0.339	**0.0001**
Column 1	8-Jun-15	18	546	6.7	36.8	0.0125	0.00265	0.00817	0.176	**0.0001**
Column 1	17-Jun-15	19	487	5.2	50.3	0.0145	0.00288	0.00965	0.378	**0.0001**
Column 1	23-Jun-15	20	532	3.42	4.39	0.0138	0.00304	0.00811	0.260	**0.0001**
Column 1	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	7-Jul-15	22	573	5.5	33.3	0.0186	0.00233	0.00912	0.381	**0.0001**
Column 1	14-Jul-15	23	611	1.32	#N/A	0.0156	0.00222	0.00697	0.265	**0.0001**
Column 1	22-Jul-15	24	706	0.206	#N/A	0.0073	0.00444	0.00566	0.111	**0.0001**
Column 2	10-Feb-15	1	796	**0.02**	3.07	**0.003**	0.00416	0.00025	0.0169	**0.0001**
Column 2	17-Feb-15	2	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	24-Feb-15	3	786	**0.02**	2.17	**0.003**	0.00427	0.00024	0.0177	**0.0001**
Column 2	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	11-Mar-15	5	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	17-Mar-15	6	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	24-Mar-15	7	772	#N/A	2.71	**0.003**	0.00426	0.00020	0.0164	**0.0001**
Column 2	31-Mar-15	8	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	7-Apr-15	9	788	**0.02**	2.40	**0.003**	0.00392	0.00022	0.0180	**0.0001**
Column 2	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	22-Apr-15	11	775	**0.02**	2.41	**0.003**	0.00357	0.00023	0.0170	**0.0001**

Speciation samples collected	No sample collected	Results discarded due to irregularities	**Bold Values are less than or equal to the MDL**
More than 15% of results are less than or equal to the MDL, no mean calculated		0-15% of values are less than or equal to the MDL, 0.5 x MDL used as replacement value in mean calculation	

	Date	Week	Sulfate (SO4)	Sulfide (as S)	Dissolved Organic Carbon	Aluminum (Al)-Dissolved	Antimony (Sb)-Dissolved	Arsenic (As)-Dissolved	Barium (Ba)-Dissolved	Beryllium (Be)-Dissolved
Column 2	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	6-May-15	13	805	**0.02**	1.04	**0.003**	0.00371	0.00023	0.0170	**0.0001**
Column 2	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	19-May-15	15	781	**0.02**	2.51	**0.003**	0.00375	0.00025	0.0180	**0.0001**
Column 2	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	2-Jun-15	17	769	**0.02**	2.82	**0.003**	0.00352	0.00023	0.0171	**0.0001**
Column 2	8-Jun-15	18	794	**0.02**	2.65	**0.003**	0.00363	0.00022	0.0174	**0.0001**
Column 2	17-Jun-15	19	780	**0.02**	2.53	**0.003**	0.00340	0.00025	0.0187	**0.0001**
Column 2	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	7-Jul-15	22	769	**0.02**	2.83	**0.003**	0.00351	0.00023	0.0188	**0.0001**
Column 2	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	22-Jul-15	24	801	**0.02**	#N/A	**0.003**	0.00329	**0.00020**	0.0190	**0.0001**
Column 5	10-Feb-15	1	754	**0.02**	165	0.0284	0.0422	0.0370	0.0455	**0.0002**
Column 5	17-Feb-15	2	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	24-Feb-15	3	524	0.88	277	0.0445	0.00306	0.00470	0.0436	**0.0002**
Column 5	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	11-Mar-15	5	248	1.56	397	0.0356	0.00183	0.00626	0.314	**0.0001**
Column 5	17-Mar-15	6	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	24-Mar-15	7	301	7.2	152	0.0251	0.00240	0.0106	0.245	**0.0001**
Column 5	31-Mar-15	8	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	7-Apr-15	9	420	10.9	97.1	0.0150	0.00463	0.0127	0.365	**0.0001**
Column 5	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	22-Apr-15	11	415	4.6	40.3	0.0167	0.00433	0.0146	0.316	**0.0001**
Column 5	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	6-May-15	13	598	0.50	8.81	0.0083	0.00601	0.0115	0.200	**0.0001**
Column 5	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	19-May-15	15	619	0.264	12.9	0.0085	0.00589	0.0107	0.158	**0.0001**
Column 5	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	2-Jun-15	17	670	0.066	9.5	0.0070	0.00512	0.00728	0.138	**0.0001**
Column 5	8-Jun-15	18	654	0.65	13.2	0.0067	0.00470	0.00912	0.122	**0.0001**
Column 5	17-Jun-15	19	588	0.194	12.1	0.0064	0.00409	0.00818	0.138	**0.0001**
Column 5	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	7-Jul-15	22	643	0.124	11.2	0.0075	0.00467	0.00717	0.131	**0.0001**
Column 5	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	22-Jul-15	24	764	0.053	#N/A	0.0054	0.00447	0.00430	0.0928	**0.0001**
Column 6	10-Feb-15	1	774	0.021	28.8	**0.003**	0.00544	0.00070	0.0189	**0.0001**
Column 6	17-Feb-15	2	778	**0.02**	28.0	**0.003**	0.00557	0.00049	0.0188	**0.0001**
Column 6	24-Feb-15	3	778	0.023	25.9	**0.003**	0.00558	0.00056	0.0190	**0.0001**
Column 6	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	11-Mar-15	5	803	**0.02**	17.5	**0.003**	0.00491	0.00073	0.0184	**0.0001**
Column 6	17-Mar-15	6	816	**0.02**	17.0	0.0052	0.00512	0.00095	0.0197	**0.0005**
Column 6	24-Mar-15	7	768	**0.02**	11.7	0.0066	0.00483	0.00074	0.0190	**0.0001**
Column 6	31-Mar-15	8	784	**0.02**	11.3	0.0051	0.00503	0.00083	0.0183	**0.0001**
Column 6	7-Apr-15	9	786	#N/A	9.39	**0.003**	0.00524	0.00081	0.0197	**0.0001**
Column 6	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	22-Apr-15	11	770	#N/A	7.16	**0.003**	0.00487	0.00070	0.0187	**0.0001**
Column 6	29-Apr-15	12	800	**0.02**	6.91	**0.003**	0.00492	0.00069	0.0181	**0.0001**
Column 6	6-May-15	13	777	**0.02**	5.56	**0.003**	0.00488	0.00067	0.0183	**0.0001**
Column 6	12-May-15	14	790	**0.02**	5.94	**0.003**	0.00548	0.00082	0.0189	**0.0001**
Column 6	19-May-15	15	782	**0.02**	4.71	**0.003**	0.00541	0.00084	0.0198	**0.0001**
Column 6	26-May-15	16	775	**0.02**	4.17	**0.003**	0.00502	0.00064	0.0185	**0.0001**
Column 6	2-Jun-15	17	780	**0.02**	4.69	**0.003**	0.00517	0.00068	0.0191	**0.0001**
Column 6	8-Jun-15	18	796	**0.02**	4.39	**0.003**	0.00568	0.00074	0.0189	**0.0001**
Column 6	17-Jun-15	19	775	**0.02**	4.56	**0.003**	0.00518	0.00073	0.0200	**0.0001**
Column 6	23-Jun-15	20	767	**0.02**	#N/A	**0.003**	0.00570	0.00071	0.0187	**0.0001**
Column 6	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	7-Jul-15	22	768	**0.02**	4.31	**0.003**	0.00622	0.00079	0.0200	**0.0001**
Column 6	14-Jul-15	23	776	**0.02**	#N/A	**0.003**	0.00570	0.00069	0.0201	**0.0001**
Column 6	22-Jul-15	24	771	**0.02**	#N/A	**0.003**	0.00504	0.00063	0.0199	**0.0001**

Speciation samples collected	No sample collected	Results discarded due to irregularities	**Bold Values are less than or equal to the MDL**
More than 15% of results are less than or equal to the MDL, no mean calculated		0-15% of values are less than or equal to the MDL, 0.5 x MDL used as replacement value in mean calculation	

	Date	Week	Bismuth (Bi)-Dissolved	Boron (B)-Dissolved	Cadmium (Cd)-Dissolved	Calcium (Ca)-Dissolved	Chromium (Cr)-Dissolved	Cobalt (Co)-Dissolved	Copper (Cu)-Dissolved	Iron (Fe)-Dissolved	Lead (Pb)-Dissolved
Inlet	10-Feb-15	1	**0.0005**	0.119	**0.00001**	189	**0.0001**	**0.00010**	0.00091	**0.03**	0.000075
Inlet	17-Feb-15	2	**0.0005**	0.119	**0.00001**	191	**0.0001**	**0.00010**	**0.0005**	**0.03**	0.000089
Inlet	24-Feb-15	3	**0.0005**	0.126	**0.00001**	191	**0.0001**	**0.00010**	**0.0005**	**0.03**	0.000114
Inlet	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	11-Mar-15	5	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	17-Mar-15	6	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	24-Mar-15	7	**0.0005**	0.119	**0.00001**	178	**0.0001**	**0.00010**	**0.0005**	**0.03**	0.000051
Inlet	31-Mar-15	8	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	7-Apr-15	9	**0.00005**	0.132	**0.000005**	188	**0.0001**	**0.00010**	**0.0005**	**0.03**	**0.00005**
Inlet	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	22-Apr-15	11	**0.00005**	0.103	**0.000005**	188	**0.0001**	**0.00010**	**0.0005**	**0.03**	**0.00005**
Inlet	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	6-May-15	13	**0.00005**	0.106	**0.000005**	187	**0.0001**	**0.00010**	**0.0005**	**0.03**	0.000082
Inlet	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	19-May-15	15	**0.00005**	0.135	**0.000005**	191	**0.0001**	**0.00010**	**0.0005**	**0.03**	**0.00005**
Inlet	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	2-Jun-15	17	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	8-Jun-15	18	**0.00005**	0.111	**0.000005**	182	**0.0001**	**0.00010**	**0.0005**	**0.03**	**0.00005**
Inlet	17-Jun-15	19	**0.00005**	0.115	**0.000005**	195	**0.0001**	**0.00010**	**0.0005**	**0.03**	**0.00005**
Inlet	23-Jun-15	20	**#N/A**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	7-Jul-15	22	**0.00005**	0.096	**0.000005**	188	**0.0001**	**0.00010**	**0.0005**	**0.03**	0.000065
Inlet	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	22-Jul-15	24	**0.00005**	0.132	**0.000005**	183	**0.0001**	**0.00010**	**0.0005**	**0.03**	**0.00005**
Column 1	10-Feb-15	1	**0.001**	0.533	0.000320	440	0.0106	0.309	0.00455	26.3	0.001170
Column 1	17-Feb-15	2	**0.001**	0.555	0.000055	542	0.00564	0.300	0.00182	25.2	0.000140
Column 1	24-Feb-15	3	**0.001**	0.446	0.000037	418	0.00426	0.0168	0.00067	20.3	0.000130
Column 1	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	11-Mar-15	5	**0.0025**	0.325	**0.00005**	557	0.00316	0.0236	**0.001**	35.2	**0.000250**
Column 1	17-Mar-15	6	**0.001**	0.314	**0.00010**	633	0.0033	0.0237	**0.001**	32.7	**0.000100**
Column 1	24-Mar-15	7	**0.001**	0.185	0.000021	320	0.00125	0.0129	0.00071	7.63	0.000220
Column 1	31-Mar-15	8	**0.0001**	0.196	0.000013	376	0.00199	0.00489	**0.0005**	4.59	**0.000100**
Column 1	7-Apr-15	9	**0.0001**	0.190	0.000014	320	0.00154	0.00352	**0.0005**	2.62	**0.000100**
Column 1	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	22-Apr-15	11	**0.00005**	0.162	0.0000113	279	0.00139	0.00246	**0.0005**	1.80	0.000100
Column 1	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	6-May-15	13	**0.00005**	0.119	0.0000113	233	0.00120	0.00293	0.00068	1.54	0.000099
Column 1	12-May-15	14	**0.00005**	0.170	0.0000143	242	0.00132	0.00342	**0.0005**	1.16	**0.000050**
Column 1	19-May-15	15	**0.00005**	0.143	0.0000094	243	0.00142	0.00173	**0.0005**	0.626	**0.000050**
Column 1	26-May-15	16	**0.00005**	0.148	0.0000118	201	0.00140	0.00069	**0.0005**	0.355	0.000053
Column 1	2-Jun-15	17	**0.00005**	0.145	0.0000064	225	0.00132	0.00067	**0.0005**	0.343	**0.000050**
Column 1	8-Jun-15	18	**0.00005**	0.142	**0.000005**	218	0.00116	0.00032	**0.0005**	0.162	**0.000050**
Column 1	17-Jun-15	19	**0.00005**	0.161	**0.000005**	231	0.00144	0.00040	**0.0005**	0.239	**0.000050**
Column 1	23-Jun-15	20	**0.00005**	0.154	0.0000131	228	0.00116	0.00042	**0.0005**	0.149	**0.000050**
Column 1	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	7-Jul-15	22	**0.00005**	0.147	0.0000092	254	0.00142	0.00039	**0.0005**	0.055	**0.000050**
Column 1	14-Jul-15	23	**0.00005**	0.160	0.0000056	249	0.00124	0.00038	**0.0005**	0.063	**0.000050**
Column 1	22-Jul-15	24	**0.00005**	0.138	**0.000005**	238	0.00042	0.00076	**0.0005**	0.835	0.000057
Column 2	10-Feb-15	1	**0.0005**	0.198	0.00165	211	**0.00010**	0.0261	0.00162	**0.03**	**0.00005**
Column 2	17-Feb-15	2	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	24-Feb-15	3	**0.0005**	0.229	0.00158	206	**0.00010**	0.0227	0.00107	**0.03**	**0.00005**
Column 2	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	11-Mar-15	5	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	17-Mar-15	6	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	24-Mar-15	7	**0.0005**	0.202	0.00173	192	**0.00010**	0.0206	0.00153	**0.03**	**0.00005**
Column 2	31-Mar-15	8	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	7-Apr-15	9	**0.00005**	0.211	0.00167	207	**0.00010**	0.0191	0.00124	**0.03**	**0.00005**
Column 2	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	22-Apr-15	11	**0.00005**	0.160	0.00131	202	**0.00010**	0.0168	**0.00100**	**0.03**	**0.00005**

Speciation samples collected | No sample collected | Results discarded due to irregularities | **Bold Values are less than or equal to the MDL**

More than 15% of results are less than or equal to the MDL, no mean calculated | 0-15% of values are less than or equal to the MDL, 0.5 x MDL used as replacement value in mean calculation

	Date	Week	Bismuth (Bi)-Dissolved	Boron (B)-Dissolved	Cadmium (Cd)-Dissolved	Calcium (Ca)-Dissolved	Chromium (Cr)-Dissolved	Cobalt (Co)-Dissolved	Copper (Cu)-Dissolved	Iron (Fe)-Dissolved	Lead (Pb)-Dissolved
Column 2	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	6-May-15	13	**0.00005**	0.142	0.00144	200	**0.00010**	0.0164	0.00120	**0.03**	**0.00005**
Column 2	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	19-May-15	15	**0.00005**	0.159	0.00146	207	**0.00010**	0.0150	0.00122	**0.03**	**0.00005**
Column 2	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	2-Jun-15	17	**0.00005**	0.165	0.00131	195	**0.00010**	0.0136	0.00103	**0.03**	**0.00005**
Column 2	8-Jun-15	18	**0.00005**	0.157	0.00118	197	**0.00010**	0.0140	0.00097	**0.03**	**0.00005**
Column 2	17-Jun-15	19	**0.00005**	0.176	0.00134	204	**0.00010**	0.0127	0.00102	**0.03**	**0.00005**
Column 2	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	7-Jul-15	22	**0.00005**	0.153	0.00125	205	**0.0001**	0.0124	0.00096	**0.03**	**0.00005**
Column 2	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	22-Jul-15	24	**0.00005**	0.178	0.00118	198	**0.00010**	0.0115	0.00089	**0.03**	**0.00005**
Column 5	10-Feb-15	1	**0.001**	0.419	0.00301	312	0.00311	0.180	0.00322	3.26	0.00057
Column 5	17-Feb-15	2	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	24-Feb-15	3	**0.001**	0.403	0.000177	328	0.00321	0.0360	0.00156	11.2	0.00028
Column 5	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	11-Mar-15	5	**0.0005**	0.306	0.000017	298	0.00282	0.00664	**0.0005**	15.7	0.000051
Column 5	17-Mar-15	6	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	24-Mar-15	7	**0.0005**	0.212	**0.000010**	232	0.00211	0.00037	0.00066	0.253	**0.00005**
Column 5	31-Mar-15	8	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	7-Apr-15	9	**0.00005**	0.206	0.0000151	229	0.00126	0.00061	**0.0005**	0.058	**0.00005**
Column 5	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	22-Apr-15	11	**0.00005**	0.159	0.0000120	233	0.00128	0.00065	**0.0005**	0.068	**0.00005**
Column 5	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	6-May-15	13	**0.00005**	0.117	0.0000078	205	0.00093	0.00196	**0.0005**	0.396	0.000061
Column 5	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	19-May-15	15	**0.00005**	0.137	0.0000080	206	0.00085	0.00261	**0.0005**	0.619	**0.00005**
Column 5	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	2-Jun-15	17	**0.00005**	0.139	0.0000062	204	0.00056	0.00287	**0.0005**	0.555	**0.00005**
Column 5	8-Jun-15	18	**0.00005**	0.140	**0.000005**	197	0.00072	0.00168	**0.0005**	0.536	**0.00005**
Column 5	17-Jun-15	19	**0.00005**	0.150	**0.000005**	207	0.00068	0.00212	**0.0005**	0.526	**0.00005**
Column 5	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	7-Jul-15	22	**0.00005**	0.131	**0.000005**	210	0.00069	0.00123	**0.0005**	0.248	**0.00005**
Column 5	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	22-Jul-15	24	**0.00005**	0.149	**0.000005**	212	0.00025	0.00116	**0.0005**	0.164	**0.00005**
Column 6	10-Feb-15	1	**0.0005**	0.224	0.00238	209	**0.0001**	0.0447	0.00123	**0.03**	0.000051
Column 6	17-Feb-15	2	**0.0005**	0.236	0.00233	210	**0.0001**	0.0413	0.00072	**0.03**	**0.00005**
Column 6	24-Feb-15	3	**0.0005**	0.248	0.00209	209	**0.0001**	0.0366	0.00115	**0.03**	**0.00005**
Column 6	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	11-Mar-15	5	**0.0005**	0.209	0.00189	199	**0.0001**	0.0330	**0.0005**	**0.03**	0.000071
Column 6	17-Mar-15	6	**0.0005**	0.252	0.00166	206	**0.0005**	0.0364	0.00113	**0.03**	0.000114
Column 6	24-Mar-15	7	**0.00005**	0.178	0.00175	198	**0.0001**	0.0340	0.00137	**0.03**	0.000173
Column 6	31-Mar-15	8	**0.00005**	0.211	0.00158	215	**0.0001**	0.0322	0.00056	**0.03**	0.000061
Column 6	7-Apr-15	9	**0.00005**	0.230	0.00136	208	**0.0001**	0.0327	0.00066	**0.03**	0.000078
Column 6	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	22-Apr-15	11	**0.00005**	0.164	0.00137	215	**0.0001**	0.0223	0.00067	**0.03**	**0.00005**
Column 6	29-Apr-15	12	**0.00005**	0.159	0.00144	202	**0.0001**	0.0198	0.00095	**0.03**	**0.000063**
Column 6	6-May-15	13	**0.00005**	0.140	0.00113	200	**0.0001**	0.0222	0.00062	**0.03**	**0.00005**
Column 6	12-May-15	14	**0.00005**	0.195	0.00120	204	**0.0001**	0.0255	0.00062	**0.03**	**0.00005**
Column 6	19-May-15	15	**0.00005**	0.167	0.00105	210	**0.0001**	0.0234	0.00054	**0.03**	**0.00005**
Column 6	26-May-15	16	**0.00005**	0.157	0.00108	180	**0.0001**	0.0184	**0.0005**	**0.03**	**0.00005**
Column 6	2-Jun-15	17	**0.00005**	0.162	0.00106	195	**0.0001**	0.0201	**0.0005**	**0.03**	**0.00005**
Column 6	8-Jun-15	18	**0.00005**	0.159	0.000977	196	**0.0001**	0.0184	**0.0005**	**0.03**	**0.00005**
Column 6	17-Jun-15	19	**0.00005**	0.167	0.000989	207	**0.0001**	0.0166	**0.0005**	**0.03**	**0.00005**
Column 6	23-Jun-15	20	**0.00005**	0.170	0.000806	199	**0.0001**	0.0182	**0.0005**	**0.03**	**0.00005**
Column 6	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	7-Jul-15	22	**0.00005**	0.153	0.000854	205	**0.0001**	0.0187	**0.0005**	**0.03**	**0.00005**
Column 6	14-Jul-15	23	**0.00005**	0.179	0.000525	203	**0.0001**	0.0178	**0.0005**	**0.03**	**0.00005**
Column 6	22-Jul-15	24	**0.00005**	0.167	0.00101	199	**0.0001**	0.0162	**0.0005**	**0.03**	**0.00005**

Speciation samples collected	No sample collected	Results discarded due to irregularities	**Bold Values are less than or equal to the MDL**
More than 15% of results are less than or equal to the MDL, no mean calculated		0-15% of values are less than or equal to the MDL, 0.5 x MDL used as replacement value in mean calculation	

	Date	Week	Lithium (Li)-Dissolved	Magnesium (Mg)-Dissolved	Manganese (Mn)-Dissolved	Molybdenum (Mo)-Dissolved	Nickel (Ni)-Dissolved	Phosphorous (P)-Dissolved	Potassium (K)-Dissolved	Selenium (Se)-Dissolved	Silicon (Si)-Dissolved
Inlet	10-Feb-15	1	0.186	111	0.000097	0.00432	0.0583	**0.3**	4.3	0.104	2.46
Inlet	17-Feb-15	2	0.178	115	0.000472	0.00433	0.0595	**0.3**	4.3	0.109	2.50
Inlet	24-Feb-15	3	0.205	110	**0.00005**	0.00424	0.0570	**0.3**	4.2	0.117	2.51
Inlet	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	11-Mar-15	5	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	17-Mar-15	6	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	24-Mar-15	7	0.208	110	0.000056	0.00415	0.0588	**0.3**	4.3	0.111	2.59
Inlet	31-Mar-15	8	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	7-Apr-15	9	0.230	107	**0.0001**	0.00402	0.0627	**0.3**	4.0	0.118	2.52
Inlet	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	22-Apr-15	11	0.174	112	**0.0001**	0.00411	0.0582	**0.3**	4.5	0.106	2.60
Inlet	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	6-May-15	13	0.171	114	**0.0001**	0.00450	0.0591	**0.3**	4.2	0.114	2.55
Inlet	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	19-May-15	15	0.215	108	**0.0001**	0.00444	0.0590	**0.3**	4.0	0.108	2.62
Inlet	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	2-Jun-15	17	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	8-Jun-15	18	0.184	111	**0.0001**	0.00430	0.0571	**0.3**	4.0	0.104	2.51
Inlet	17-Jun-15	19	0.181	108	**0.0001**	0.00390	0.0536	**0.3**	4.2	0.109	2.59
Inlet	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	7-Jul-15	22	0.195	109	**0.0001**	0.00428	0.0537	**0.3**	3.9	0.108	2.58
Inlet	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	22-Jul-15	24	0.204	110	**0.0001**	0.00441	0.0527	**0.3**	4.1	0.107	2.50
Column 1	10-Feb-15	1	0.232	104	1.24	0.0269	1.20	0.91	139	0.0494	16.1
Column 1	17-Feb-15	2	0.202	111	1.27	0.0143	1.07	0.62	108	0.00273	20.0
Column 1	24-Feb-15	3	0.201	90.0	0.820	0.00082	0.0748	1.23	64.0	0.00167	24.2
Column 1	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	11-Mar-15	5	0.211	135	0.790	0.00128	0.0723	1.19	47.0	0.00569	19.0
Column 1	17-Mar-15	6	0.224	129	0.774	0.00077	0.0940	1.17	41.4	0.0057	19.1
Column 1	24-Mar-15	7	0.201	103	0.261	0.00499	0.0958	0.3	23.7	0.0187	12.4
Column 1	31-Mar-15	8	0.176	113	0.252	0.00199	0.0413	0.59	23.8	0.00580	14.7
Column 1	7-Apr-15	9	0.229	104	0.185	0.00300	0.0360	0.32	17.8	0.0110	12.4
Column 1	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	22-Apr-15	11	0.194	95.2	0.121	0.00316	0.0265	**0.3**	15.8	0.0115	12.9
Column 1	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	6-May-15	13	0.147	85.4	0.0801	0.00433	0.0356	**0.3**	12.0	0.0172	10.6
Column 1	12-May-15	14	0.211	95.1	0.0847	0.00498	0.0368	**0.3**	12.2	0.0114	11.4
Column 1	19-May-15	15	0.195	98.4	0.0877	0.00273	0.0285	**0.3**	11.6	0.0110	11.8
Column 1	26-May-15	16	0.206	109	0.0848	0.00151	0.0187	0.34	10.2	0.00661	10.9
Column 1	2-Jun-15	17	0.212	91.3	0.0852	0.00189	0.0144	0.34	10.7	0.0134	11.0
Column 1	8-Jun-15	18	0.184	103	0.0840	0.000888	0.0114	**0.3**	9.0	0.00859	9.59
Column 1	17-Jun-15	19	0.196	96.2	0.0851	0.000779	0.0117	**0.3**	9.6	0.00905	10.9
Column 1	23-Jun-15	20	0.205	108	0.0905	0.00135	0.0117	**0.3**	9.0	0.0167	9.62
Column 1	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	7-Jul-15	22	0.202	103	0.107	0.000818	0.00829	**0.3**	12.4	0.0177	12.7
Column 1	14-Jul-15	23	0.209	102	0.122	0.000905	0.00698	**0.3**	10.1	0.0128	10.2
Column 1	22-Jul-15	24	0.205	102	0.115	0.00295	0.0103	**0.3**	6.9	0.0319	6.45
Column 2	10-Feb-15	1	0.249	92.5	0.0805	0.0241	0.143	**0.3**	4.6	0.137	2.14
Column 2	17-Feb-15	2	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	24-Feb-15	3	0.238	100	0.0991	0.0206	0.139	**0.3**	4.9	0.113	2.31
Column 2	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	11-Mar-15	5	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	17-Mar-15	6	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	24-Mar-15	7	0.227	103	0.128	0.0150	0.125	**0.3**	5.0	0.111	2.36
Column 2	31-Mar-15	8	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	7-Apr-15	9	0.246	106	0.131	0.0129	0.115	**0.3**	4.8	0.112	2.34
Column 2	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	22-Apr-15	11	0.196	109	0.127	0.0121	0.102	**0.3**	5.4	0.101	2.44

Speciation samples collected

No sample collected

Results discarded due to irregularities

Bold Values are less than or equal to the MDL

More than 15% of results are less than or equal to the MDL, no mean calculated

0-15% of values are less than or equal to the MDL, 0.5 x MDL used as replacement value in mean calculation

	Date	Week	Lithium (Li)-Dissolved	Magnesium (Mg)-Dissolved	Manganese (Mn)-Dissolved	Molybdenum (Mo)-Dissolved	Nickel (Ni)-Dissolved	Phosphorous (P)-Dissolved	Potassium (K)-Dissolved	Selenium (Se)-Dissolved	Silicon (Si)-Dissolved
Column 2	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	6-May-15	13	0.162	113	0.124	0.0120	0.0984	**0.3**	4.8	0.111	2.31
Column 2	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	19-May-15	15	0.202	108	0.125	0.0107	0.0928	**0.3**	4.9	0.108	2.49
Column 2	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	2-Jun-15	17	0.221	102	0.122	0.00987	0.0821	**0.3**	4.5	0.101	2.24
Column 2	8-Jun-15	18	0.182	110	0.125	0.0104	0.0873	**0.3**	4.7	0.0913	2.33
Column 2	17-Jun-15	19	0.201	101	0.123	0.0101	0.0810	**0.3**	4.6	0.0951	2.34
Column 2	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	7-Jul-15	22	0.205	107	0.130	0.0102	0.0802	**0.3**	4.8	0.0895	2.50
Column 2	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	22-Jul-15	24	0.213	108	0.119	0.00964	0.0728	**0.3**	4.5	0.0902	2.32
Column 5	10-Feb-15	1	0.217	90.0	0.887	0.0570	0.918	0.55	67.4	0.102	10.7
Column 5	17-Feb-15	2	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	24-Feb-15	3	0.209	89.4	0.753	0.0109	0.252	1.74	38.0	0.00230	20.1
Column 5	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	11-Mar-15	5	0.195	90.2	0.547	0.00125	0.0351	2.14	25.7	0.00471	20.0
Column 5	17-Mar-15	6	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	24-Mar-15	7	0.200	87.4	0.269	0.000753	0.0153	1.76	17.5	0.00501	16.0
Column 5	31-Mar-15	8	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	7-Apr-15	9	0.234	96.2	0.177	0.00240	0.0207	0.95	11.5	0.0198	10.4
Column 5	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	22-Apr-15	11	0.184	95.5	0.149	0.00198	0.0234	1.06	11.6	0.00637	11.2
Column 5	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	6-May-15	13	0.147	104	0.112	0.00498	0.0281	0.65	9.6	0.0178	8.40
Column 5	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	19-May-15	15	0.194	104	0.0911	0.00524	0.0381	0.38	8.1	0.0161	7.36
Column 5	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	2-Jun-15	17	0.207	99.2	0.0864	0.00506	0.0366	**0.3**	7.6	0.0223	6.42
Column 5	8-Jun-15	18	0.187	107	0.0721	0.00434	0.0296	0.36	7.4	0.00898	6.74
Column 5	17-Jun-15	19	0.185	102	0.0714	0.00378	0.0328	**0.3**	7.3	0.00787	6.85
Column 5	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	7-Jul-15	22	0.204	106	0.0850	0.00488	0.0184	**0.3**	7.1	0.00939	6.93
Column 5	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	22-Jul-15	24	0.203	106	0.0945	0.00582	0.0183	**0.3**	6.1	0.0139	5.46
Column 6	10-Feb-15	1	0.216	93.5	0.247	0.0212	0.233	**0.3**	5.8	0.119	2.51
Column 6	17-Feb-15	2	0.206	102	0.239	0.0212	0.212	**0.3**	6.1	0.0998	2.64
Column 6	24-Feb-15	3	0.228	99.7	0.251	0.0206	0.187	**0.3**	5.3	0.0947	2.65
Column 6	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	11-Mar-15	5	0.191	96.7	0.225	0.0180	0.174	**0.3**	5.5	0.0665	2.62
Column 6	17-Mar-15	6	0.213	94.9	0.267	0.0212	0.188	**0.3**	5.19	0.0578	2.80
Column 6	24-Mar-15	7	0.201	103	0.266	0.0175	0.182	**0.3**	5.4	0.0595	2.70
Column 6	31-Mar-15	8	0.191	106	0.252	0.0167	0.173	**0.3**	5.3	0.0599	2.70
Column 6	7-Apr-15	9	0.241	99.0	0.258	0.0173	0.177	**0.3**	4.9	0.0512	2.57
Column 6	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	22-Apr-15	11	0.187	104	0.184	0.0145	0.134	0.3	5.1	0.0456	2.56
Column 6	29-Apr-15	12	0.177	107	0.165	0.0156	0.127	**0.3**	4.7	0.0407	2.46
Column 6	6-May-15	13	0.165	110	0.167	0.0145	0.122	**0.3**	4.9	0.0398	2.45
Column 6	12-May-15	14	0.213	103	0.190	0.0158	0.117	**0.3**	4.8	0.0319	2.58
Column 6	19-May-15	15	0.206	106	0.178	0.0145	0.117	**0.3**	5.0	0.0304	2.67
Column 6	26-May-15	16	0.215	116	0.159	0.0121	0.102	**0.3**	4.8	0.0326	2.41
Column 6	2-Jun-15	17	0.215	98.6	0.169	0.0125	0.101	**0.3**	4.7	0.0313	2.36
Column 6	8-Jun-15	18	0.192	107	0.159	0.0136	0.104	**0.3**	4.9	0.0234	2.52
Column 6	17-Jun-15	19	0.194	103	0.157	0.0124	0.0985	**0.3**	4.9	0.0276	2.53
Column 6	23-Jun-15	20	0.213	117	0.167	0.0136	0.103	**0.3**	5.2	0.0234	2.52
Column 6	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	7-Jul-15	22	0.218	105	0.181	0.0145	0.101	**0.3**	5.0	0.0249	2.65
Column 6	14-Jul-15	23	0.215	105	0.166	0.0136	0.0984	**0.3**	4.7	0.0232	2.47
Column 6	22-Jul-15	24	0.206	109	0.151	0.0117	0.0896	**0.3**	4.7	0.0422	2.42

Speciation samples collected	No sample collected	Results discarded due to irregularities	**Bold Values are less than or equal to the MDL**
More than 15% of results are less than or equal to the MDL, no mean calculated		0-15% of values are less than or equal to the MDL, 0.5 x MDL used as replacement value in mean calculation	

	Date	Week	Silver (Ag)-Dissolved	Sodium (Na)-Dissolved	Strontium (Sr)-Dissolved	Thallium (Tl)-Dissolved	Tin (Sn)-Dissolved	Titanium (Ti)-Dissolved	Uranium (U)-Dissolved	Vanadium (V)-Dissolved	Zinc (Zn)-Dissolved
Inlet	**10-Feb-15**	**1**	**0.00001**	101	0.339	0.000024	**0.0001**	0.012	0.0202	**0.001**	**0.003**
Inlet	**17-Feb-15**	**2**	**0.00001**	104	0.345	0.000031	**0.0001**	0.013	0.0196	**0.001**	**0.003**
Inlet	**24-Feb-15**	**3**	**0.00001**	103	0.333	0.000049	**0.0001**	0.020	0.0211	**0.001**	**0.003**
Inlet	**2-Mar-15**	**4**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**11-Mar-15**	**5**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**17-Mar-15**	**6**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**24-Mar-15**	**7**	**0.00001**	101	0.348	0.000044	**0.0001**	**0.01**	0.0198	**0.001**	**0.003**
Inlet	**31-Mar-15**	**8**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**7-Apr-15**	**9**	**0.00001**	96.2	0.332	0.000046	**0.0001**	0.015	0.0200	**0.0005**	**0.003**
Inlet	**14-Apr-15**	**10**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**22-Apr-15**	**11**	**0.00001**	105	0.332	0.000046	**0.0001**	0.013	0.0190	**0.0005**	**0.003**
Inlet	**29-Apr-15**	**12**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**6-May-15**	**13**	**0.00001**	97.4	0.343	0.000066	**0.0001**	**0.01**	0.0220	**0.0005**	**0.003**
Inlet	**12-May-15**	**14**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**19-May-15**	**15**	**0.00001**	101	0.341	0.000025	**0.0001**	0.012	0.0205	**0.0005**	**0.003**
Inlet	**26-May-15**	**16**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**2-Jun-15**	**17**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**8-Jun-15**	**18**	**0.00001**	98.6	0.327	0.000023	**0.0001**	**0.01**	0.0204	**0.0005**	**0.003**
Inlet	**17-Jun-15**	**19**	**0.00001**	103	0.311	0.000021	**0.0001**	**0.01**	0.0175	**0.0005**	**0.003**
Inlet	**23-Jun-15**	**20**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**30-Jun-15**	**21**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**7-Jul-15**	**22**	**0.00001**	104	0.331	0.000022	**0.0001**	**0.01**	0.0203	**0.0005**	**0.003**
Inlet	**14-Jul-15**	**23**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Inlet	**22-Jul-15**	**24**	**0.00001**	99.7	0.340	0.000023	**0.0001**	**0.01**	0.0199	**0.0005**	**0.003**
Column 1	**10-Feb-15**	**1**	**0.00002**	131	0.785	0.000548	0.00055	0.018	0.00409	0.0156	1.81
Column 1	**17-Feb-15**	**2**	**0.00002**	104	0.953	0.000047	0.00034	0.016	0.00291	0.0106	0.0252
Column 1	**24-Feb-15**	**3**	**0.00002**	98.0	0.800	**0.00002**	**0.0002**	0.031	0.00229	0.0103	0.0077
Column 1	**2-Mar-15**	**4**	#N/A	#N/A	#N/A	#N/A	**#N/A**	#N/A	#N/A	#N/A	#N/A
Column 1	**11-Mar-15**	**5**	**0.00005**	103	1.20	**0.00005**	**0.0005**	0.013	0.00513	0.0061	0.005
Column 1	**17-Mar-15**	**6**	**0.00002**	112	1.15	**0.0002**	**0.0002**	0.020	0.00503	0.0070	0.006
Column 1	**24-Mar-15**	**7**	**0.00002**	97.7	0.580	**0.00002**	**0.0002**	**0.01**	0.0110	0.0032	0.0062
Column 1	**31-Mar-15**	**8**	**0.00002**	105	0.612	**0.00002**	**0.0002**	0.020	0.00872	0.0050	**0.003**
Column 1	**7-Apr-15**	**9**	**0.00002**	98.1	0.553	**0.00002**	**0.0002**	0.020	0.00967	0.0045	0.0040
Column 1	**14-Apr-15**	**10**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	**22-Apr-15**	**11**	**0.00001**	101	0.517	**0.00001**	**0.0001**	0.016	0.00939	0.00463	0.0054
Column 1	**29-Apr-15**	**12**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	**6-May-15**	**13**	**0.00001**	92.0	0.449	**0.00001**	**0.0001**	**0.01**	0.0156	0.00355	0.0053
Column 1	**12-May-15**	**14**	**0.00001**	97.9	0.458	**0.00001**	**0.0001**	0.013	0.0123	0.00417	0.0034
Column 1	**19-May-15**	**15**	**0.00001**	99.3	0.415	**0.00001**	**0.0001**	0.013	0.0102	0.00433	0.0063
Column 1	**26-May-15**	**16**	**0.00001**	95.2	0.406	**0.00001**	**0.0001**	**0.01**	0.0112	0.00479	0.0031
Column 1	**2-Jun-15**	**17**	**0.00001**	97.6	0.418	**0.00001**	**0.0001**	**0.01**	0.00878	0.00430	0.0031
Column 1	**8-Jun-15**	**18**	**0.00001**	99.6	0.385	**0.00001**	**0.0001**	**0.01**	0.00895	0.00412	**0.003**
Column 1	**17-Jun-15**	**19**	**0.00001**	97.7	0.395	**0.00001**	**0.0001**	**0.01**	0.00616	0.00449	**0.003**
Column 1	**23-Jun-15**	**20**	**0.00001**	99.1	0.406	**0.00001**	**0.0001**	**0.01**	0.00917	0.00422	**0.003**
Column 1	**30-Jun-15**	**21**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 1	**7-Jul-15**	**22**	**0.00001**	104	0.432	**0.00001**	**0.0001**	**0.01**	0.00285	0.00478	**0.003**
Column 1	**14-Jul-15**	**23**	**0.00001**	97.9	0.445	**0.00001**	**0.0001**	**0.01**	0.00654	0.00405	0.0055
Column 1	**22-Jul-15**	**24**	**0.00001**	97.4	0.419	**0.00001**	**0.0001**	**0.01**	0.0107	0.00204	0.0032
Column 2	**10-Feb-15**	**1**	**0.00001**	129	0.352	0.000085	**0.0001**	0.012	0.0192	**0.001**	0.0808
Column 2	**17-Feb-15**	**2**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**24-Feb-15**	**3**	**0.00001**	117	0.351	0.000094	**0.0001**	0.021	0.0200	**0.001**	0.0909
Column 2	**2-Mar-15**	**4**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**11-Mar-15**	**5**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**17-Mar-15**	**6**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**24-Mar-15**	**7**	**0.00001**	105	0.353	0.000085	**0.0001**	**0.01**	0.0189	**0.001**	0.0830
Column 2	**31-Mar-15**	**8**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**7-Apr-15**	**9**	**0.00001**	101	0.338	0.000084	**0.0001**	0.016	0.0184	**0.0005**	0.0767
Column 2	**14-Apr-15**	**10**	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	**22-Apr-15**	**11**	**0.00001**	103	0.341	0.000080	**0.0001**	0.013	0.0151	**0.0005**	0.0700

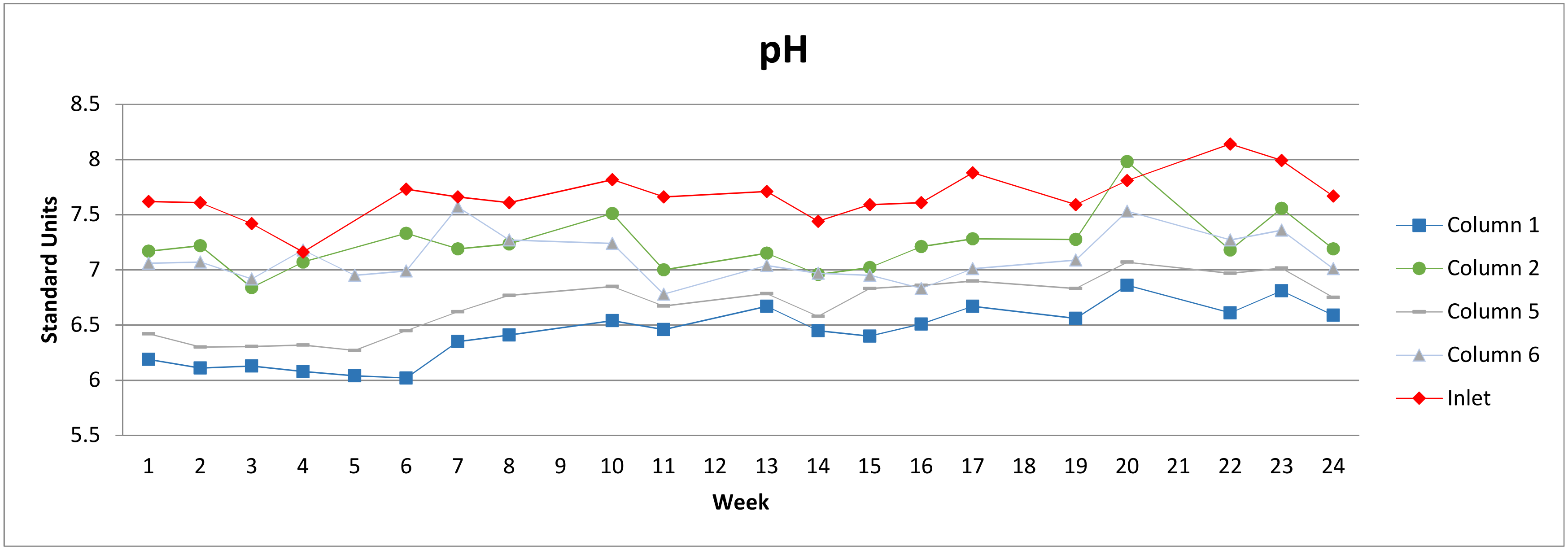
Speciation samples collected	No sample collected	Results discarded due to irregularities	**Bold Values are less than or equal to the MDL**
More than 15% of results are less than or equal to the MDL, no mean calculated		0-15% of values are less than or equal to the MDL, 0.5 x MDL used as replacement value in mean calculation	

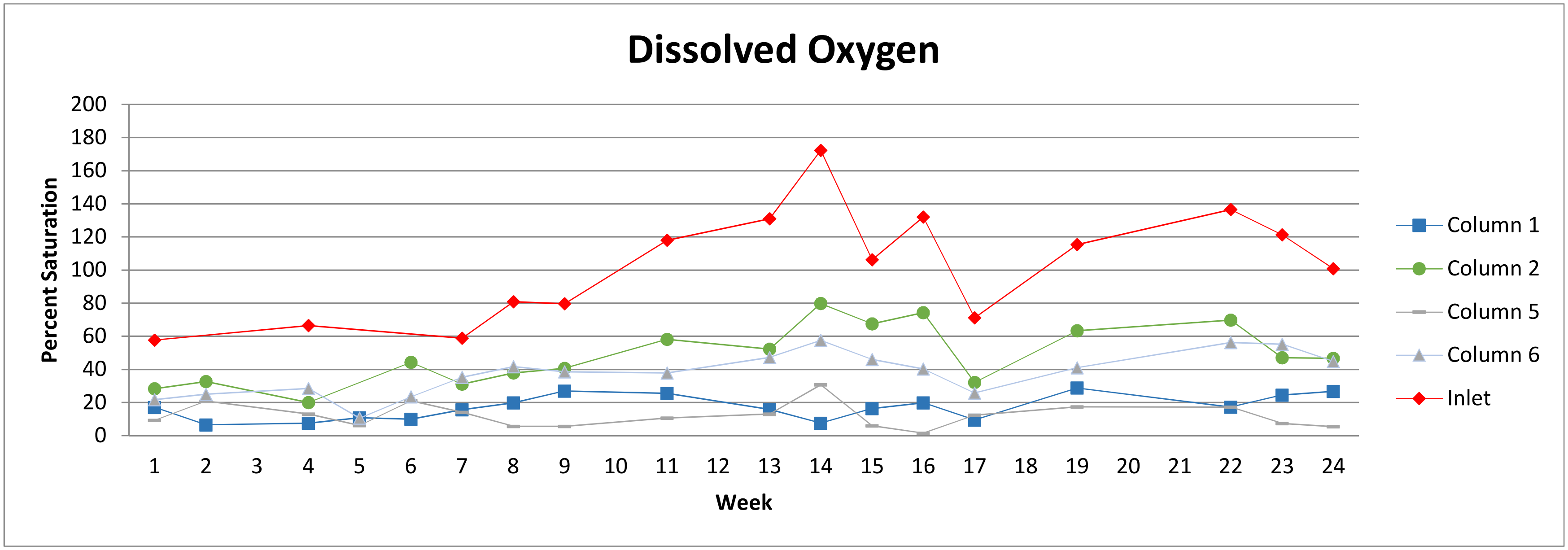
0-Jan-00	Date	Week	Silver (Ag)-Dissolved	Sodium (Na)-Dissolved	Strontium (Sr)-Dissolved	Thallium (Tl)-Dissolved	Tin (Sn)-Dissolved	Titanium (Ti)-Dissolved	Uranium (U)-Dissolved	Vanadium (V)-Dissolved	Zinc (Zn)-Dissolved
Column 2	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	6-May-15	13	**0.00001**	97.8	0.356	0.000084	**0.0001**	**0.01**	0.0197	**0.0005**	0.0696
Column 2	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	19-May-15	15	**0.00001**	101	0.339	0.000087	**0.0001**	0.014	0.0180	**0.0005**	0.0624
Column 2	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	2-Jun-15	17	**0.00001**	98.0	0.341	0.000087	**0.0001**	**0.01**	0.0180	**0.0005**	0.0574
Column 2	8-Jun-15	18	**0.00001**	100	0.323	0.000084	**0.0001**	**0.01**	0.0176	**0.0005**	0.0623
Column 2	17-Jun-15	19	**0.00001**	98.5	0.328	0.000084	**0.0001**	**0.01**	0.0161	**0.0005**	0.0574
Column 2	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	7-Jul-15	22	**0.00001**	106	0.339	0.000090	**0.0001**	**0.01**	0.0174	**0.0005**	0.0600
Column 2	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 2	22-Jul-15	24	**0.00001**	99.0	0.349	0.000087	**0.0001**	**0.01**	0.0170	**0.0005**	0.0498
Column 5	10-Feb-15	1	**0.00002**	121	0.548	0.000511	**0.0002**	0.015	0.0146	0.0087	0.911
Column 5	17-Feb-15	2	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	24-Feb-15	3	**0.00002**	102	0.522	**0.00002**	0.00042	**0.030**	0.00571	0.0148	0.0083
Column 5	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	11-Mar-15	5	**0.00001**	97.5	0.584	**0.00001**	0.00028	0.014	0.00363	0.0125	**0.003**
Column 5	17-Mar-15	6	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	24-Mar-15	7	**0.00001**	98.5	0.469	**0.00001**	0.00012	**0.01**	0.00580	0.0086	**0.003**
Column 5	31-Mar-15	8	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	7-Apr-15	9	**0.00001**	97.5	0.441	**0.00001**	**0.0001**	0.017	0.0112	0.00639	0.0031
Column 5	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	22-Apr-15	11	**0.00001**	98.1	0.444	**0.00001**	**0.0001**	0.015	0.00906	0.00743	**0.003**
Column 5	29-Apr-15	12	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	6-May-15	13	**0.00001**	93.7	0.403	**0.00001**	**0.0001**	**0.01**	0.0122	0.00463	**0.003**
Column 5	12-May-15	14	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	19-May-15	15	**0.00001**	98.4	0.359	**0.00001**	**0.0001**	0.013	0.0135	0.00468	0.0040
Column 5	26-May-15	16	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	2-Jun-15	17	**0.00001**	98.3	0.371	**0.00001**	**0.0001**	**0.01**	0.0124	0.00379	0.0040
Column 5	8-Jun-15	18	**0.00001**	99.8	0.351	**0.00001**	**0.0001**	**0.01**	0.0153	0.00434	**0.003**
Column 5	17-Jun-15	19	**0.00001**	100	0.335	**0.00001**	**0.0001**	**0.01**	0.0111	0.00388	**0.003**
Column 5	23-Jun-15	20	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	7-Jul-15	22	**0.00001**	104	0.373	**0.00001**	**0.0001**	**0.01**	0.0118	0.00403	0.0049
Column 5	14-Jul-15	23	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 5	22-Jul-15	24	**0.00001**	97.0	0.383	**0.00001**	**0.0001**	**0.01**	0.0128	0.00309	0.0064
Column 6	10-Feb-15	1	**0.00001**	128	0.352	0.000067	**0.0001**	0.012	0.0204	**0.001**	0.127
Column 6	17-Feb-15	2	0.000025	126	0.342	0.000098	**0.0001**	0.013	0.0198	**0.001**	0.121
Column 6	24-Feb-15	3	**0.00001**	121	0.342	0.000063	**0.0001**	0.022	0.0217	**0.001**	0.116
Column 6	2-Mar-15	4	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	11-Mar-15	5	**0.00001**	110	0.324	0.000054	**0.0001**	0.012	0.0200	**0.001**	0.114
Column 6	17-Mar-15	6	**0.00001**	110	0.343	**0.0001**	**0.0001**	0.017	0.0227	0.0011	0.113
Column 6	24-Mar-15	7	**0.00001**	106	0.345	0.000063	**0.0001**	**0.01**	0.0208	0.00091	0.113
Column 6	31-Mar-15	8	**0.00001**	111	0.339	0.000066	**0.0001**	0.015	0.0205	0.00073	0.106
Column 6	7-Apr-15	9	**0.00001**	97.9	0.341	0.000068	**0.0001**	0.016	0.0199	0.00101	0.102
Column 6	14-Apr-15	10	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	22-Apr-15	11	**0.00001**	102	0.349	0.000064	**0.0001**	0.014	0.0180	0.00057	0.0834
Column 6	29-Apr-15	12	**0.00001**	96.2	0.354	0.000070	**0.0001**	**0.01**	0.0202	0.00068	0.0790
Column 6	6-May-15	13	**0.00001**	97.8	0.360	0.000068	**0.0001**	**0.01**	0.0215	0.0005	0.0786
Column 6	12-May-15	14	**0.00001**	101	0.365	0.000073	**0.0001**	0.013	0.0200	0.00059	0.0730
Column 6	19-May-15	15	**0.00001**	103	0.342	0.000072	**0.0001**	0.012	0.0192	0.00052	0.0705
Column 6	26-May-15	16	**0.00001**	97.2	0.344	0.000068	**0.0001**	**0.01**	0.0188	**0.0005**	0.0647
Column 6	2-Jun-15	17	**0.00001**	98.7	0.344	0.000073	**0.0001**	**0.01**	0.0187	0.00054	0.0616
Column 6	8-Jun-15	18	**0.00001**	101	0.339	0.000075	**0.0001**	**0.01**	0.0198	**0.0005**	0.0635
Column 6	17-Jun-15	19	**0.00001**	101	0.321	0.000071	**0.0001**	**0.01**	0.0170	**0.0005**	0.0630
Column 6	23-Jun-15	20	**0.00001**	104	0.336	0.000077	**0.0001**	**0.01**	0.0196	**0.0005**	0.0648
Column 6	30-Jun-15	21	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Column 6	7-Jul-15	22	**0.00001**	108	0.362	0.000087	**0.0001**	**0.01**	0.0206	0.00055	0.0637
Column 6	14-Jul-15	23	**0.00001**	99.1	0.359	0.000080	**0.0001**	**0.01**	0.0199	**0.0005**	0.0609
Column 6	22-Jul-15	24	**0.00001**	100	0.356	0.000075	**0.0001**	**0.01**	0.0177	0.00057	0.0581

Speciation samples collected	No sample collected	Results discarded due to irregularities	**Bold Values are less than or equal to the MDL**
More than 15% of results are less than or equal to the MDL, no mean calculated		0-15% of values are less than or equal to the MDL, 0.5 x MDL used as replacement value in mean calculation	

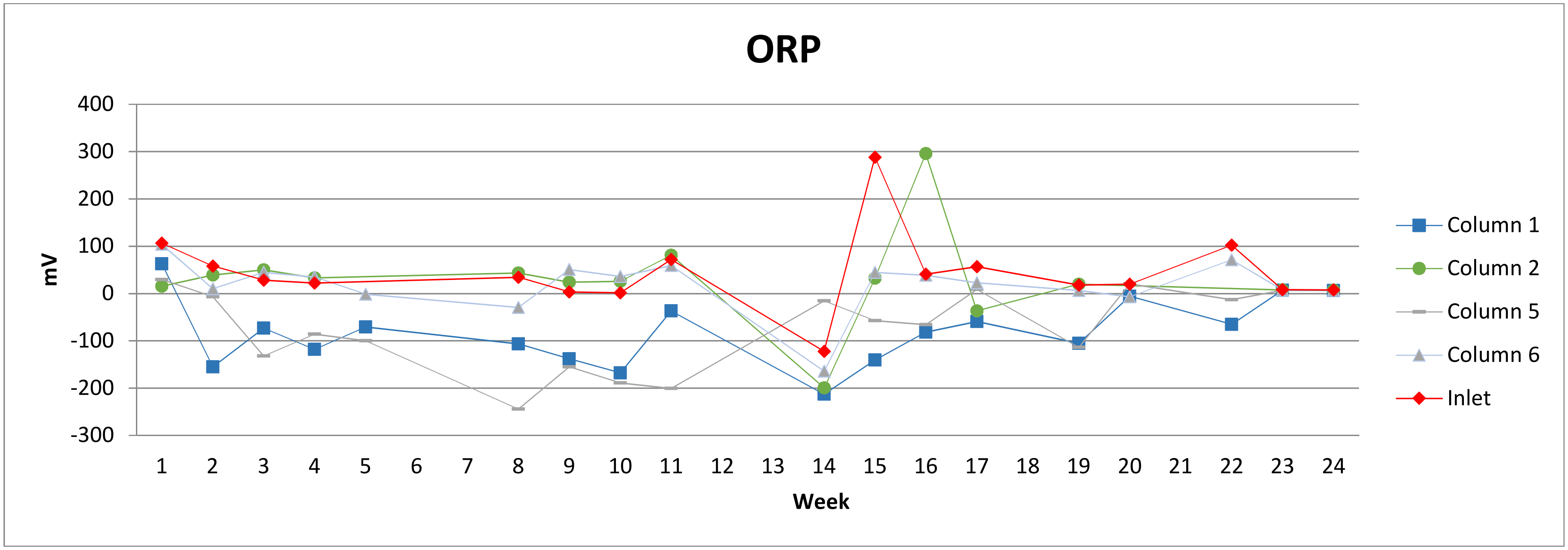
Appendix D.10

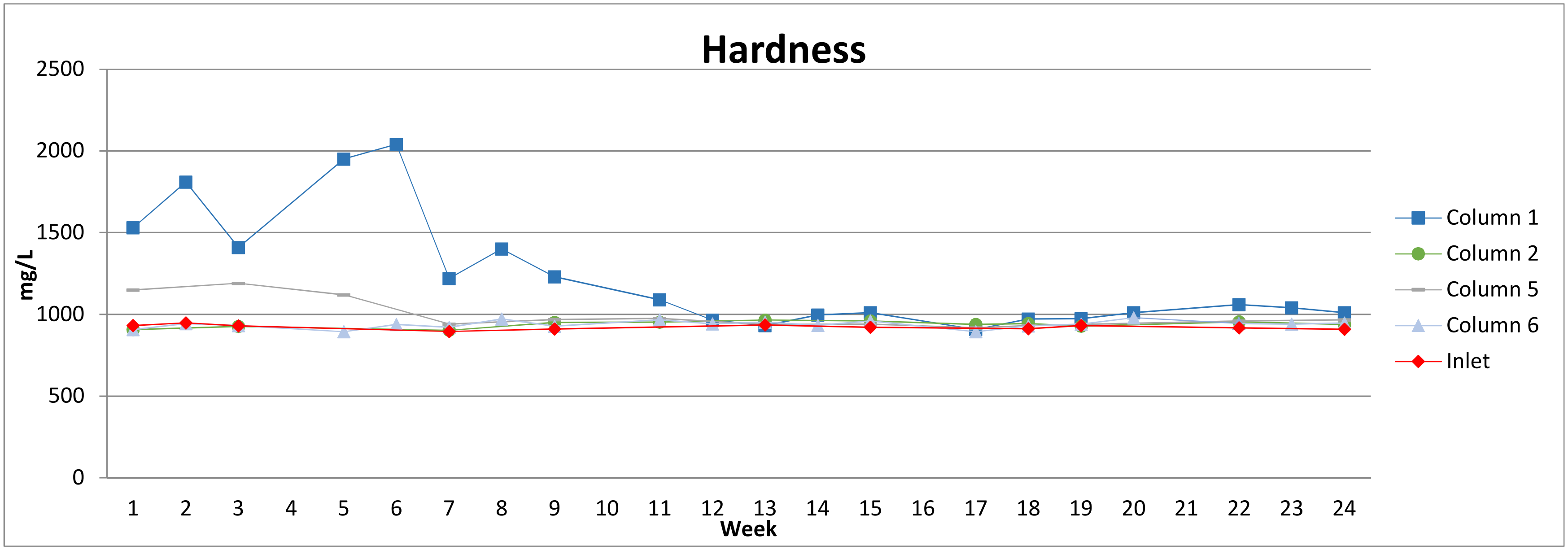
Combined Water Quality Results Graphed



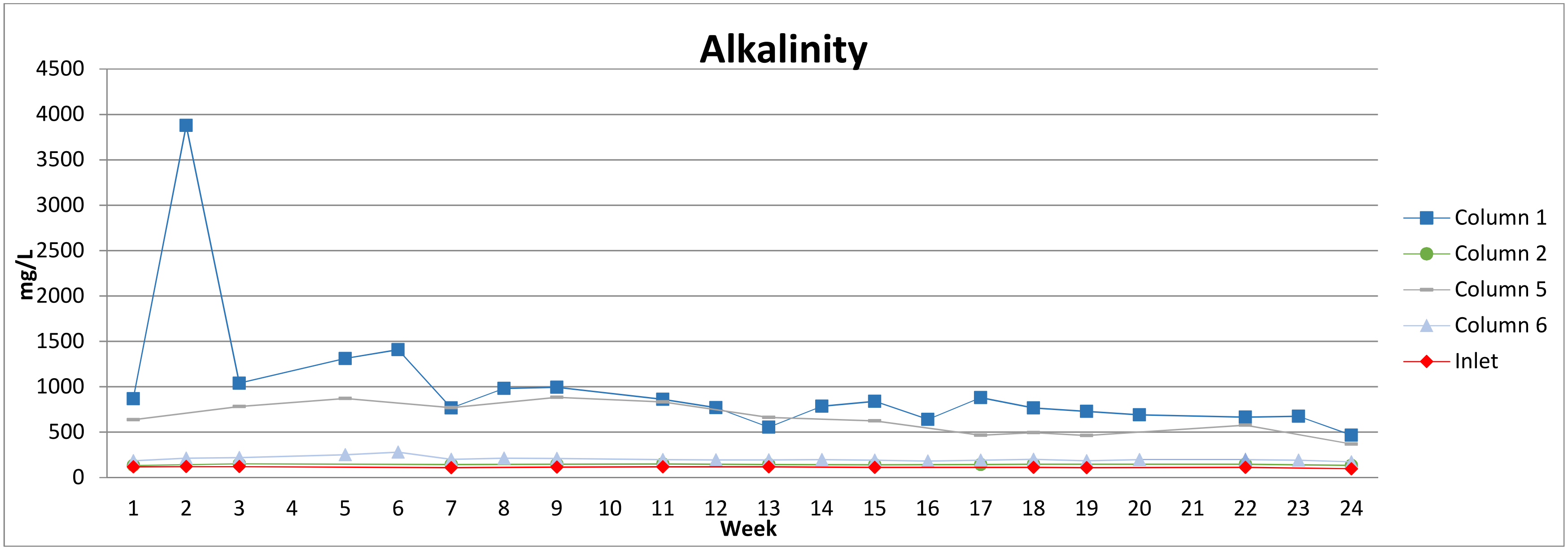


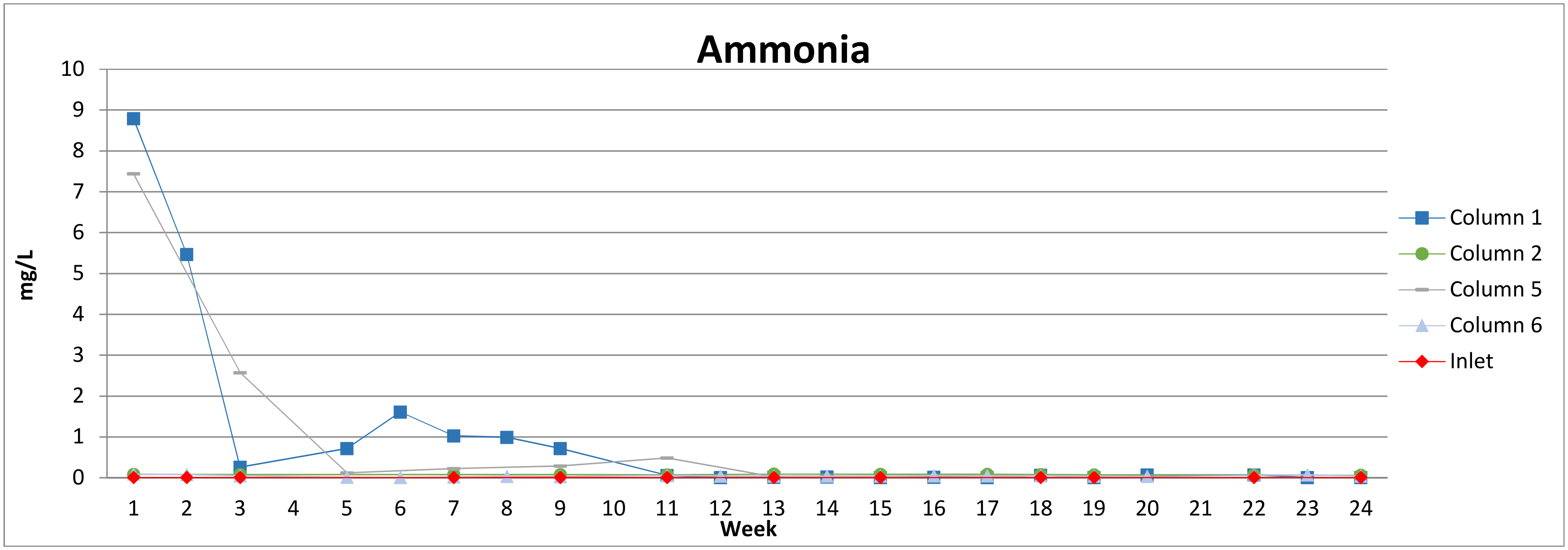
Combined Water Quality Results Graphed



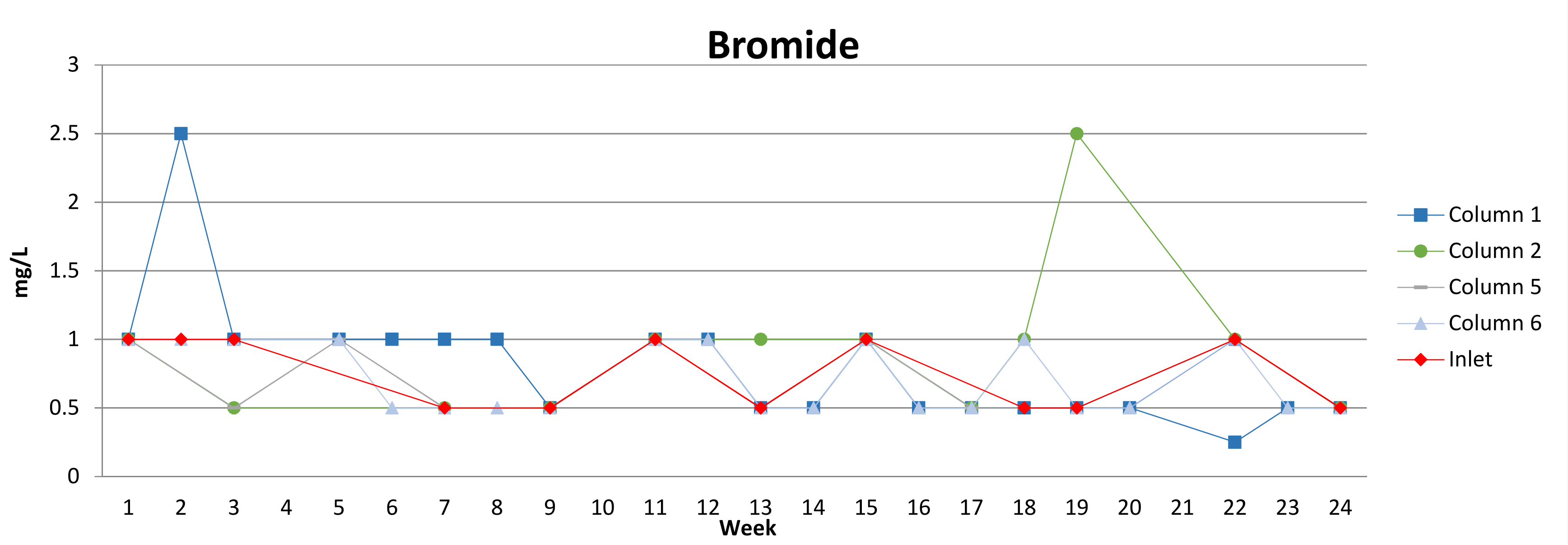


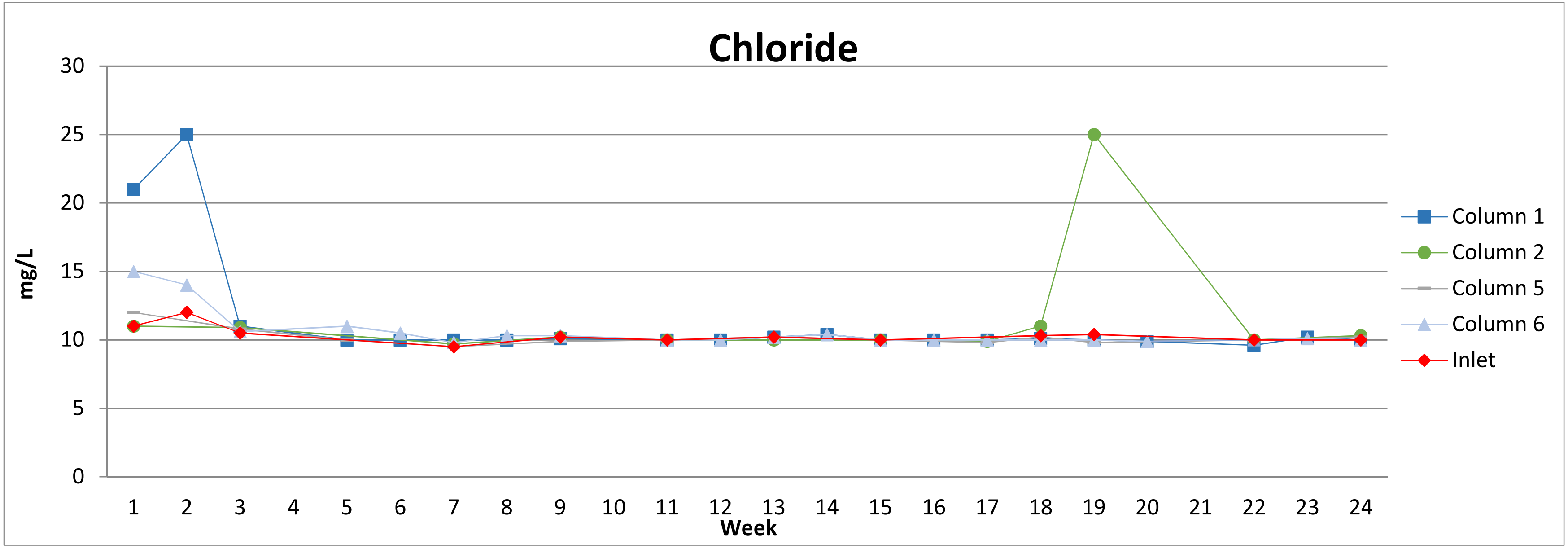
Combined Water Quality Results Graphed





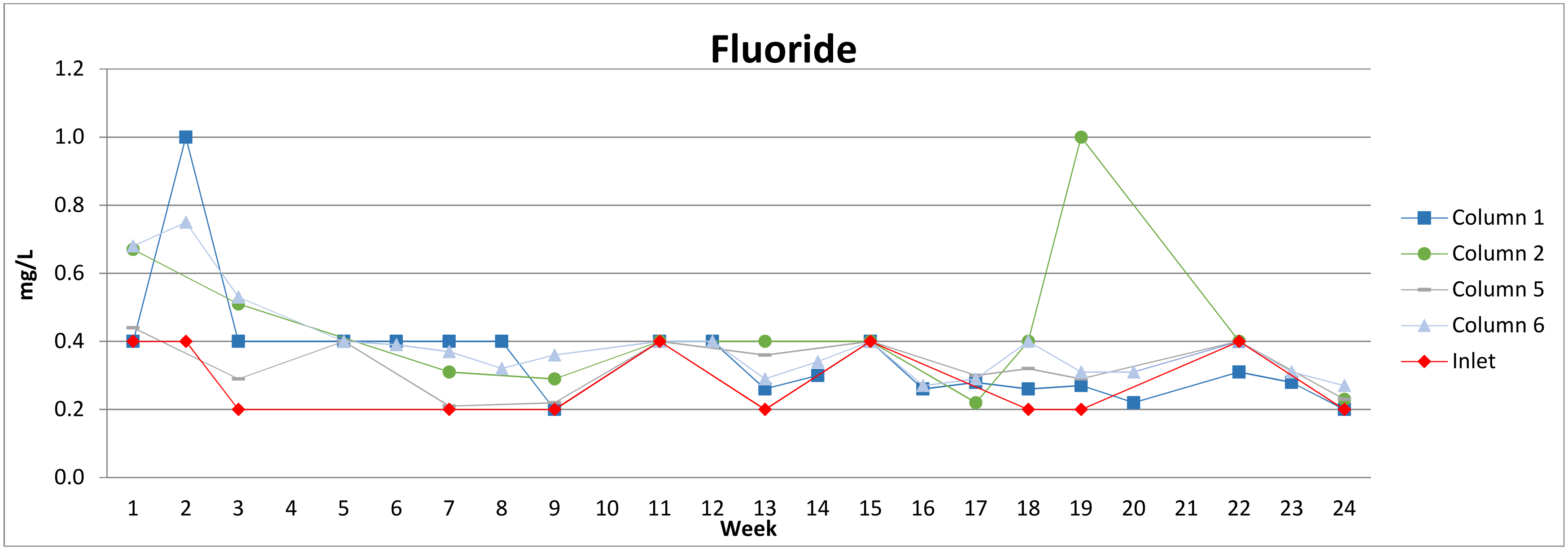
Combined Water Quality Results Graphed

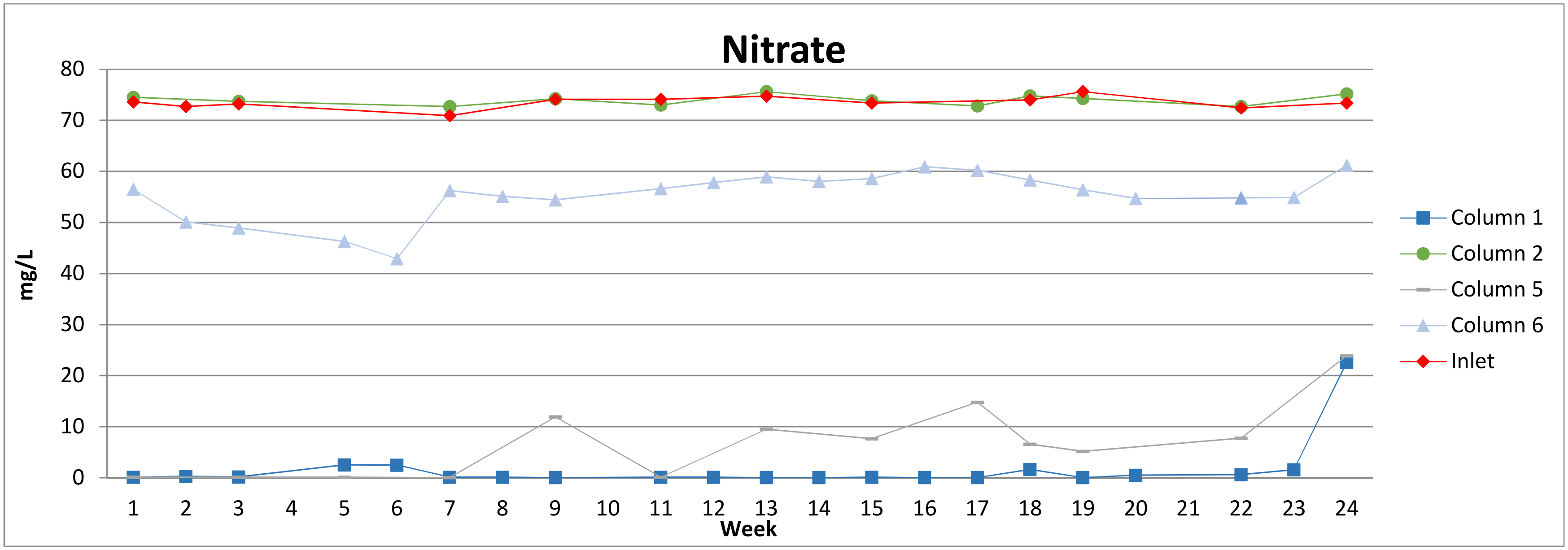




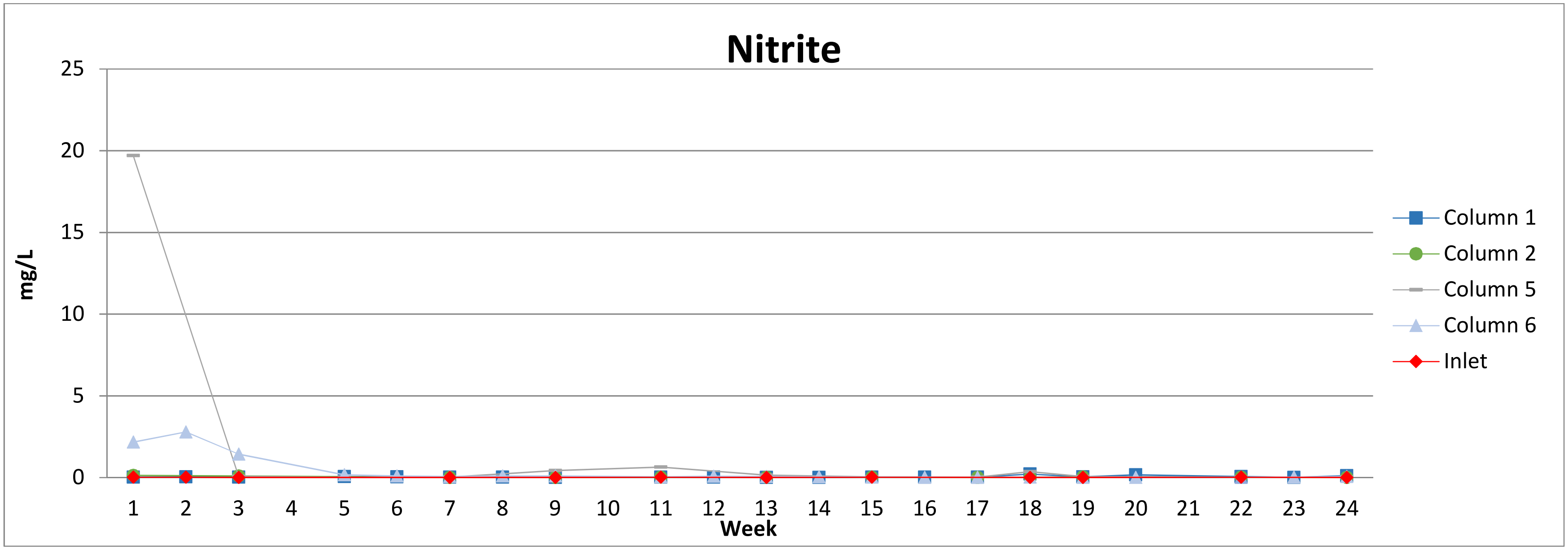
Appendix D.10

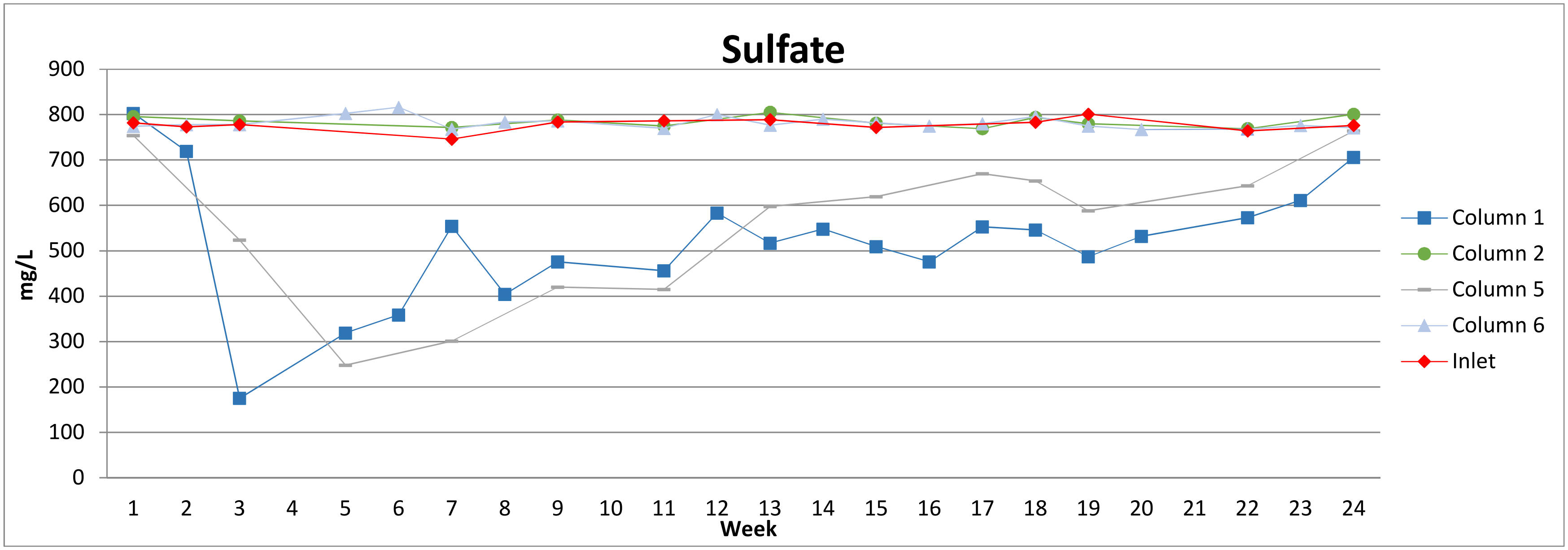
Combined Water Quality Results Graphed



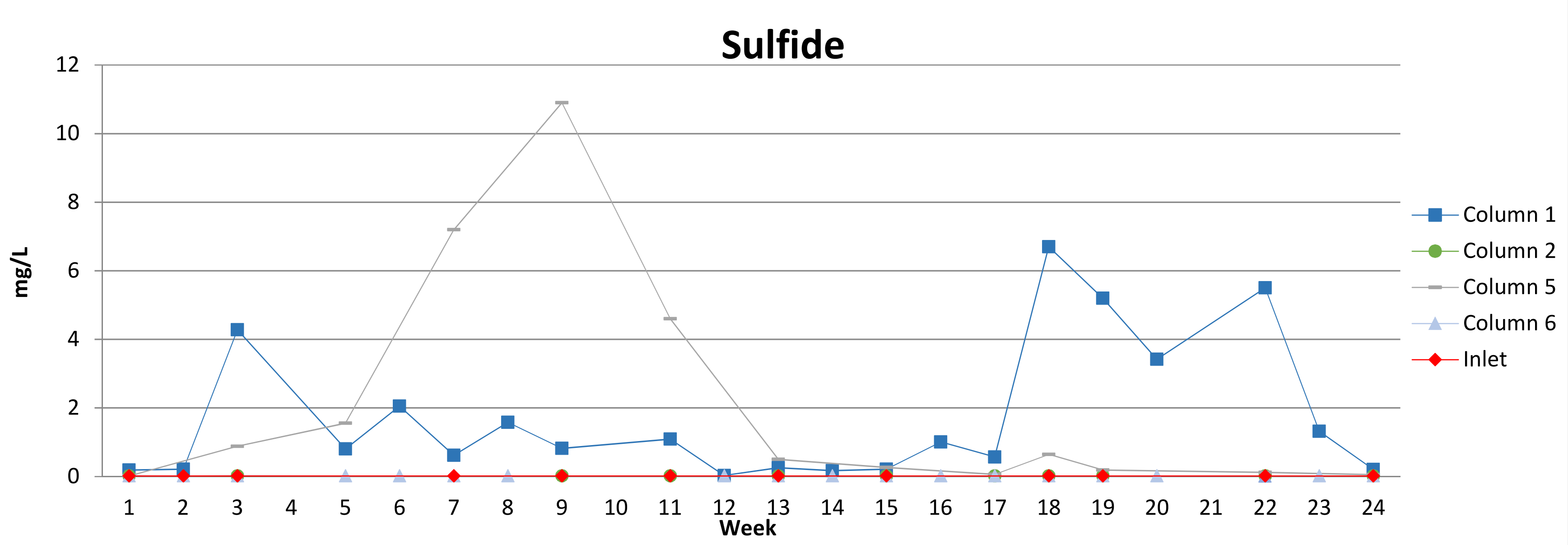


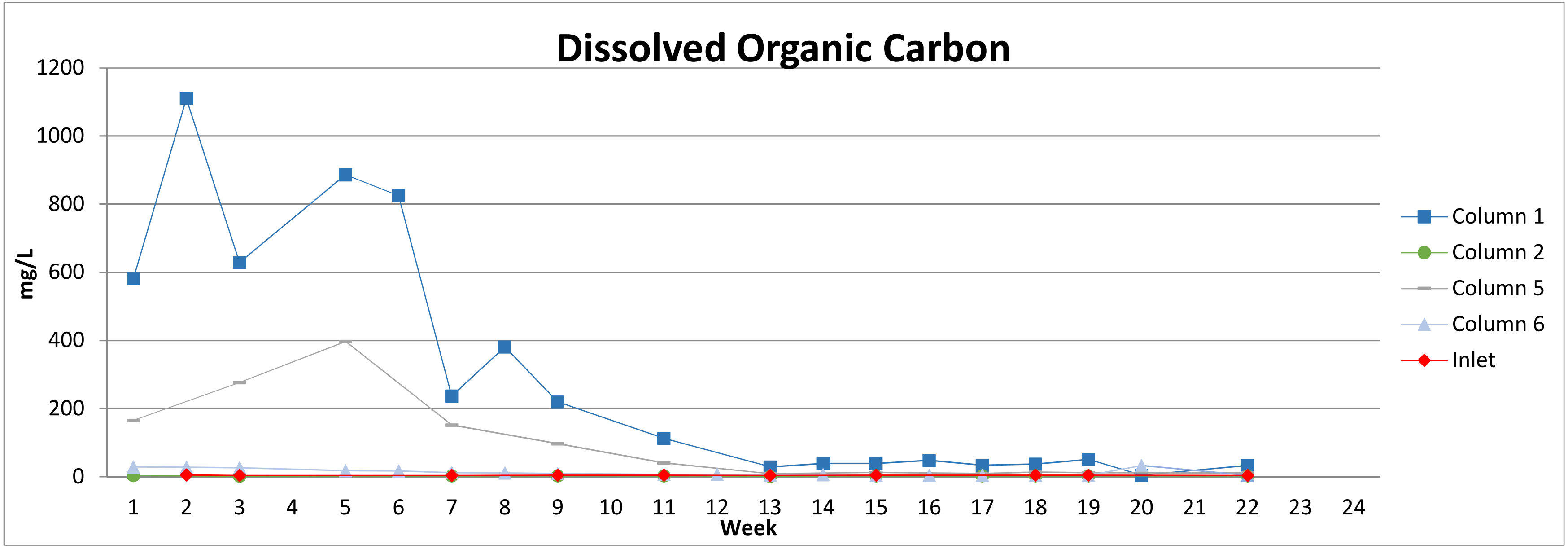
Combined Water Quality Results Graphed

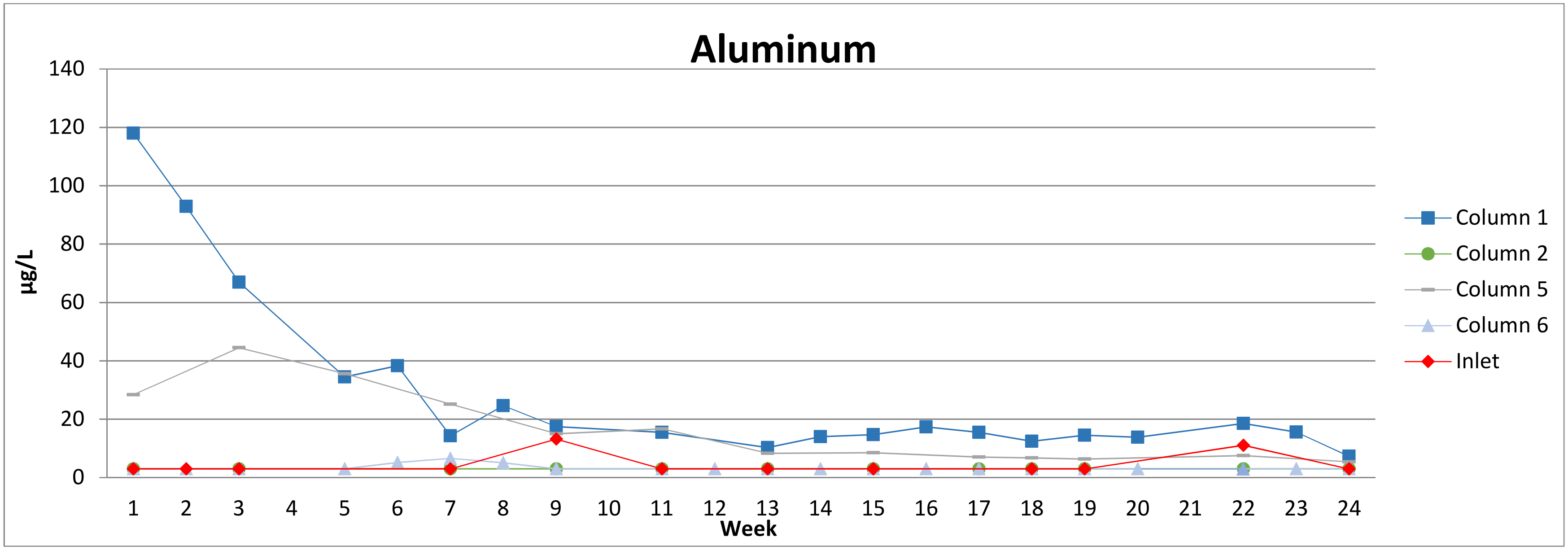


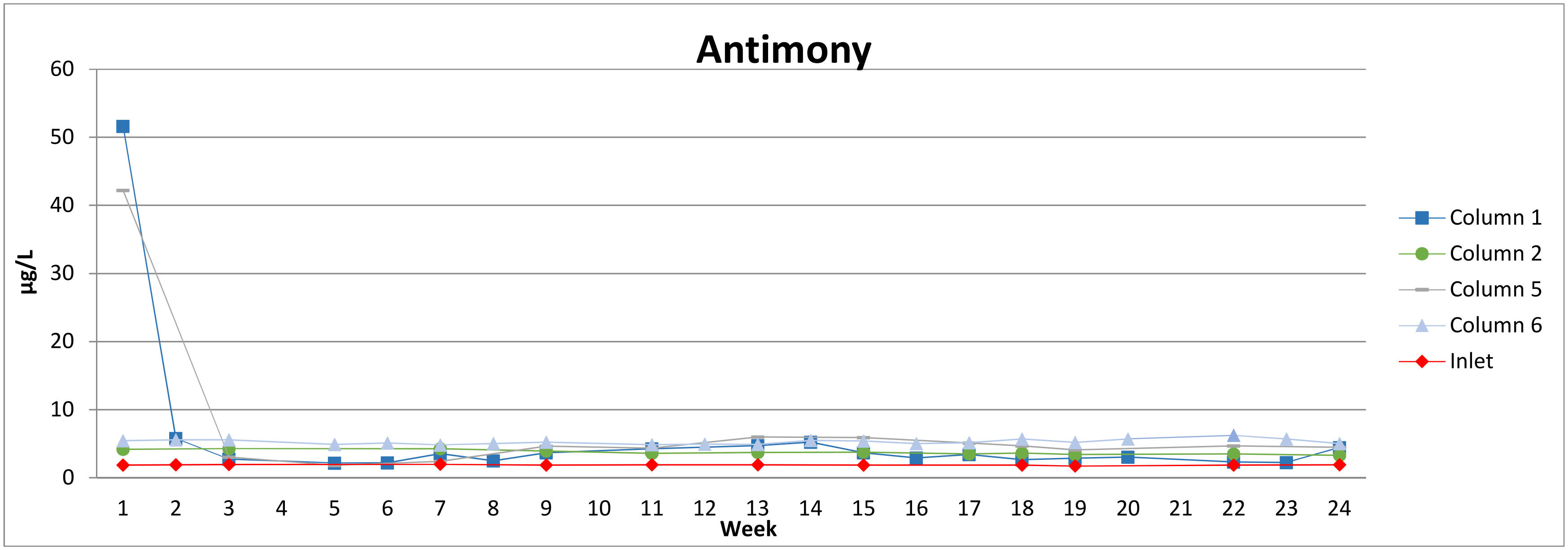


Combined Water Quality Results Graphed

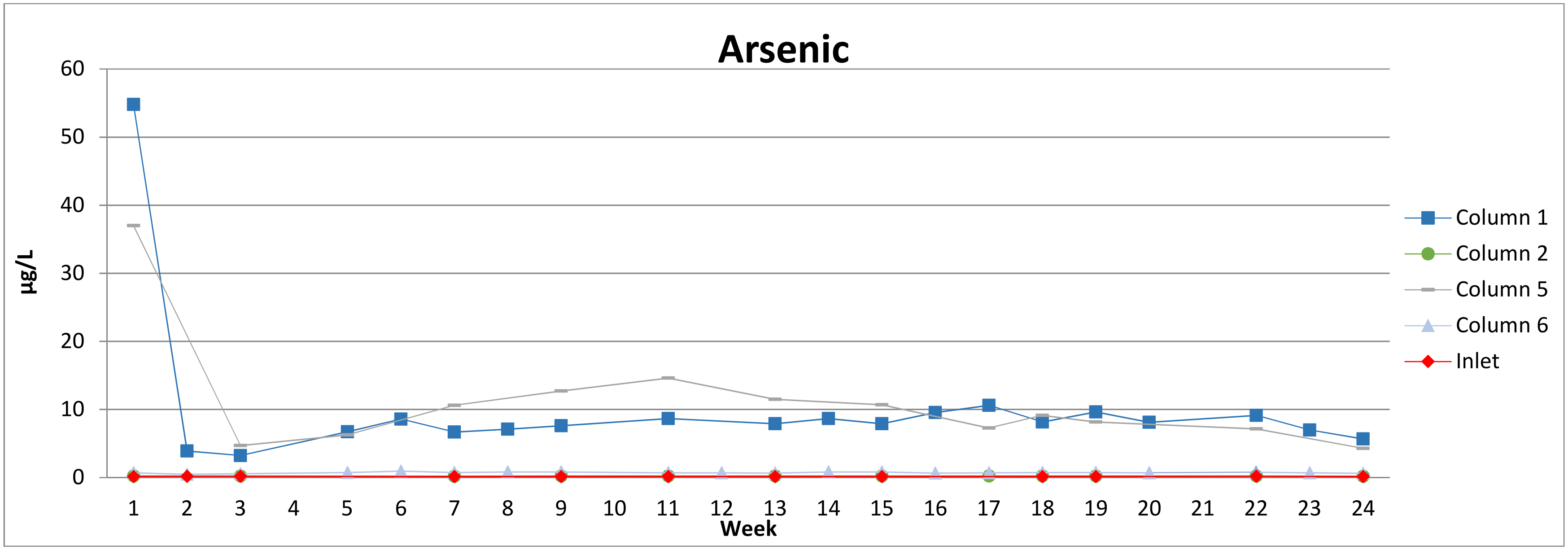


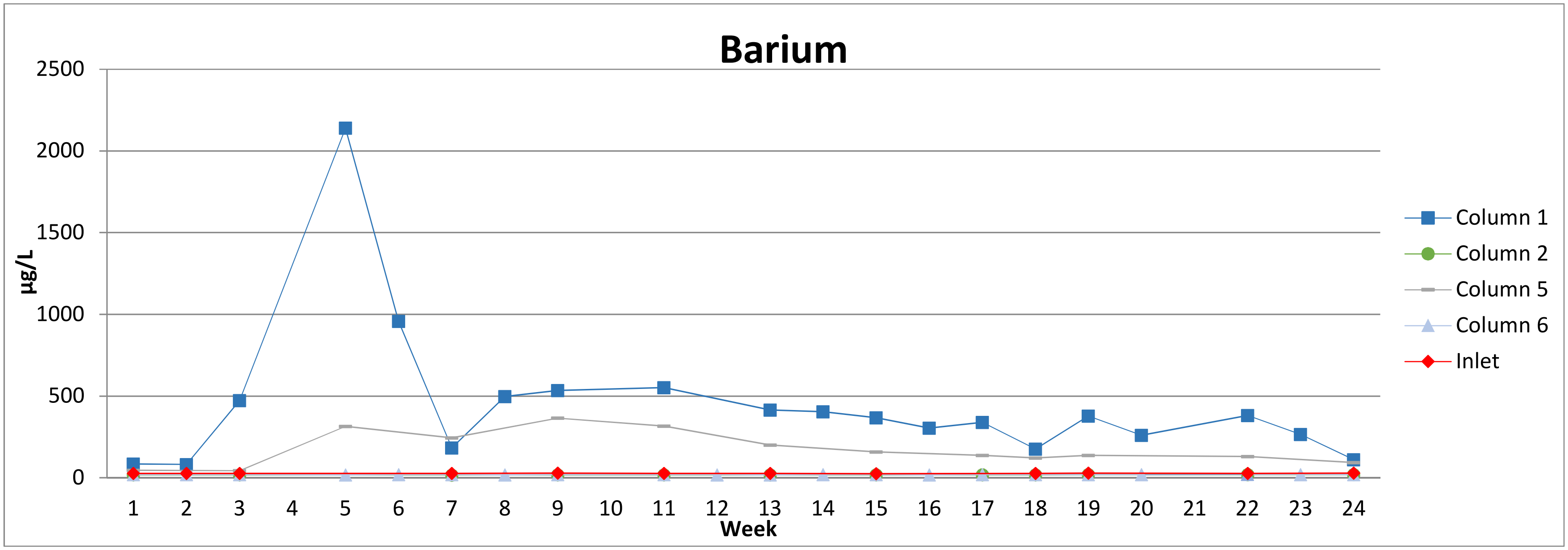



Aluminum
µg/L
0
20
40
60
80
100
120
140
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Week
Column 1
Column 2
Column 5
Column 6
Inlet

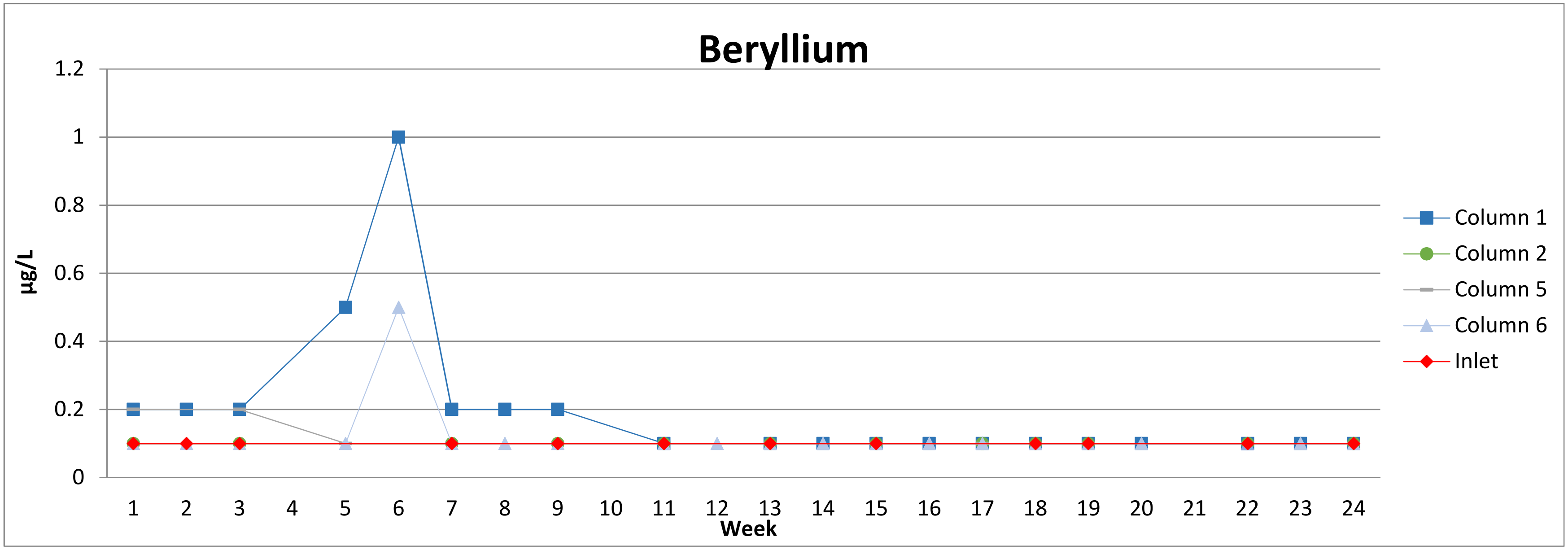

Antimony
µg/L
0
10
20
30
40
50
60
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Week
Column 1
Column 2
Column 5
Column 6
Inlet

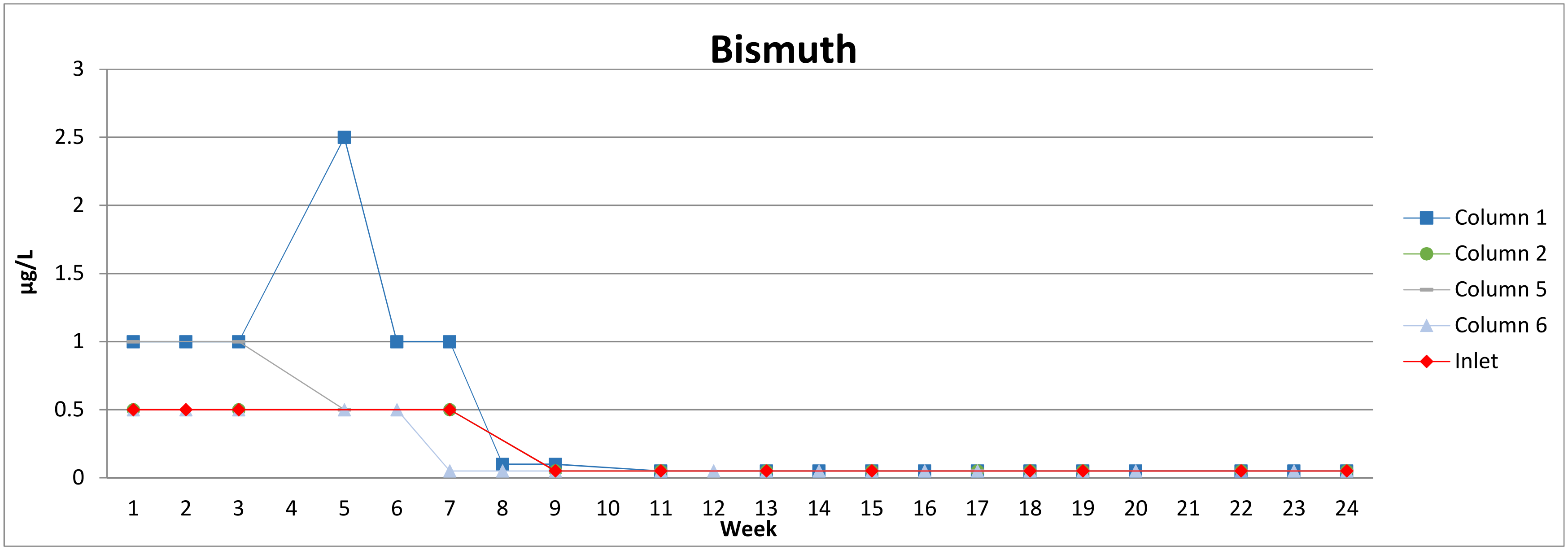
Combined Water Quality Results Graphed



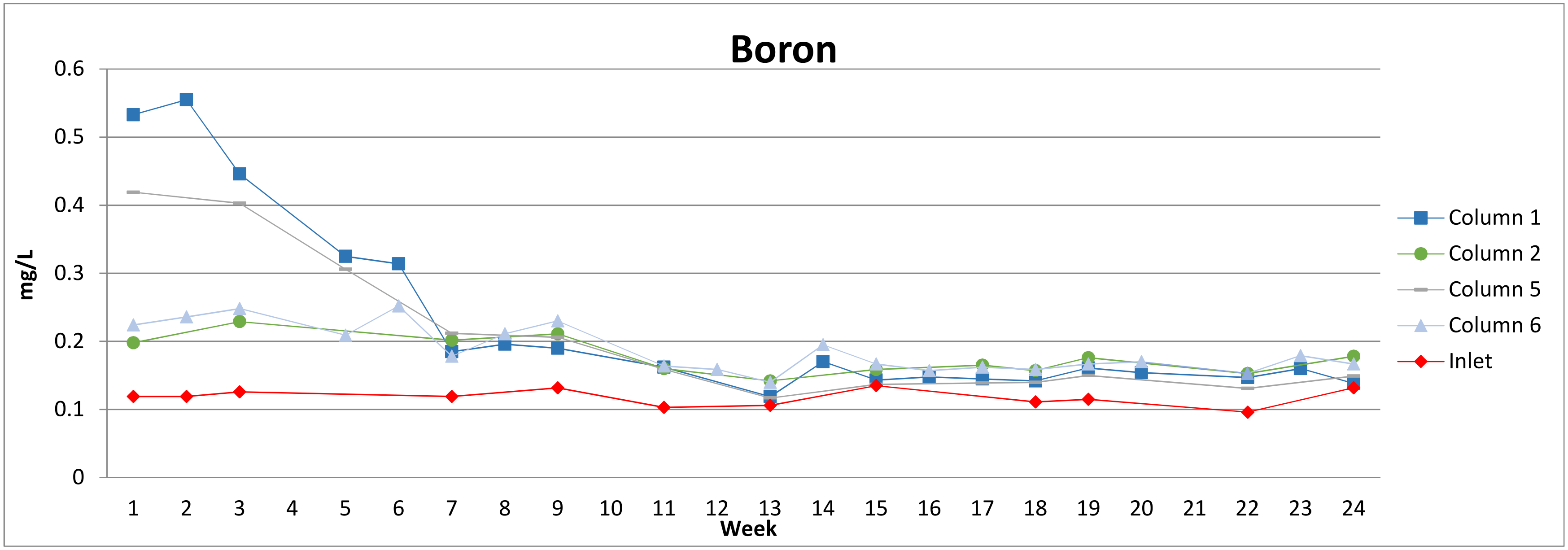


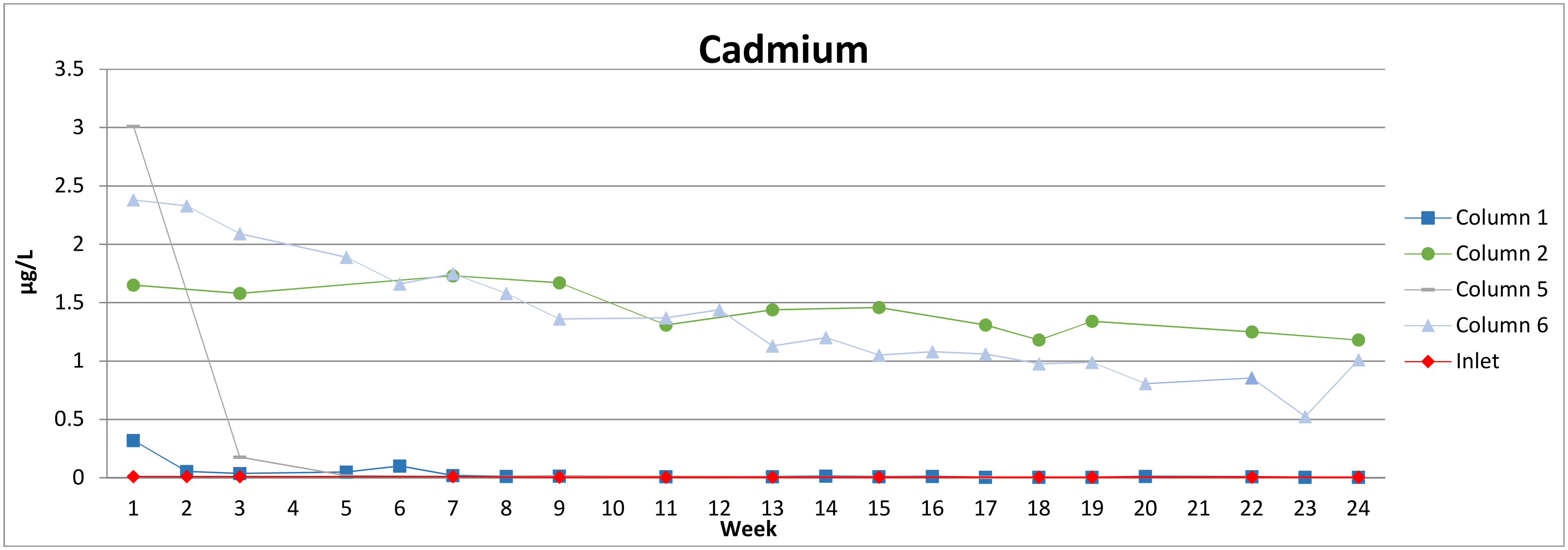
Combined Water Quality Results Graphed



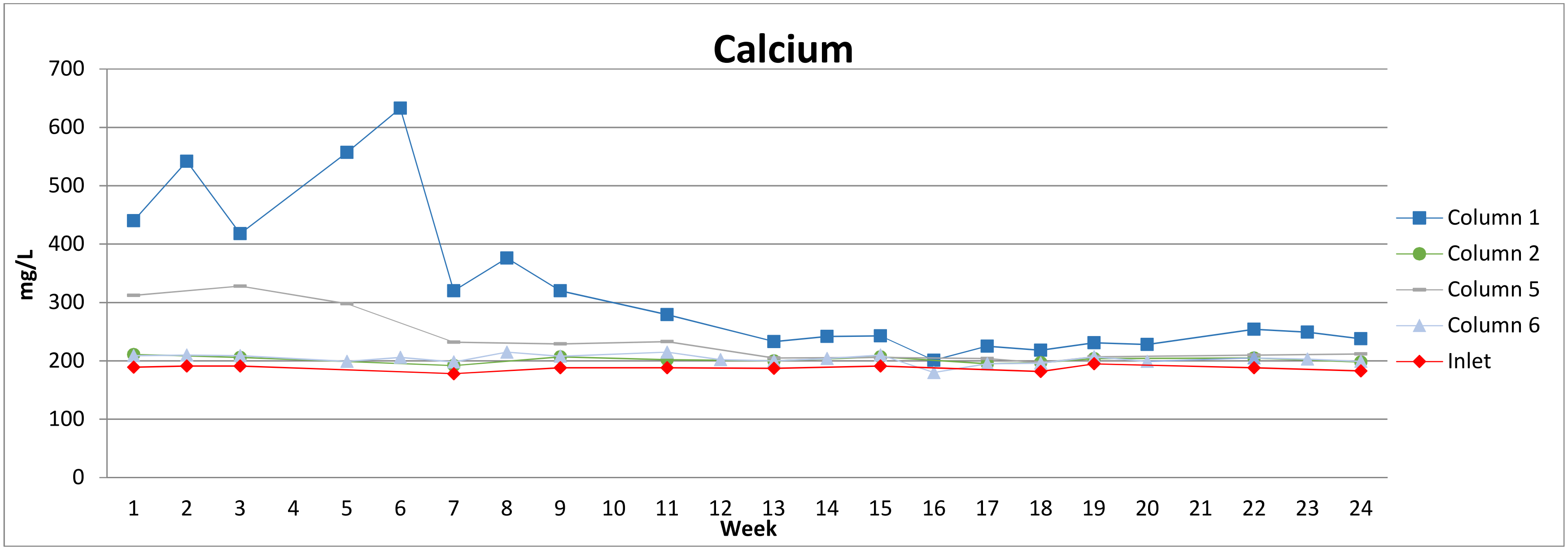


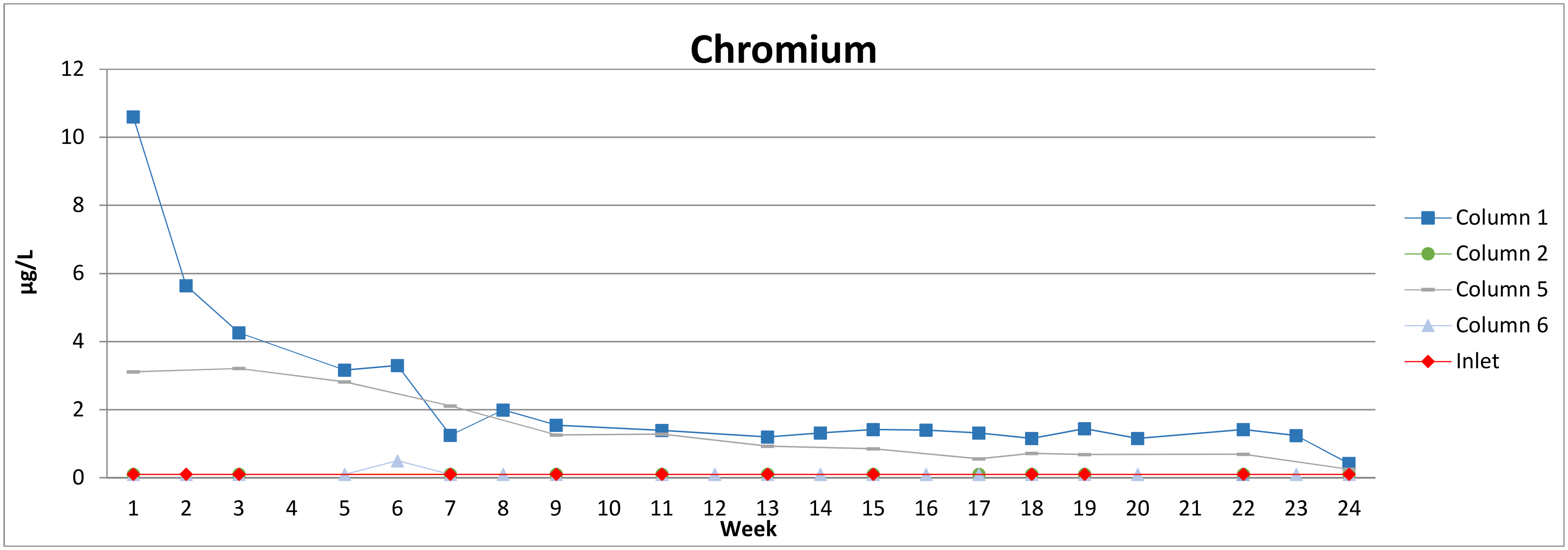
Combined Water Quality Results Graphed



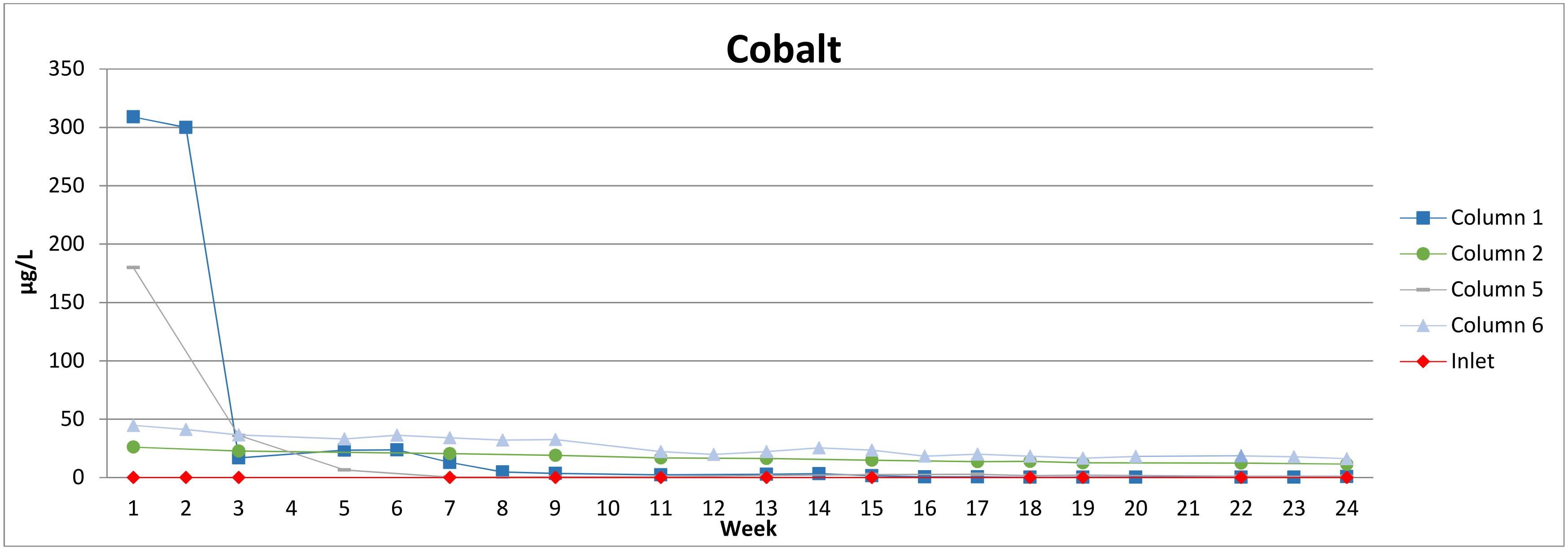


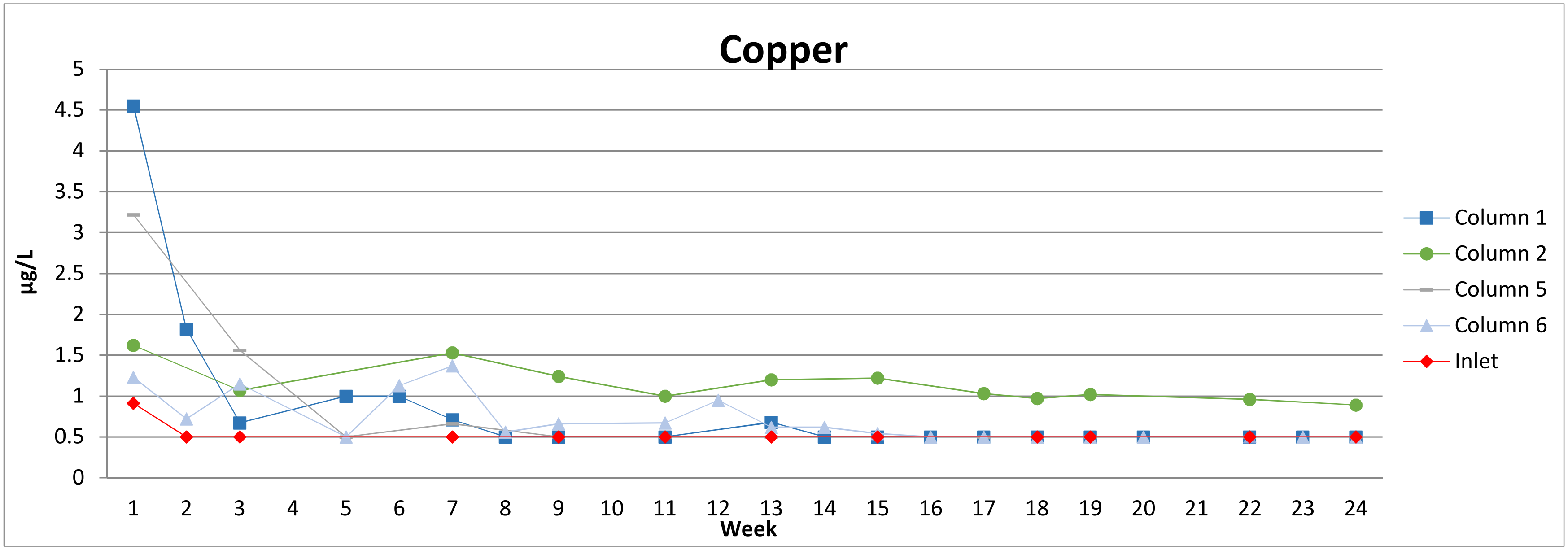
Combined Water Quality Results Graphed



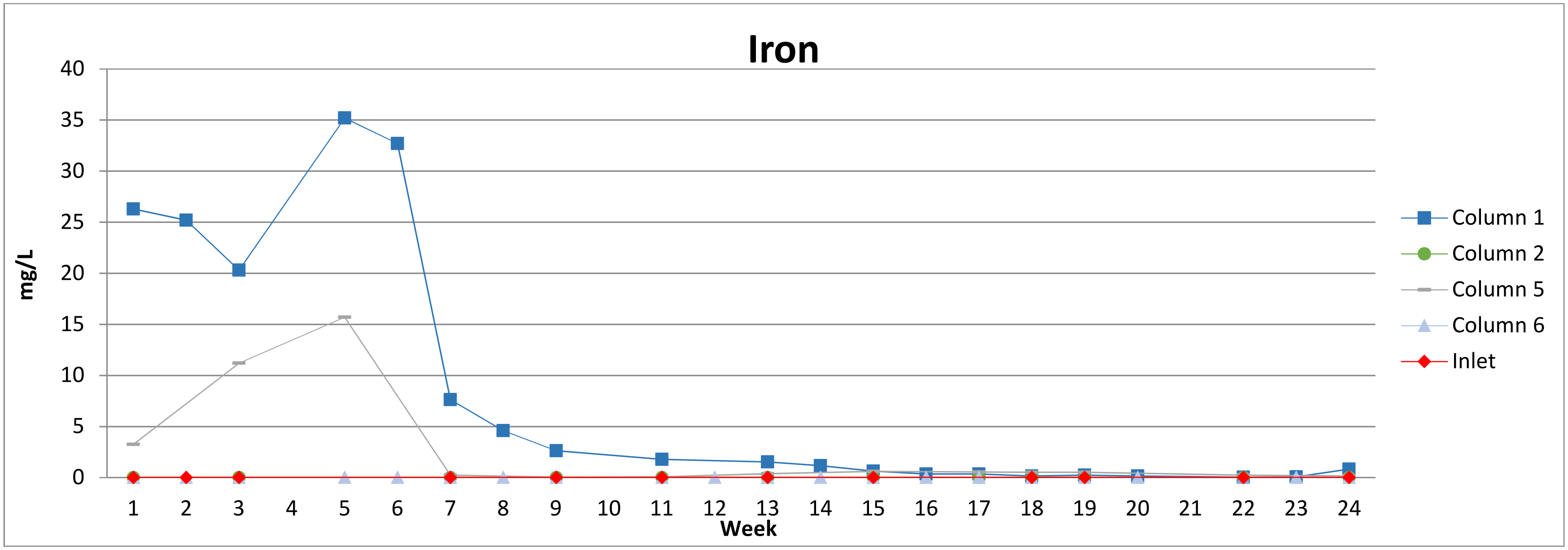


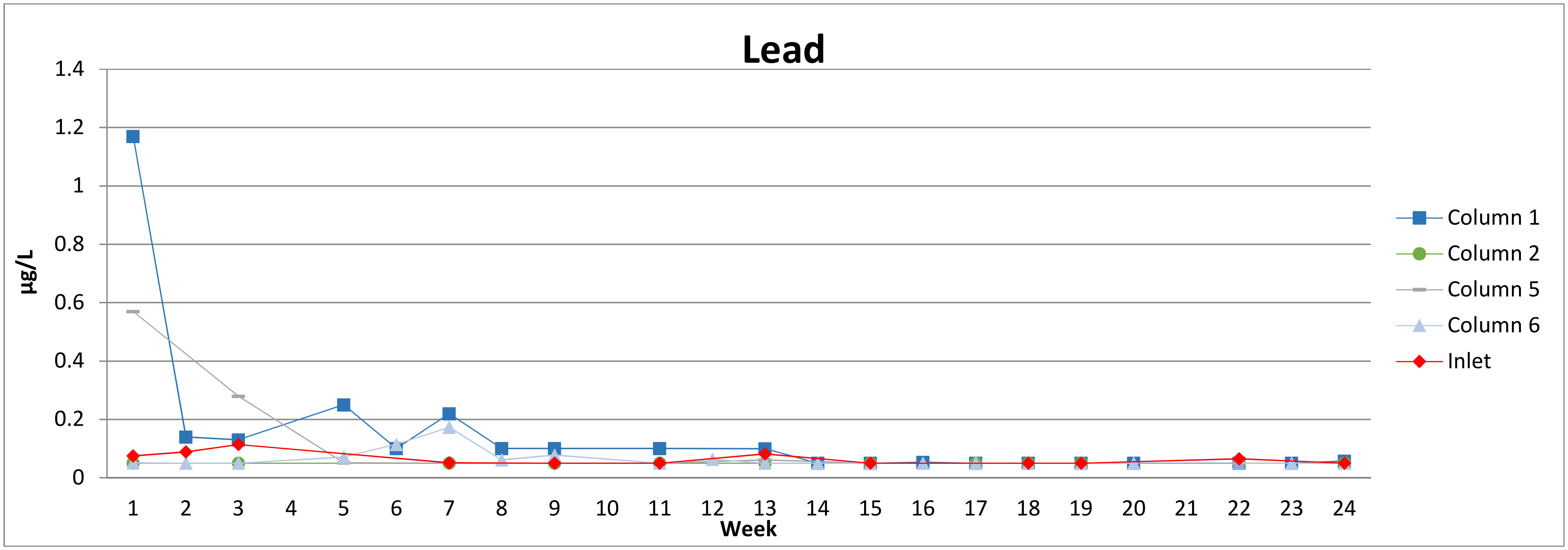
Combined Water Quality Results Graphed



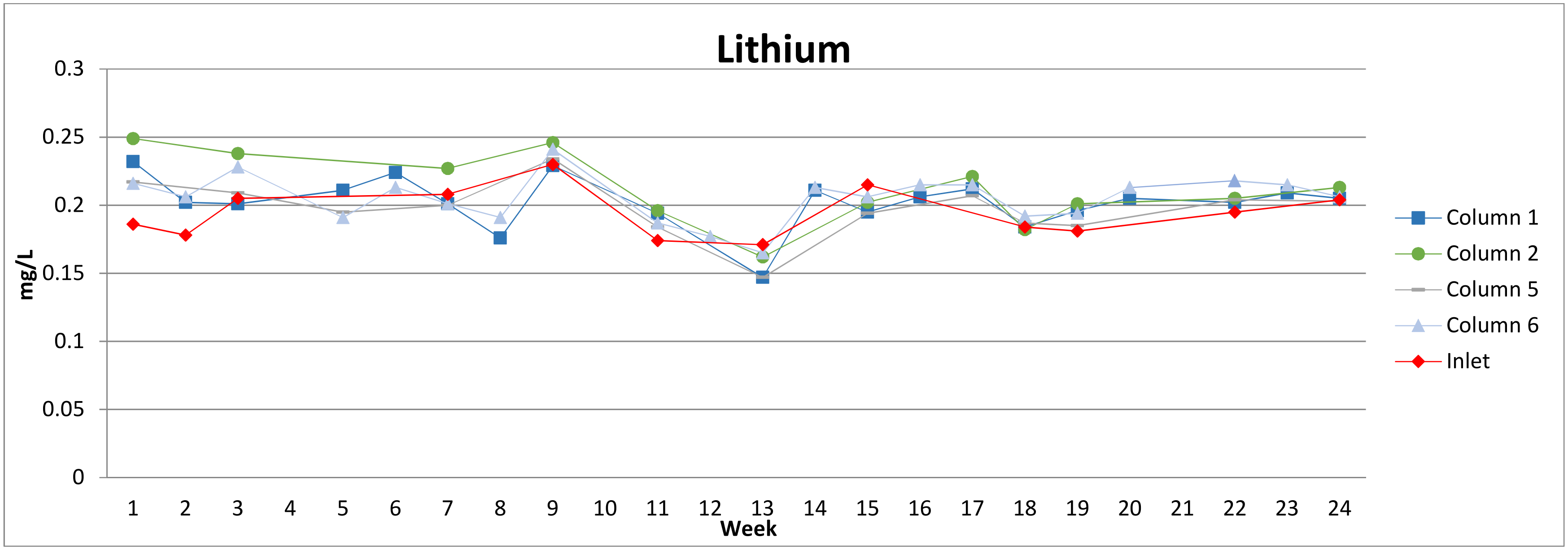


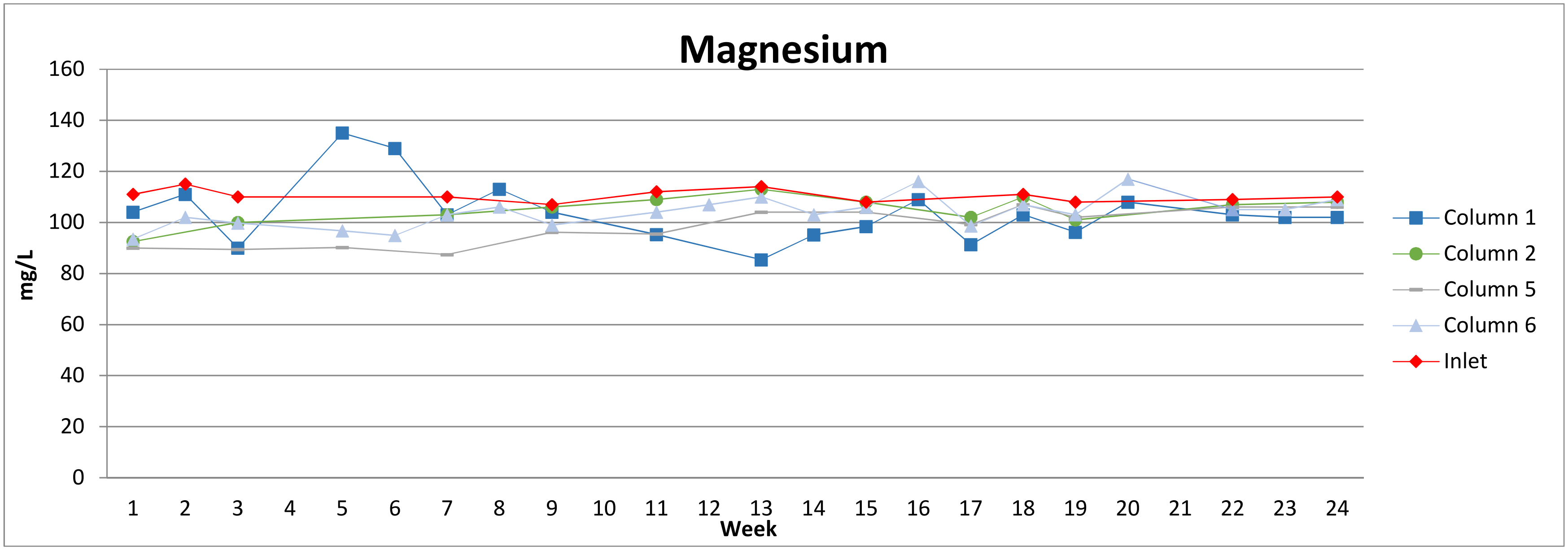
Combined Water Quality Results Graphed



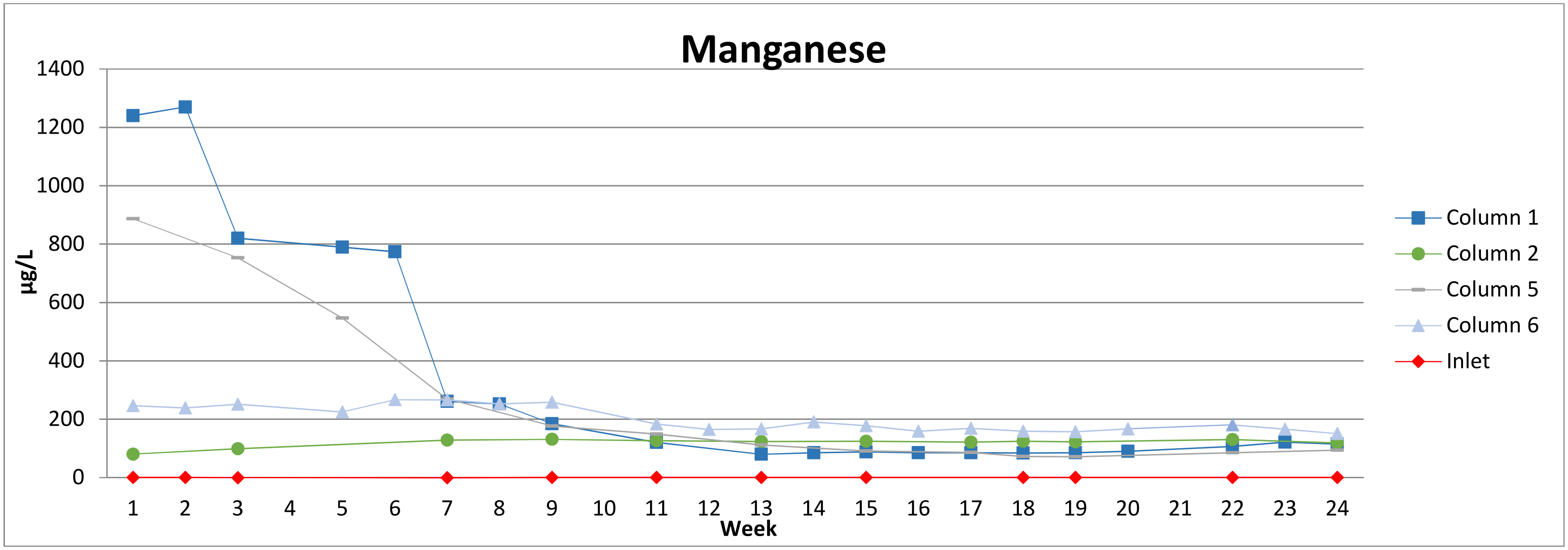


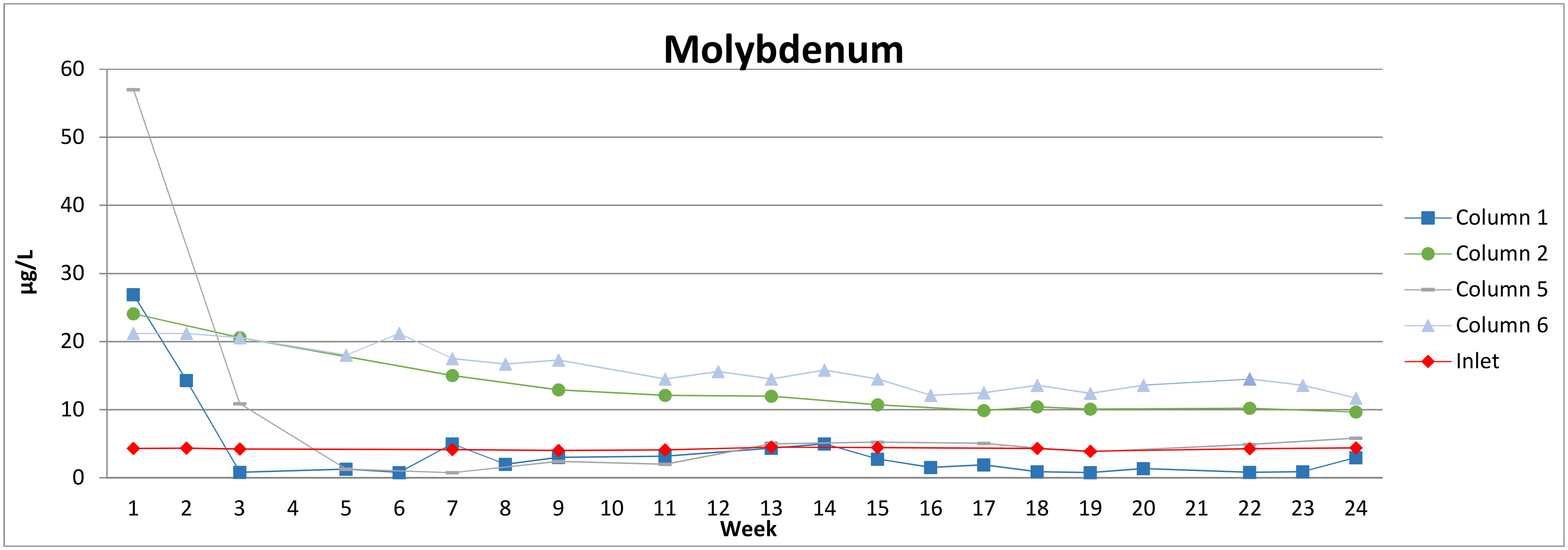
Combined Water Quality Results Graphed



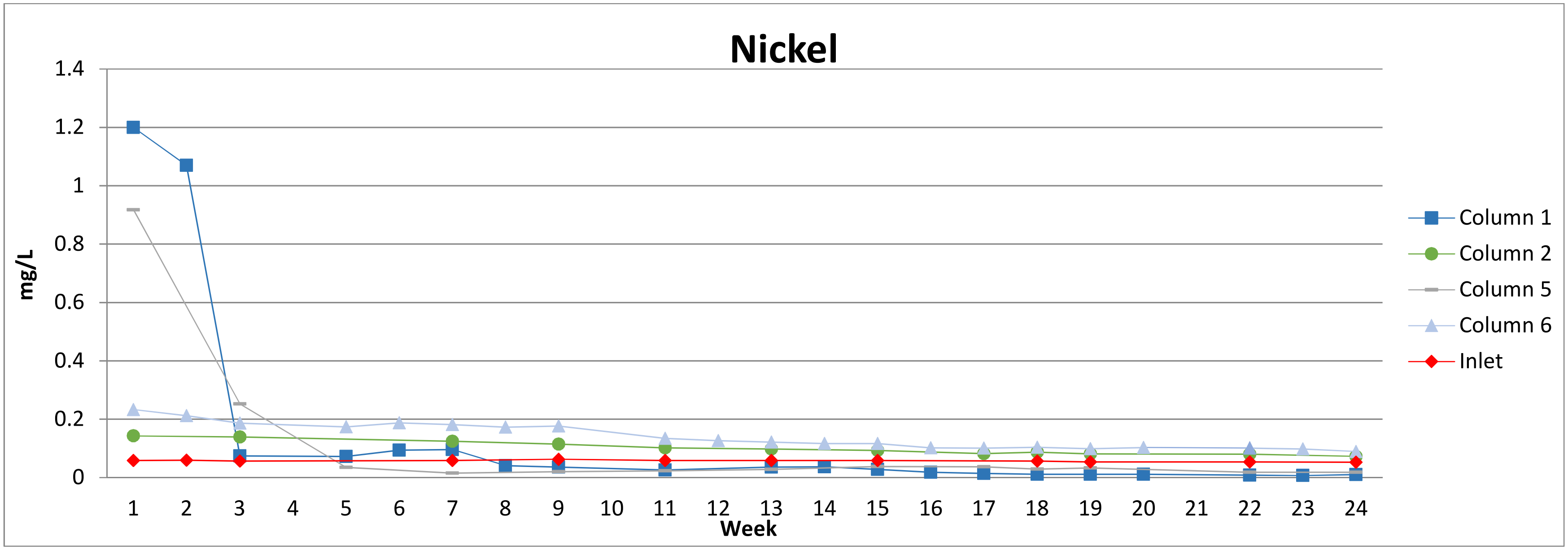


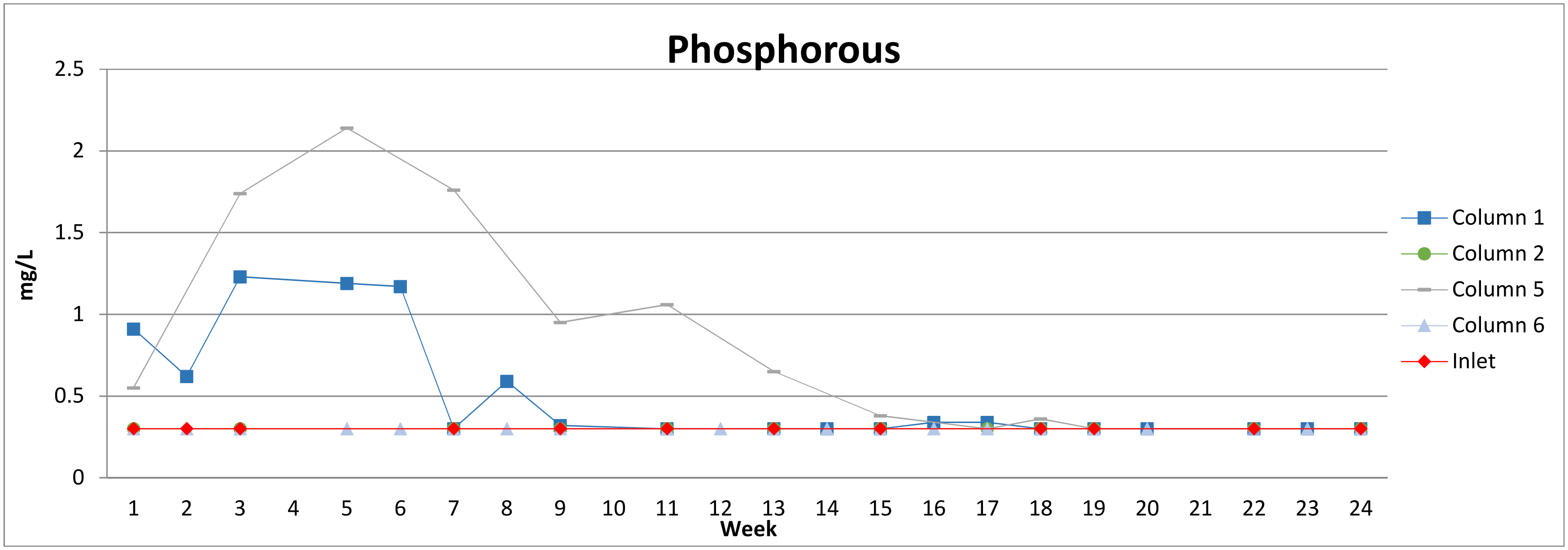
Combined Water Quality Results Graphed



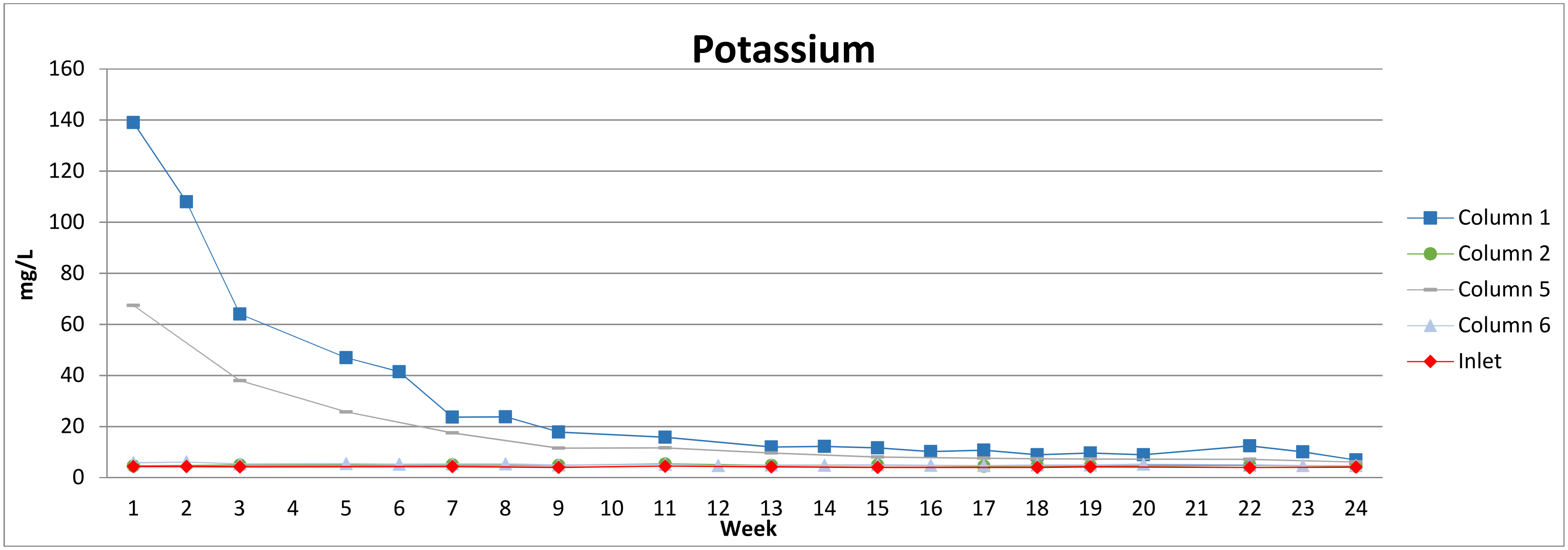


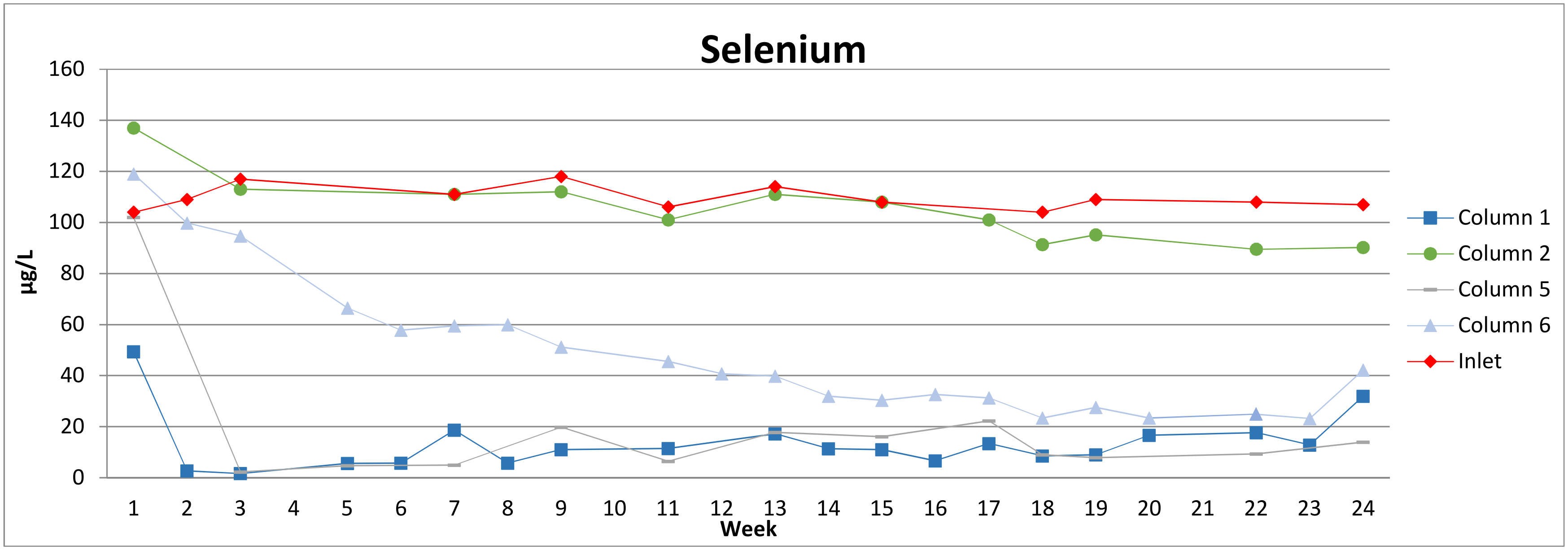
Combined Water Quality Results Graphed



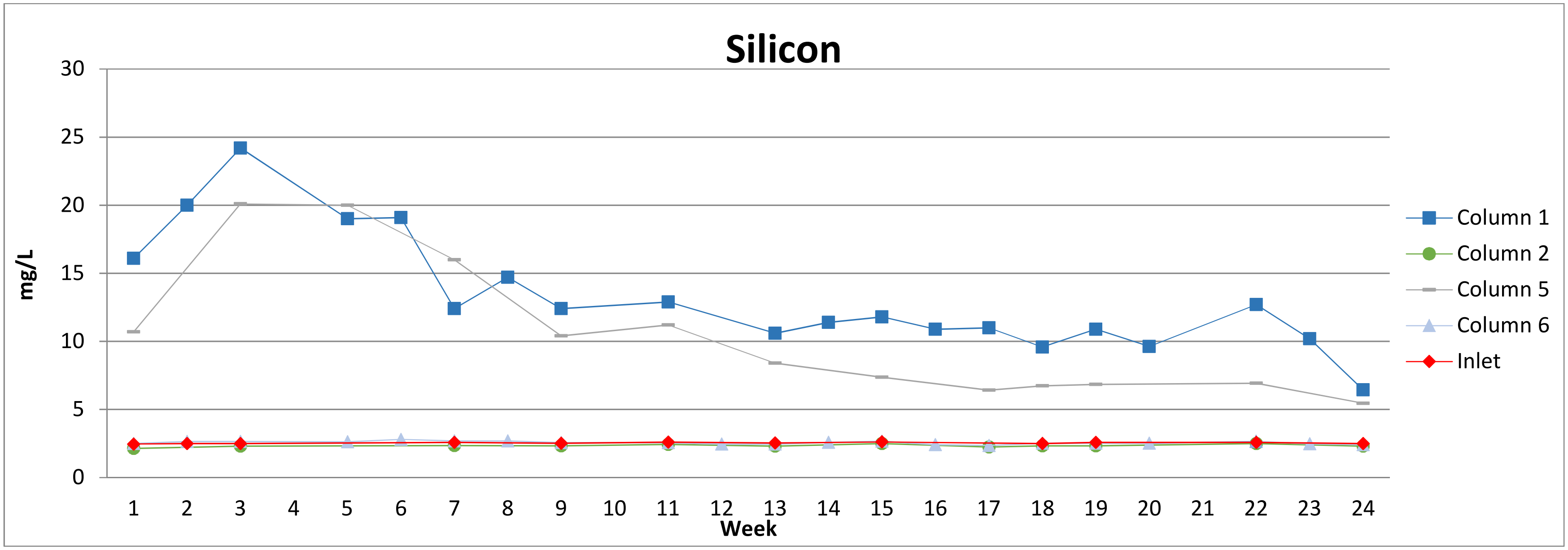


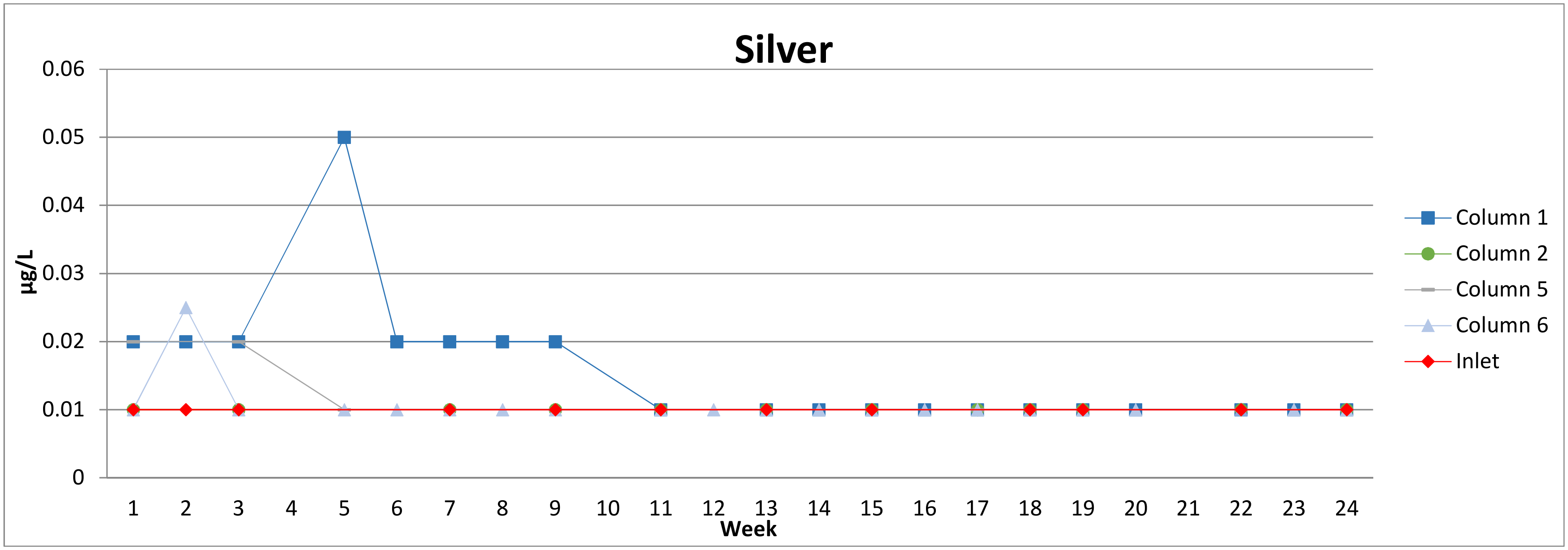
Combined Water Quality Results Graphed



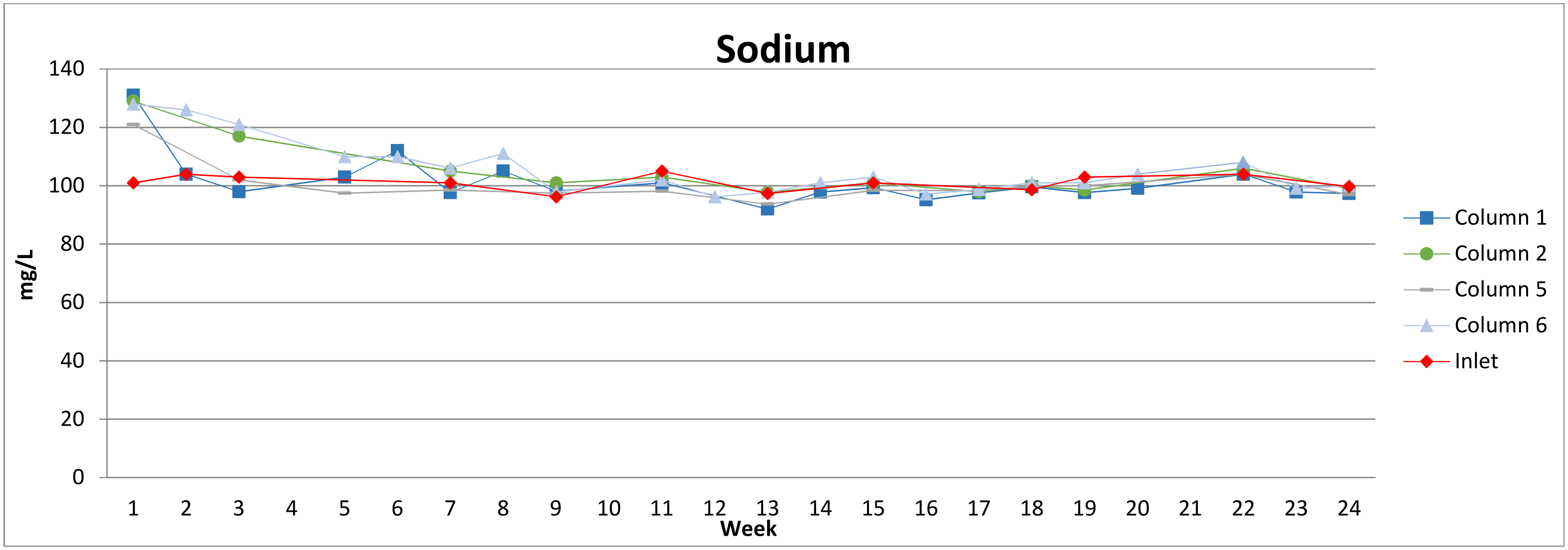


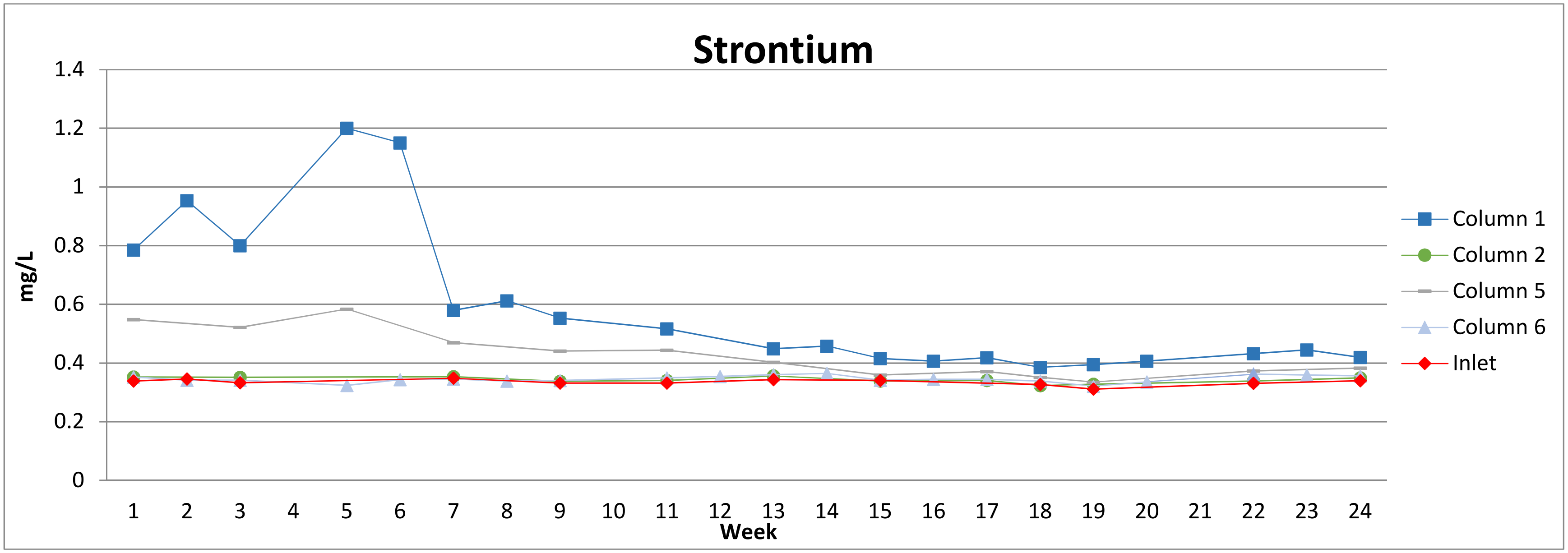
Combined Water Quality Results Graphed



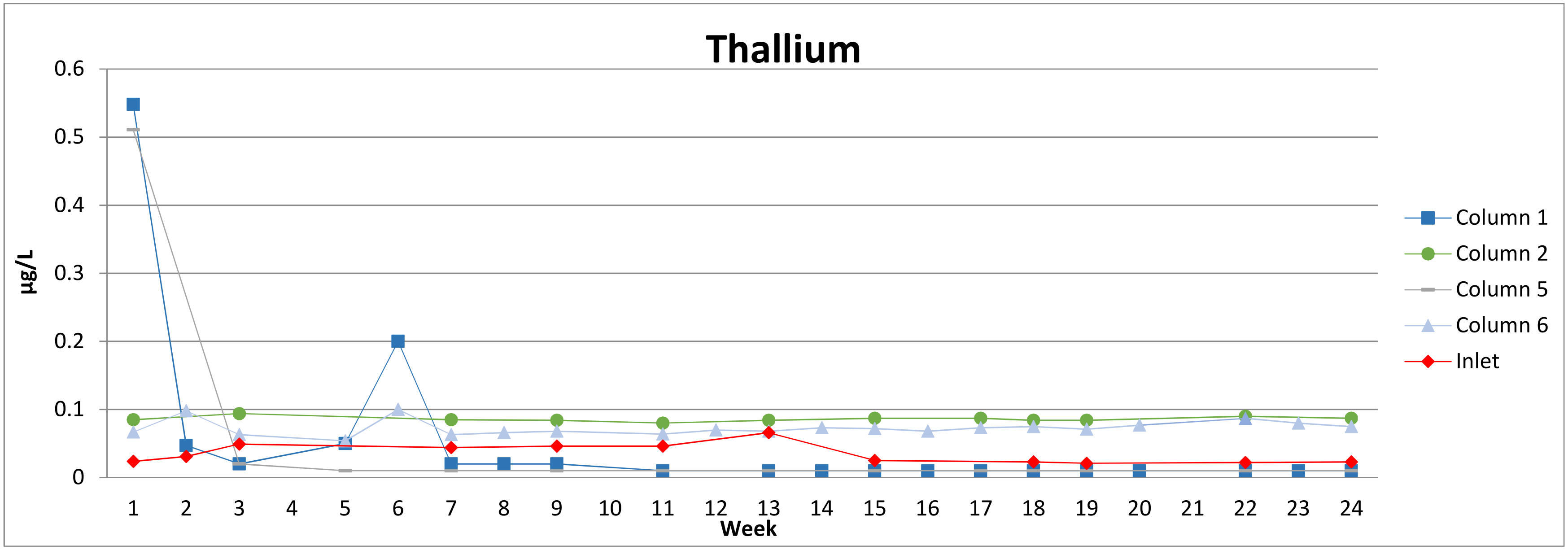


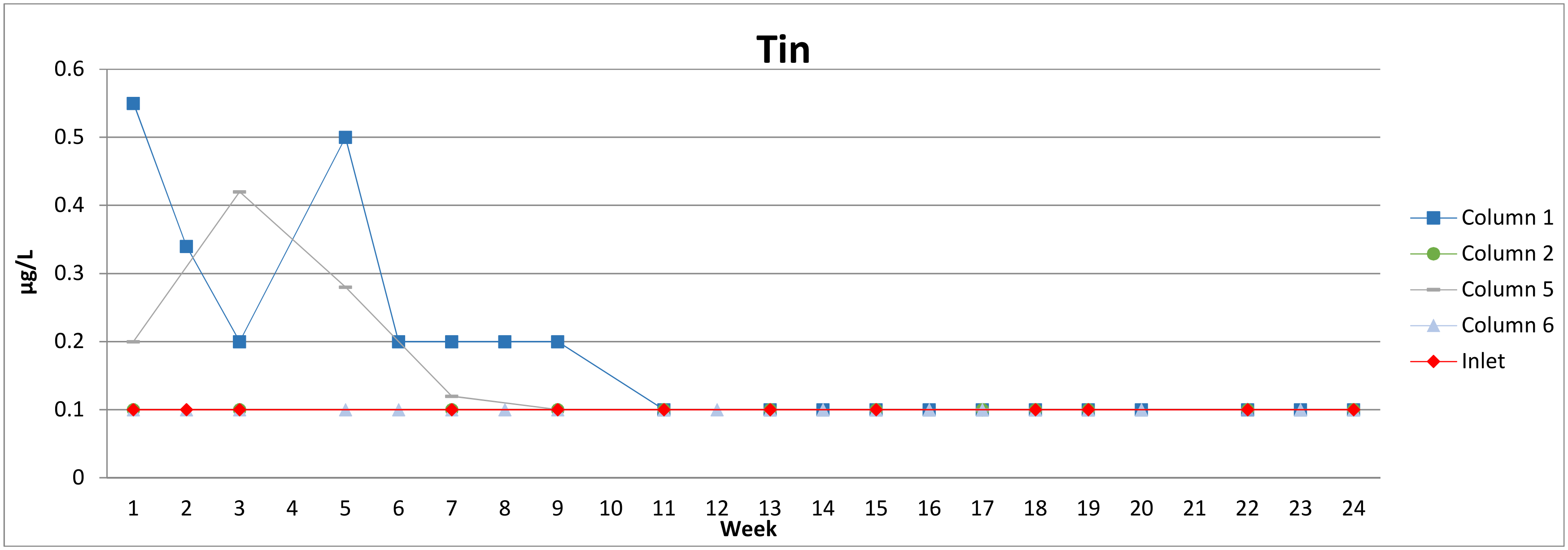
Combined Water Quality Results Graphed



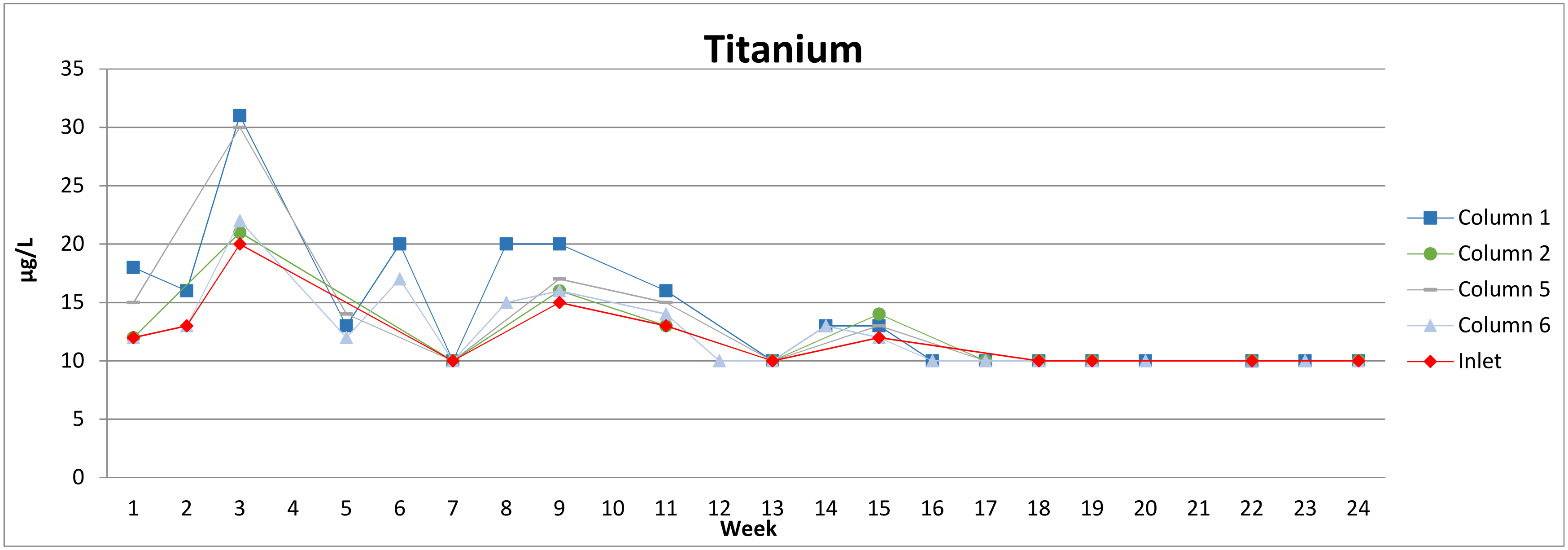


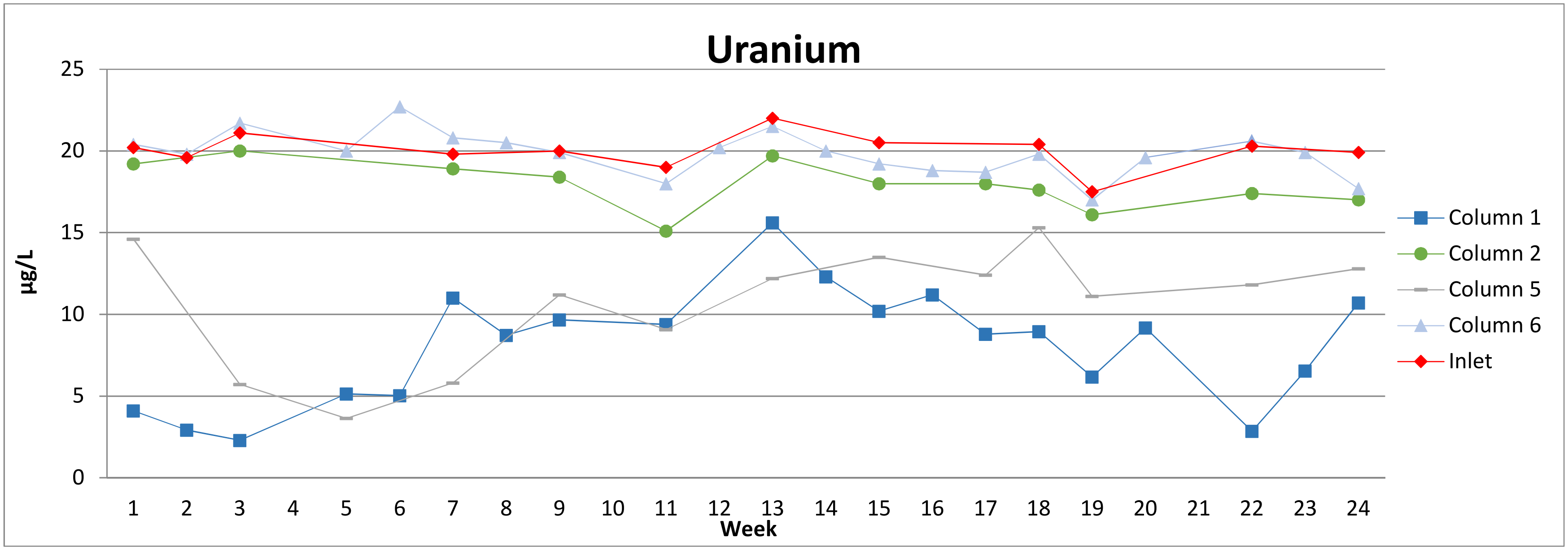
Combined Water Quality Results Graphed



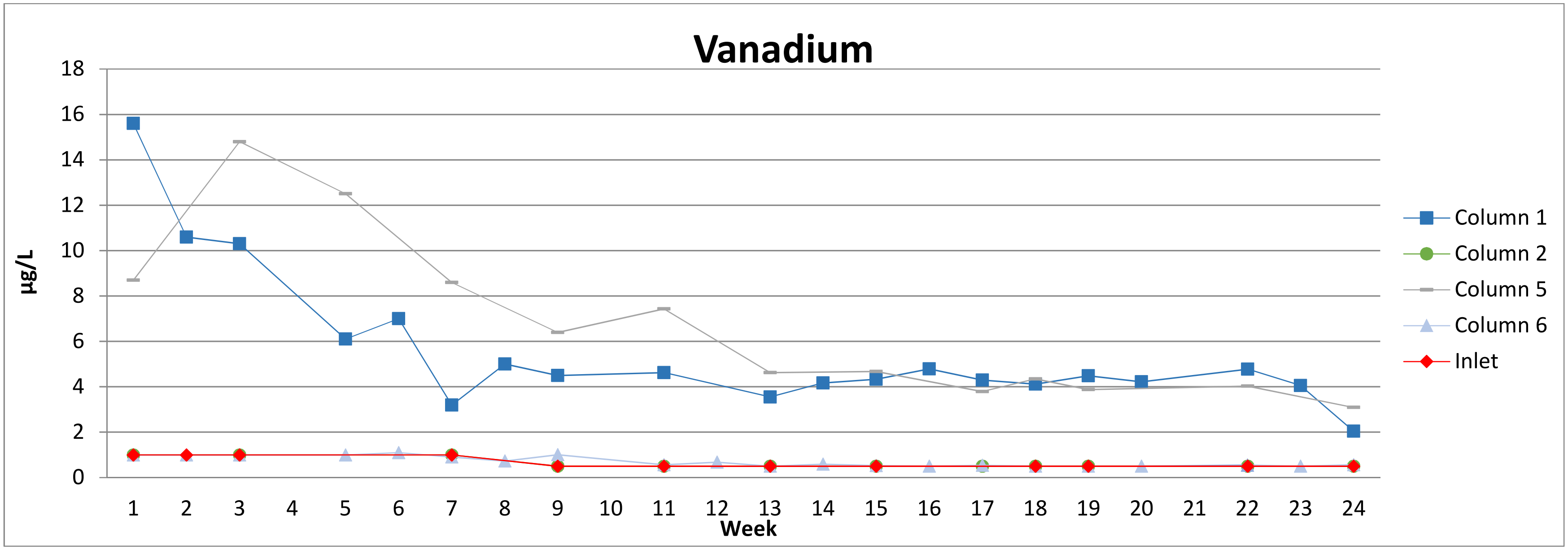


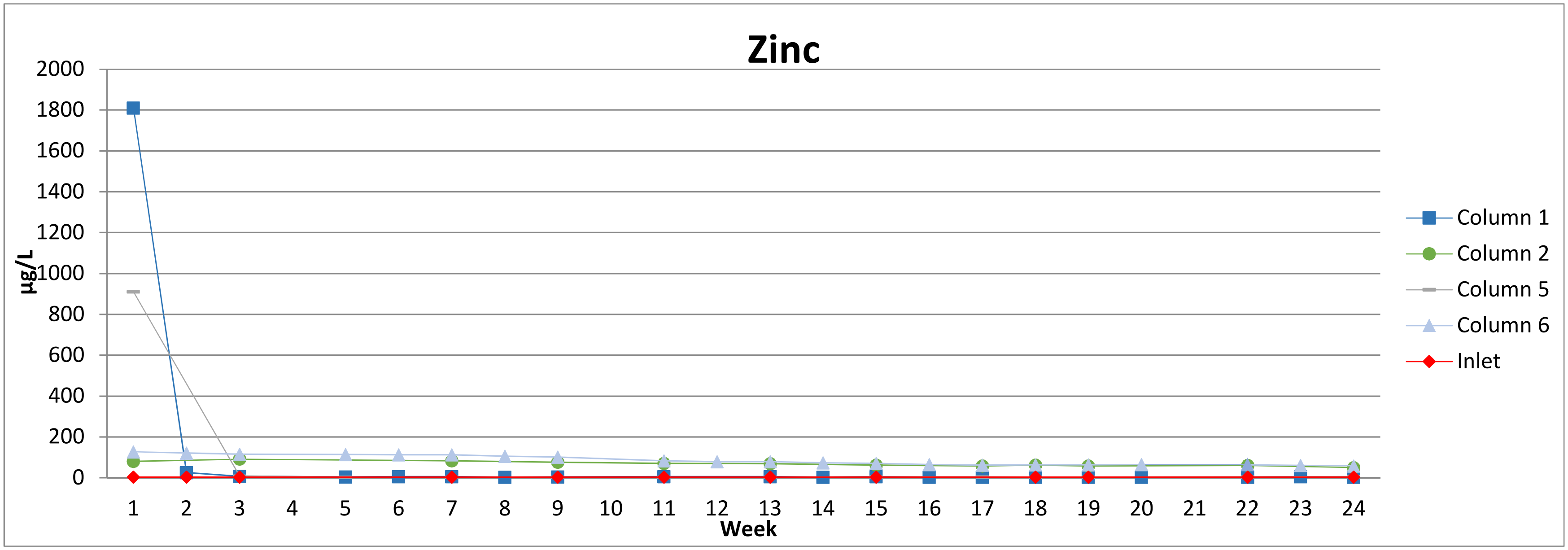
Combined Water Quality Results Graphed





Combined Water Quality Results Graphed





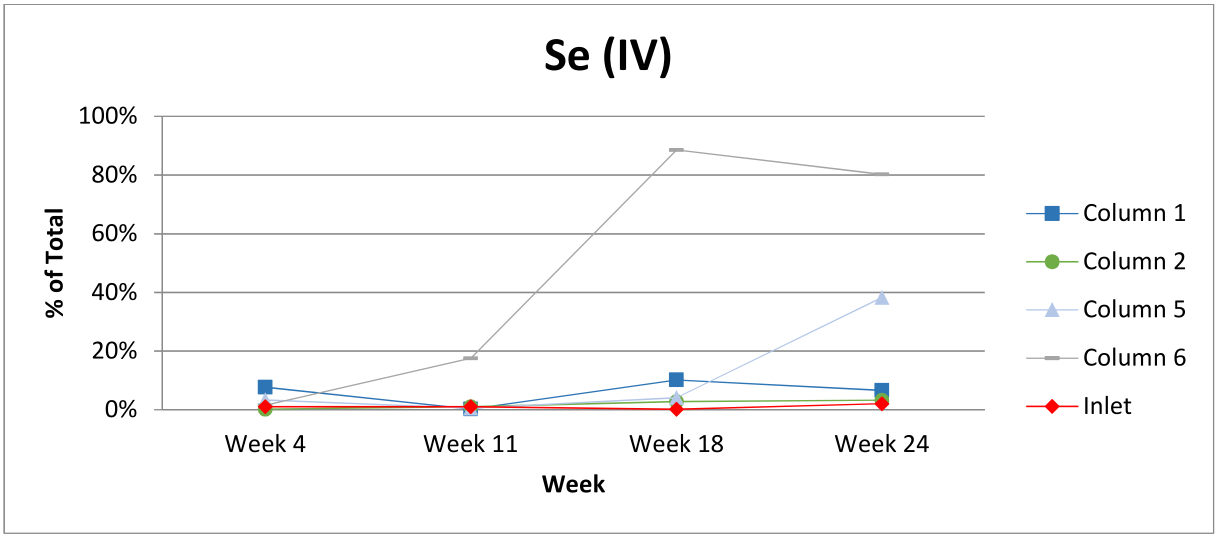
Appendix D.11

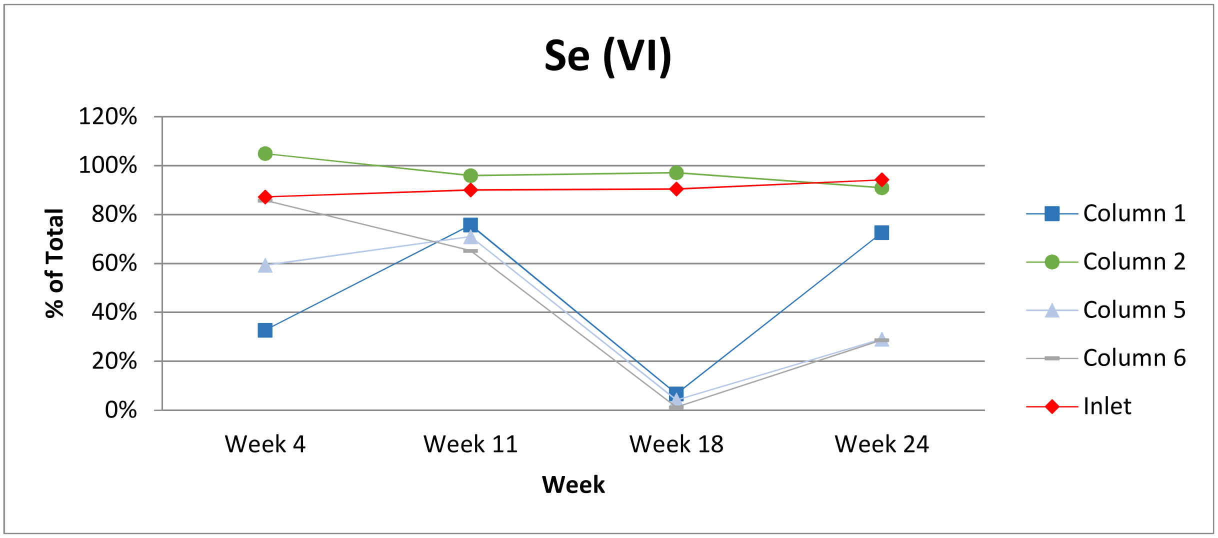
Liquid Phase Selenium Speciation Results Tabulated

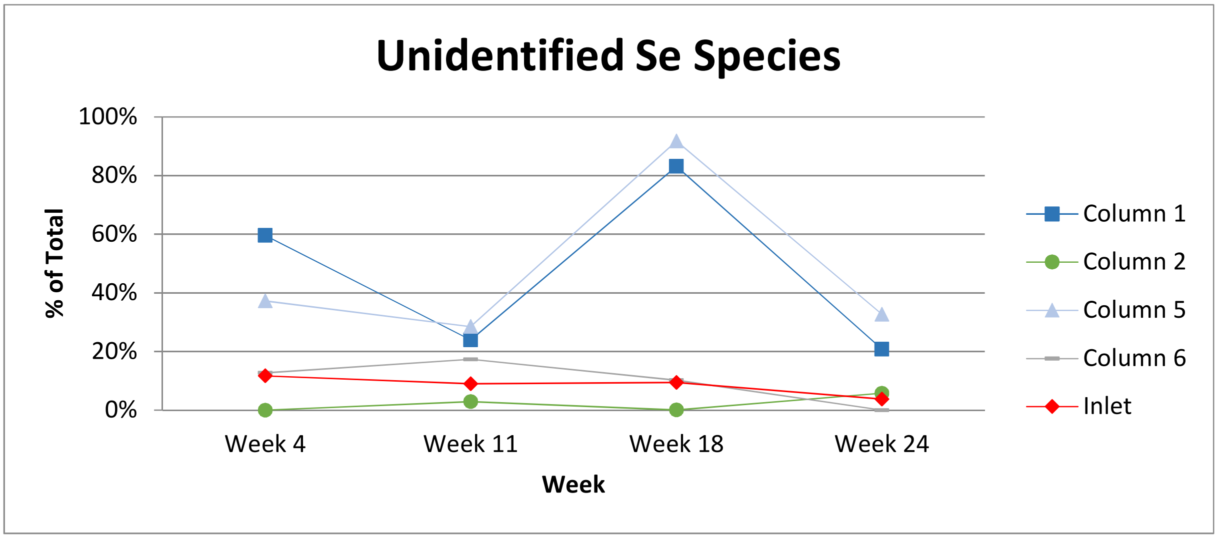
		Results in ppb				Results as a % of Total		
Sample	**Date**	**Se(IV)**	**Se(VI)**	**Unidentified**	**Total**	**Se(IV)**	**Se(VI)**	**Unidentified**
Inlet	Week 4	1.1	87.1	11.7	99.9	1.10%	87.19%	11.71%
Inlet	Week 11	**1**	88	8.8	97.8	1.02%	89.98%	9.00%
Inlet	Week 18	**0.20**	91.5	9.53108623	101.2	0.20%	90.38%	9.42%
Inlet	Week 24	2.0	90.1	3.60580007	95.7	2.07%	94.16%	3.77%
Column 1	Week 4	0.4	1.7	3.1	5.2	7.69%	32.69%	59.62%
Column 1	Week 11	**0.05**	13.1	4.15	17.3	0.29%	75.72%	23.99%
Column 1	Week 18	0.5	0.3	3.82419641	4.6	10.21%	6.65%	83.13%
Column 1	Week 24	**0.4**	4.4	1.25325007	6.0	6.62%	72.65%	20.73%
Column 2	Week 4	0.2	100	0	95.3	0.21%	104.93%	0.00%
Column 2	Week 11	**1**	85	2.6	88.6	1.13%	95.94%	2.93%
Column 2	Week 18	2.4	81.6	0.06283525	84	2.82%	97.11%	0.07%
Column 2	Week 24	2.6	71.7	4.53280217	78.9	3.29%	90.96%	5.75%
Column 5	Week 4	0.2	3.5	2.2	5.9	3.39%	59.32%	37.29%
Column 5	Week 11	**0.05**	6.6	2.65	9.3	0.54%	70.97%	28.49%
Column 5	Week 18	**0.2**	0.2	4.4961756	4.9	4.08%	4.16%	91.76%
Column 5	Week 24	1.2	0.9	1.0490365	3.2	38.27%	29.07%	32.66%
Column 6	Week 4	1.1	62	9.2	72.3	1.52%	85.75%	12.72%
Column 6	Week 11	8.4	31.2	8.3	47.9	17.54%	65.14%	17.33%
Column 6	Week 18	14.5	**0.2**	1.68178559	16.4	88.53%	1.22%	10.25%
Column 6	Week 24	16.5	5.9	0	20.6	80.24%	28.62%	0.00%

Bold text indicates result at or below method detection limit

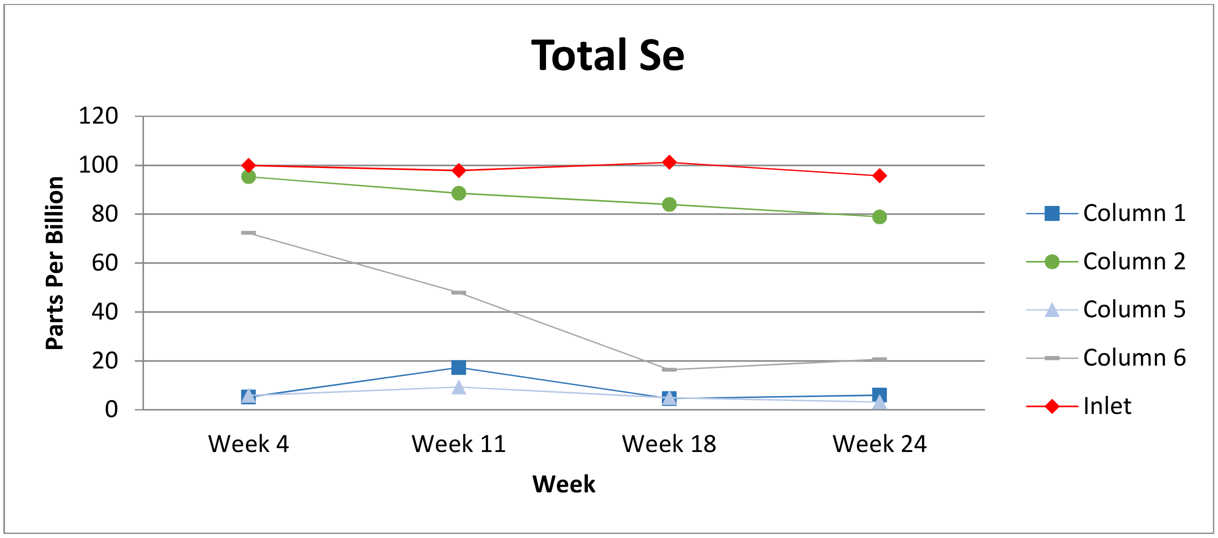
Highlighted column indicates that majority concentration of Se is in this species

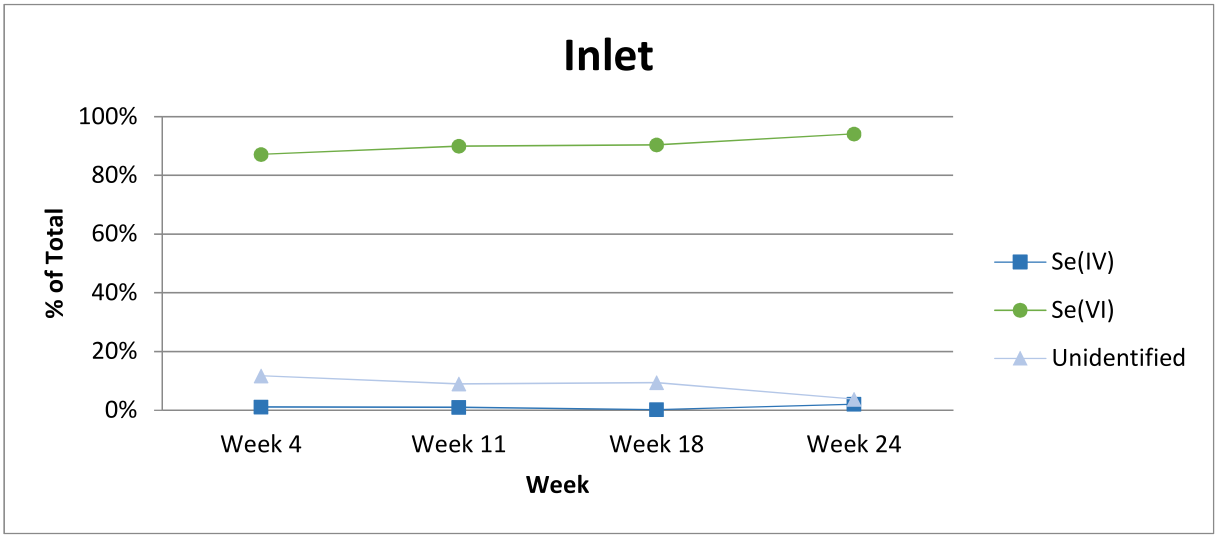

Se (IV)
100%
80%
60%
40%
20%
0%
% of Total
Week 4
Week 11
Week 18
Week 24
Week
Column 1
Column 2
Column 5
Column 6
Inlet

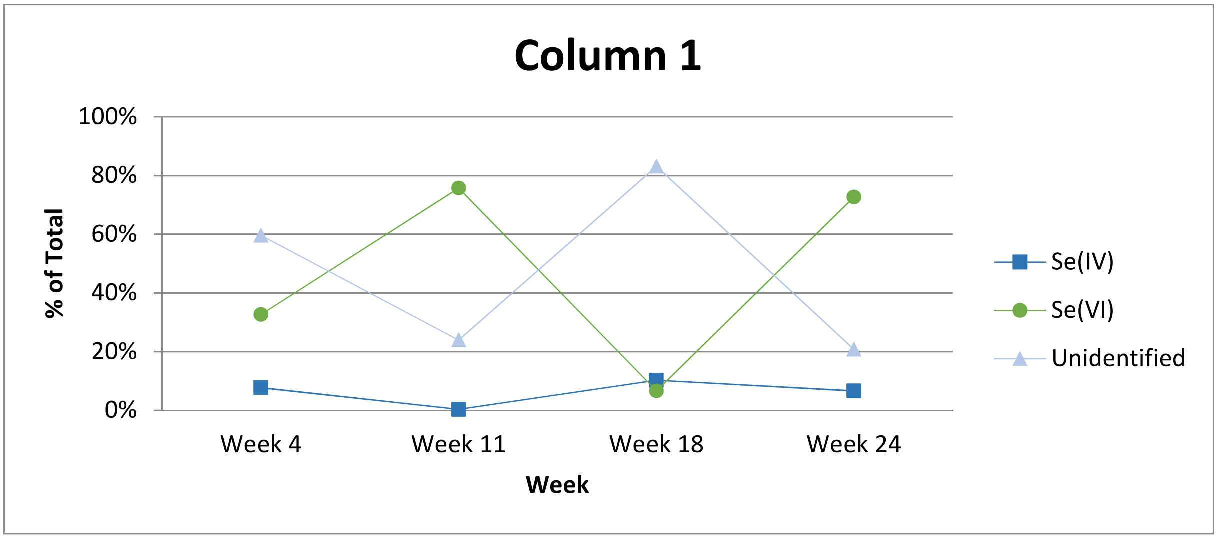

Se (VI)
120%
100%
80%
60%
40%
20%
0%
% of Total
Week 4
Week 11
Week 18
Week 24
Week
Column 1
Column 2
Column 5
Column 6
Inlet


Unidentified Se Species
100%
80%
60%
40%
20%
0%
% of Total
Week 4
Week 11
Week 18
Week 24
Week
Column 1
Column 2
Column 5
Column 6
Inlet

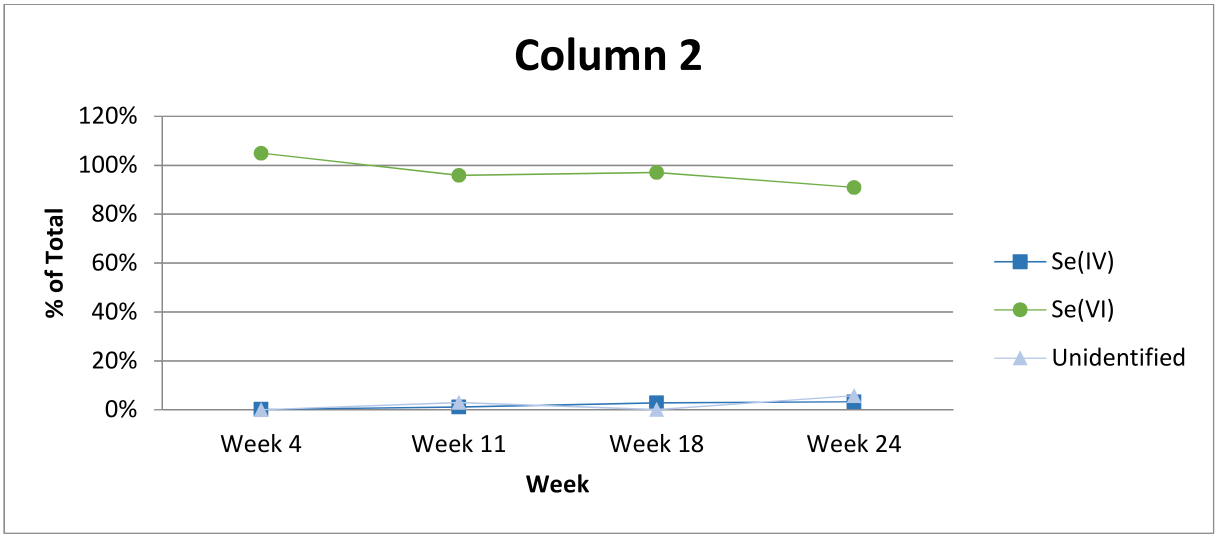
Appendix D.12 Graphed Liquid Phase Selenium Speciation Results

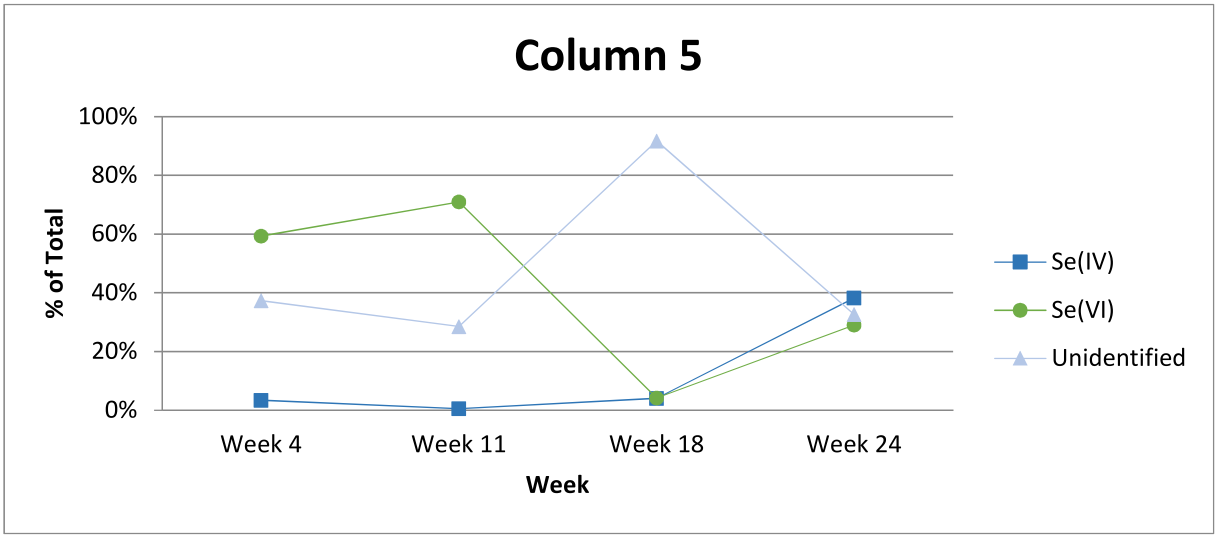


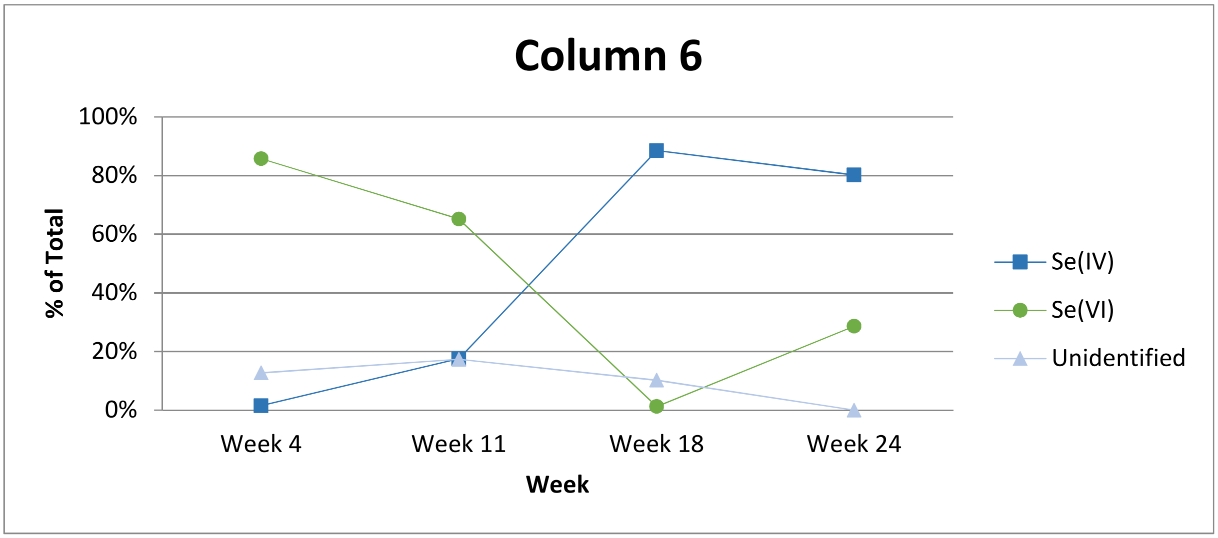




Appendix D.12 Graphed Liquid Phase Selenium Speciation Results

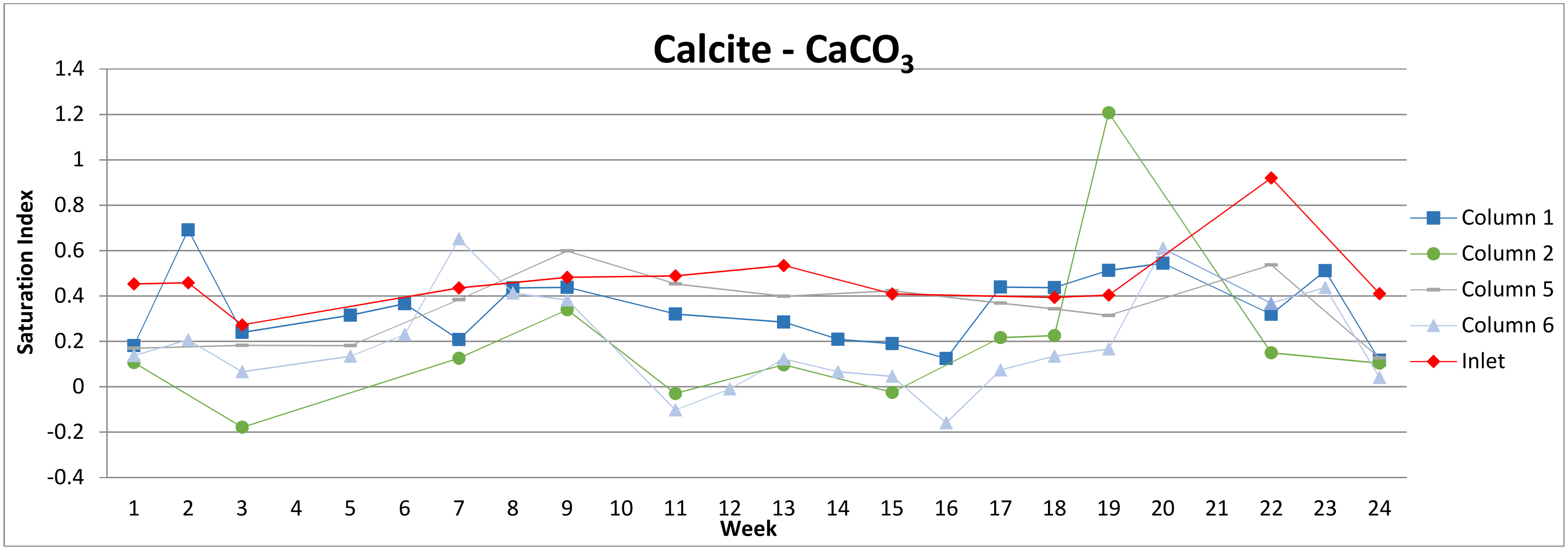


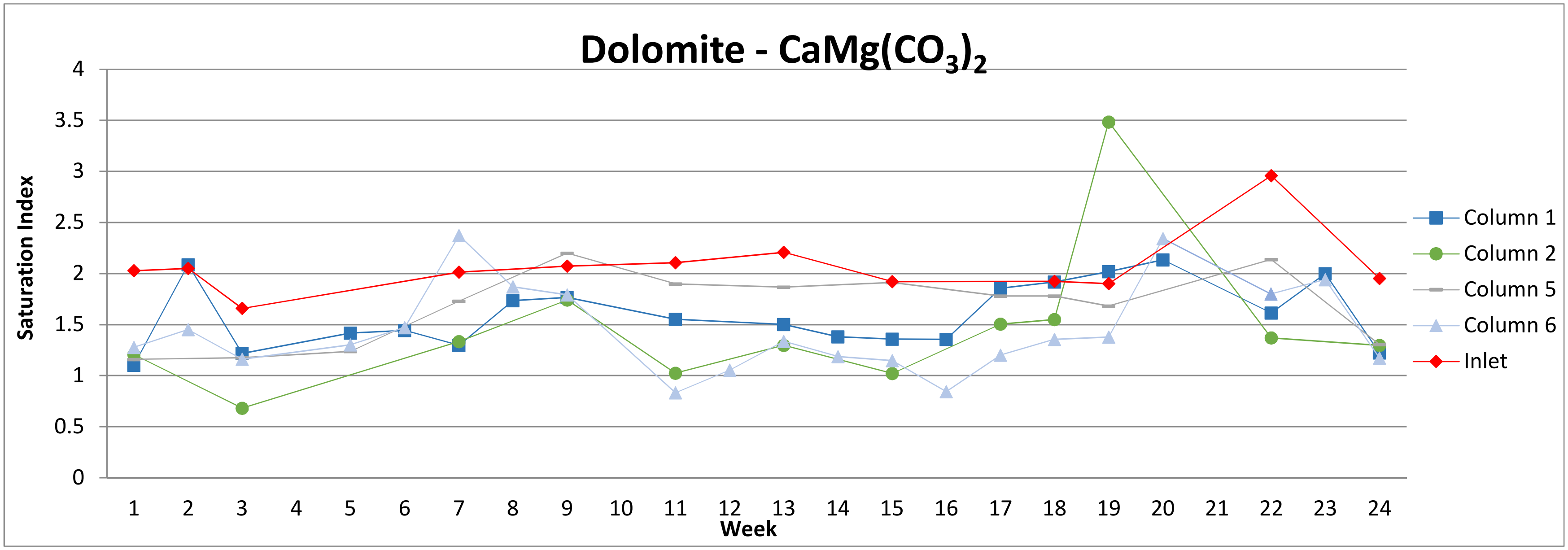




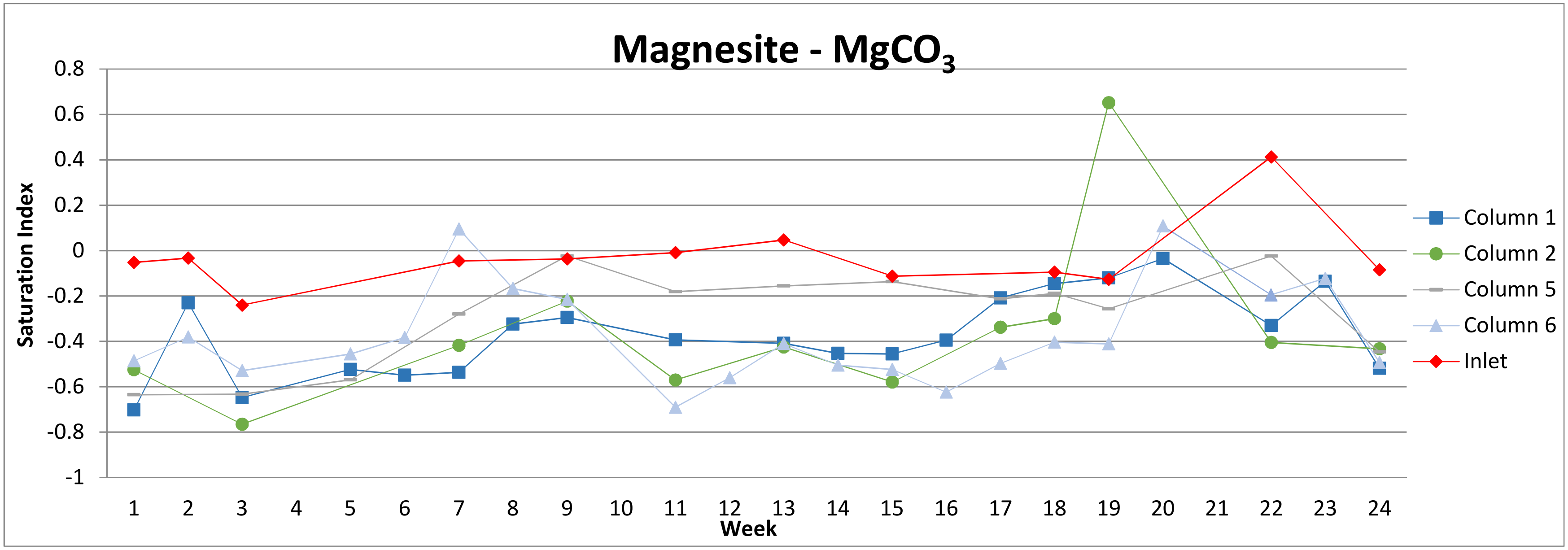
Appendix D.13

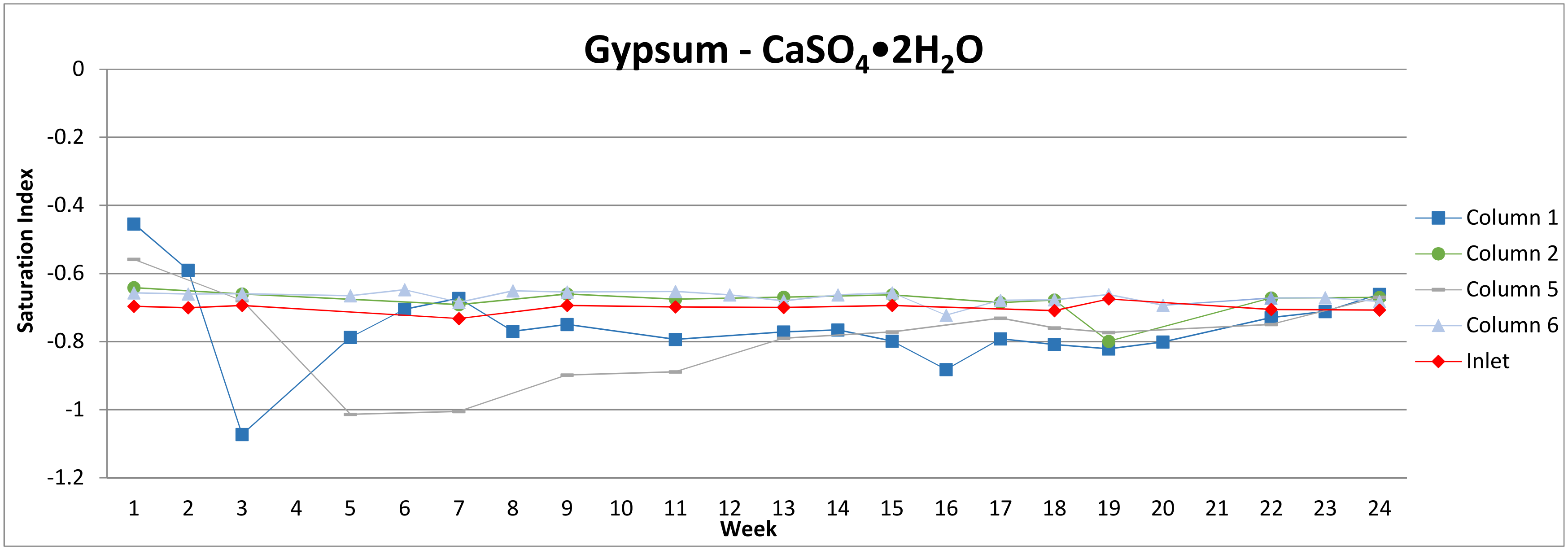
PHREEQC Modelled Saturation Indices for Minerals of Interest



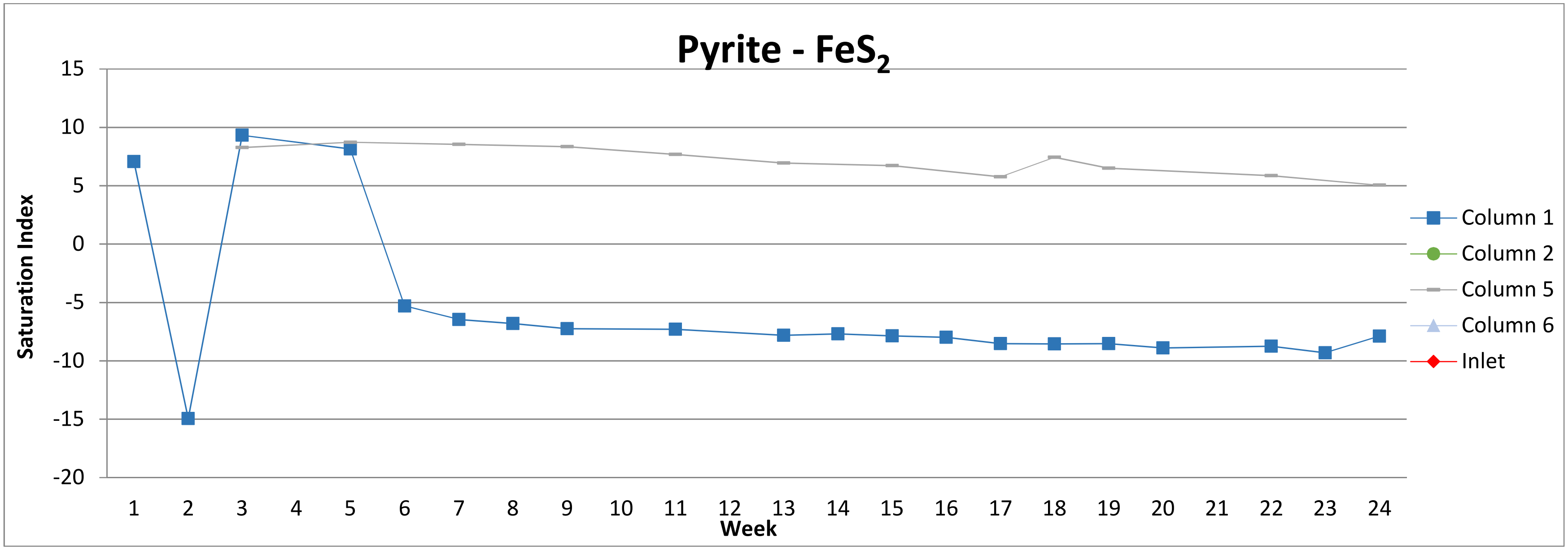


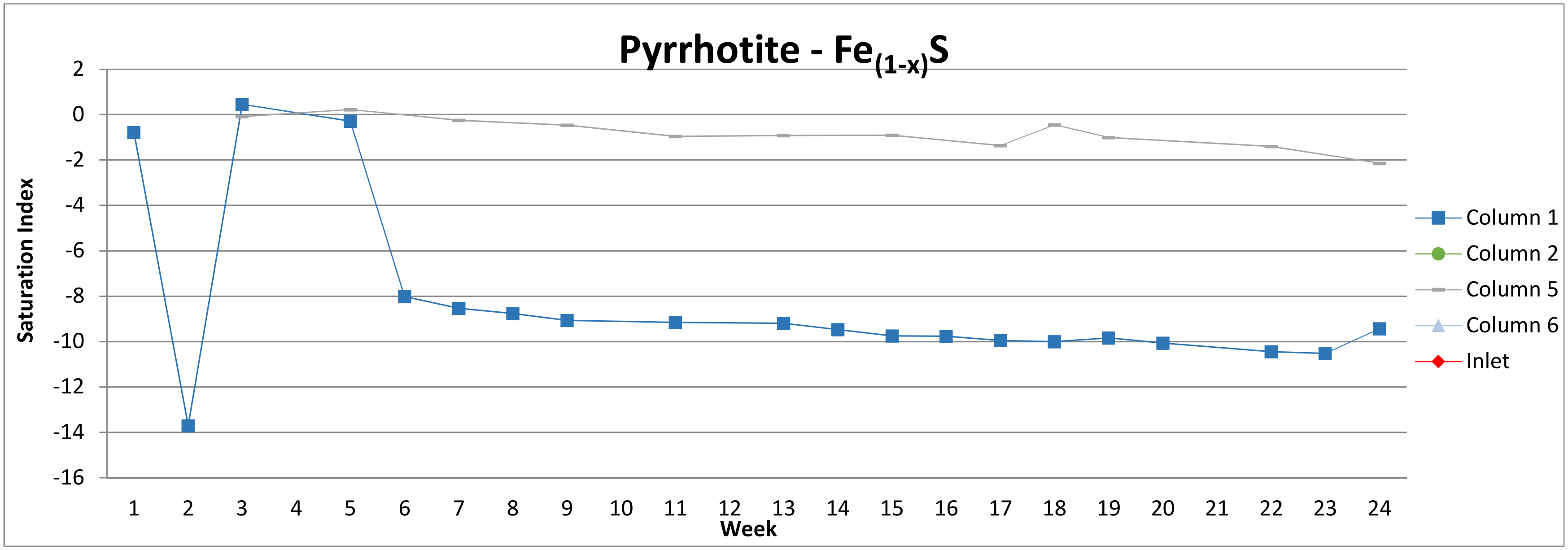
Appendix D.13 PHREEQC Modelled Saturation Indices for Minerals of Interest



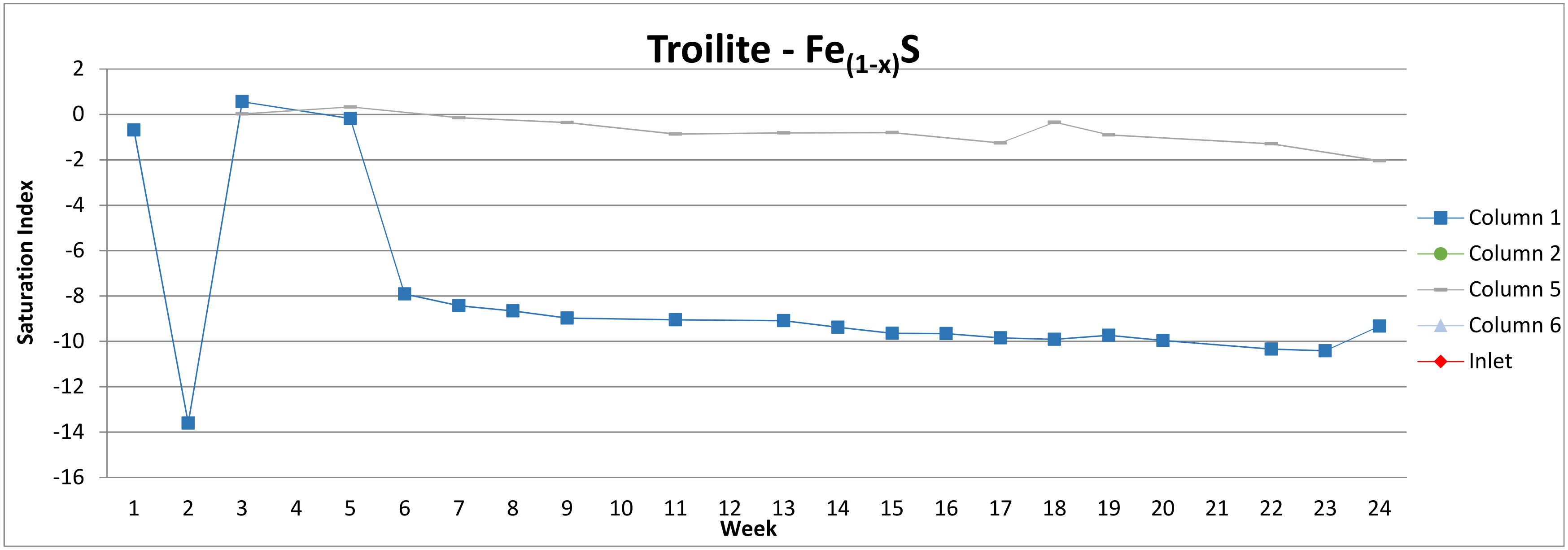


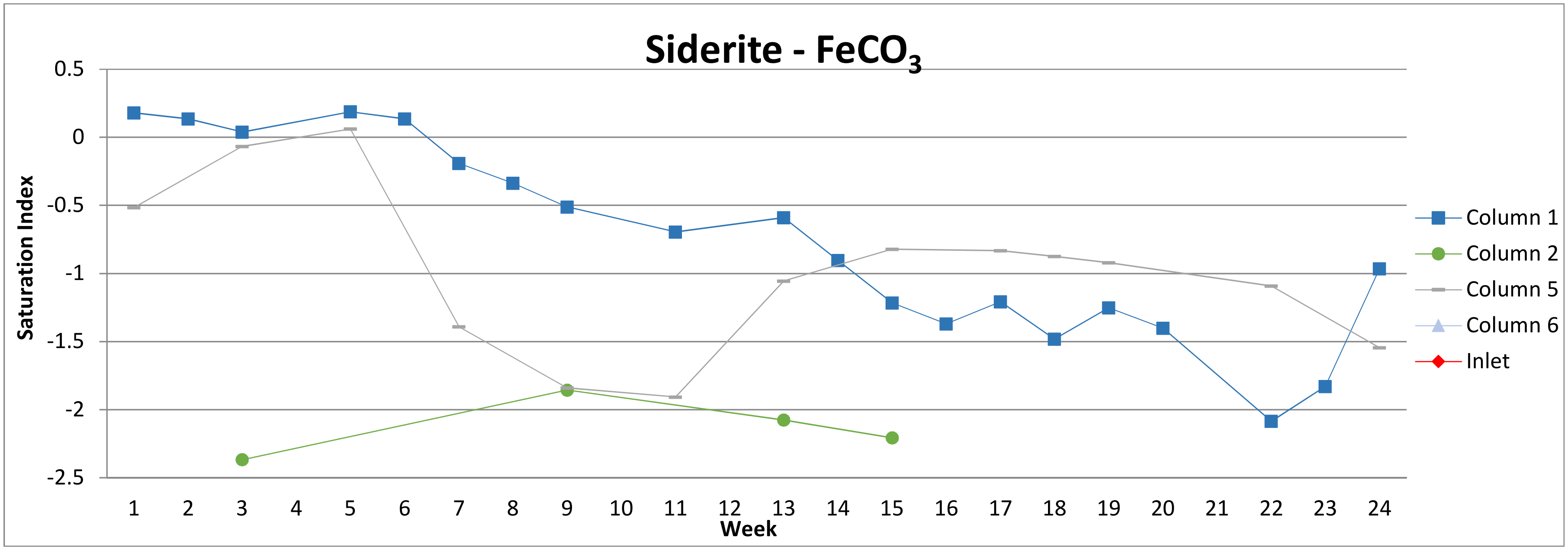
PHREEQC Modelled Saturation Indices for Minerals of Interest



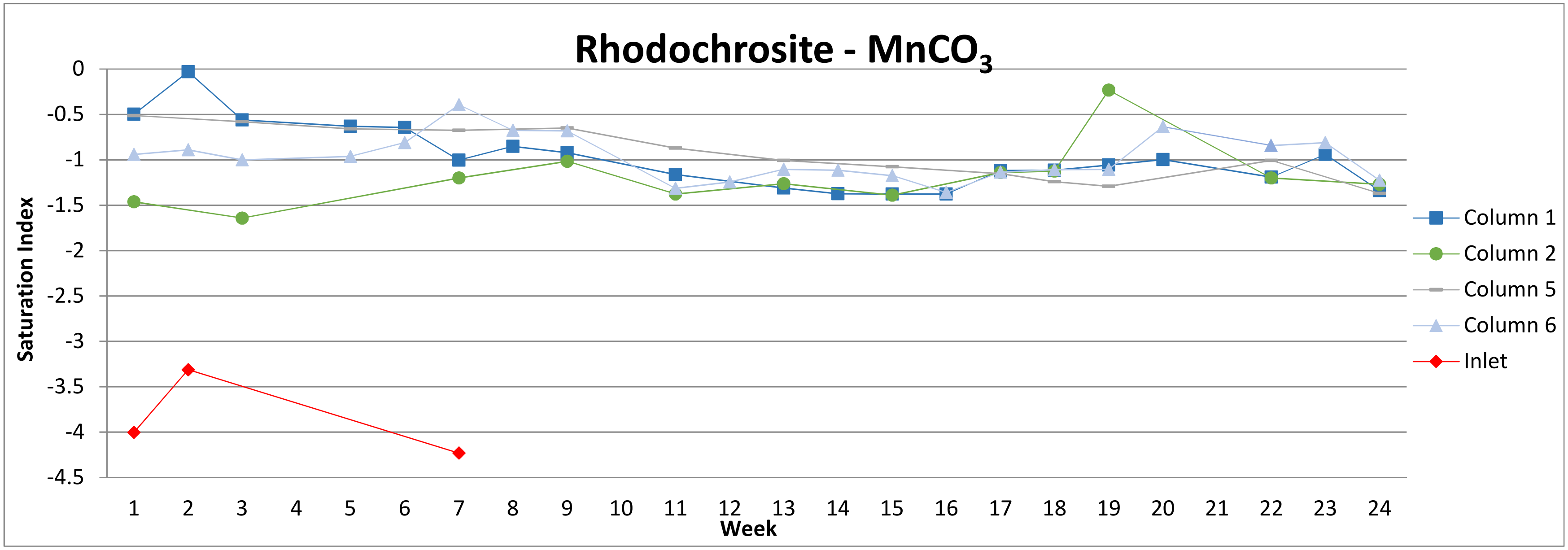


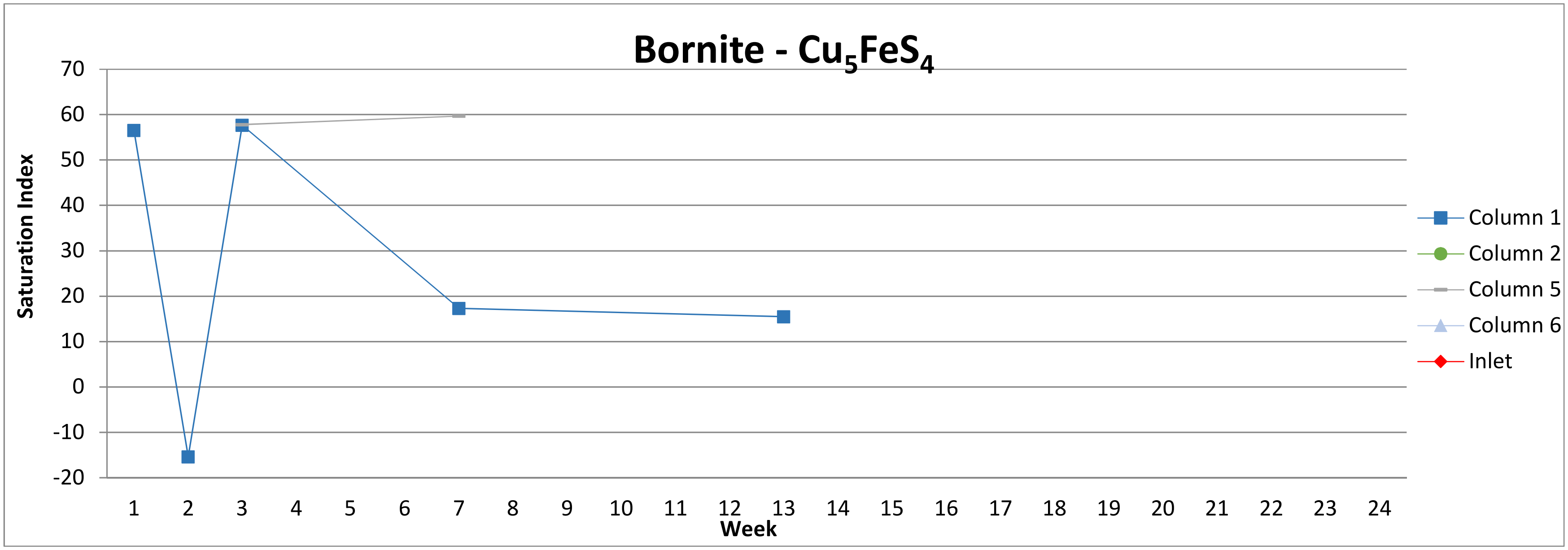
PHREEQC Modelled Saturation Indices for Minerals of Interest



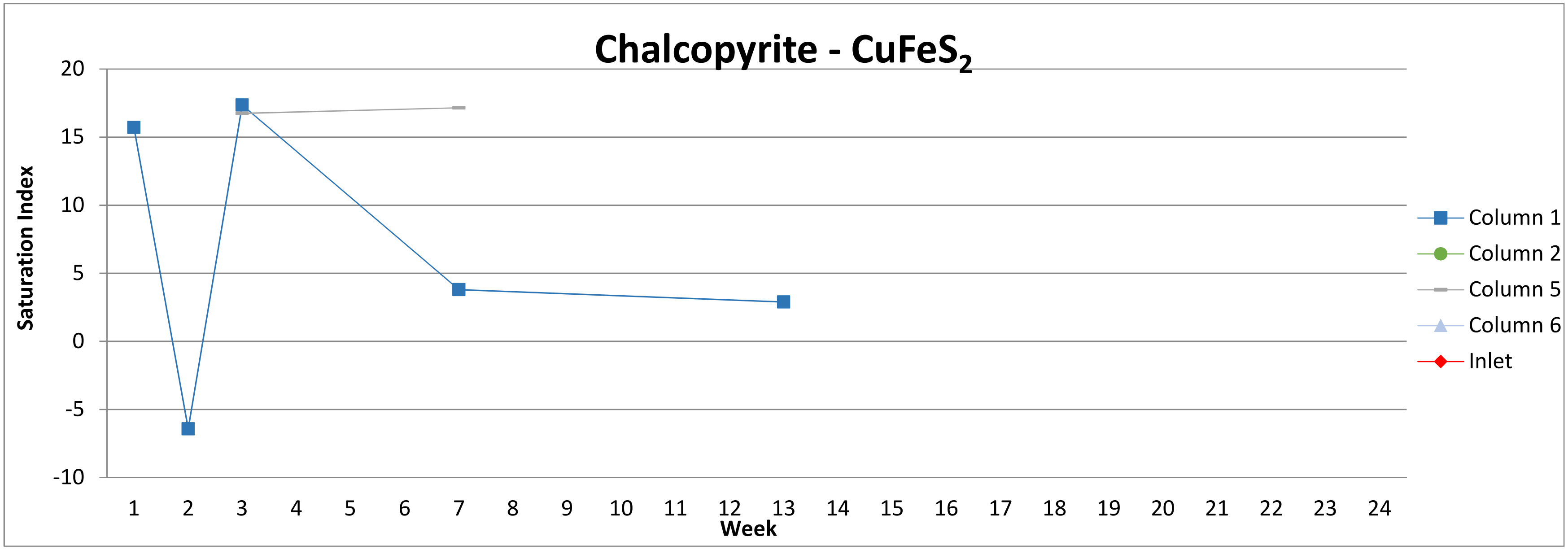


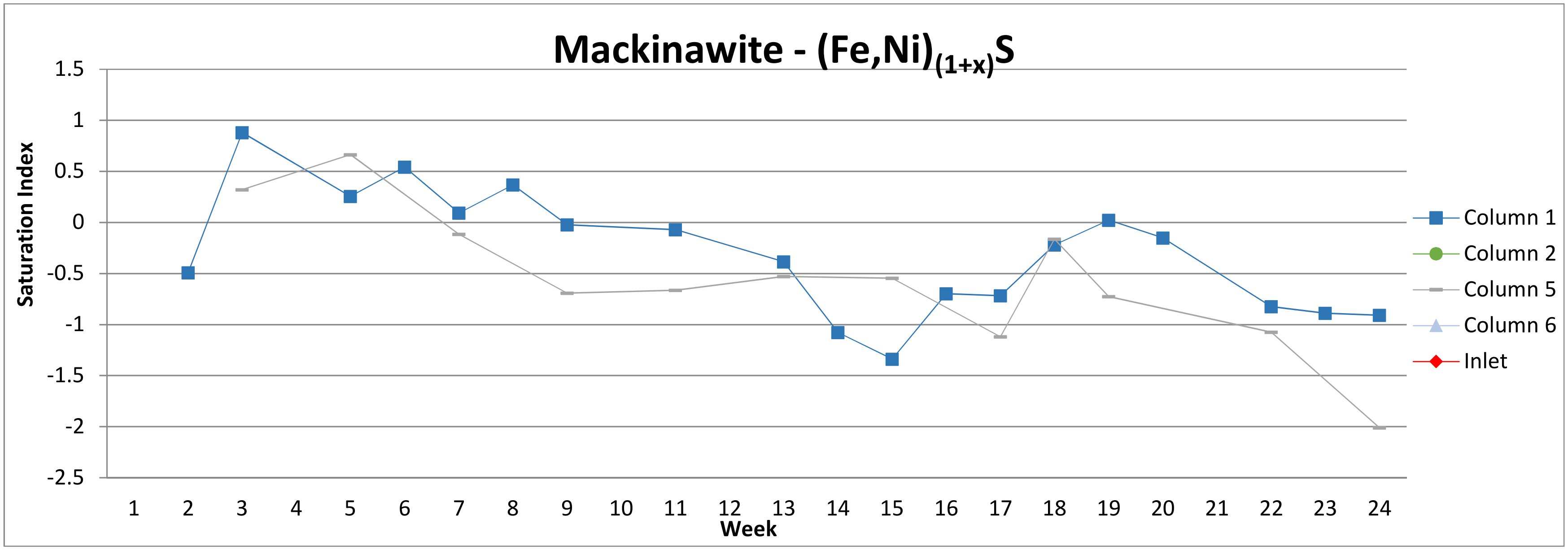
PHREEQC Modelled Saturation Indices for Minerals of Interest





PHREEQC Modelled Saturation Indices for Minerals of Interest





Comparison of Column 1 Effluent and British Columbia Water Quality Guidelines

All results in mg/L	**BC WQG**		**Column 1**	**Column 1**	**Column 1**	**Column 1**	**Column 1**	**Column 1**	**Column 1**	**Column 1**	**Column 1**
Week	**N/A**		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
pH	**Guideline a function of upstream concentrations**		6.19	6.11	6.13	6.08	6.04	6.02	6.35	6.41	
Dissolved Oxygen	**DO > 5**			0.54		0.653333333	0.93	1.195	1.41	2.083333333	2.38
Hardness (as CaCO3)	**N/A**		1530	1810	1410	""	1950	2040	1220	1400	1230
Alkalinity Total (as CaCO3)	**N/A**		869	3880	1040	""	1310	1410	768	981	995
Ammonia, Total (as N)	**A function of pH and temperature, using an average temp of 20 C, minimum pH shown in guidelines is 6.5. Guideline is inversely related to temperature**		8.79	5.47	0.258	""	0.72	1.61	1.03	0.991	0.715
Bromide (Br)			**1**	**2.5**	**1**	""	**1**	**1**	**1**	**1**	**0.5**
Chloride (Cl)	**Total Cl^- < 600**		21.0	**25.0**	11.0	""	**10.0**	**10.0**	**10.0**	**10.0**	10.1
Fluoride (F)	**Total Fl^- = [-51.73 + 92.57 log(10) (hardness*)] × 0.01, valid for 10-385 mg/L CaCO3 hardness, above which point a site-specific assessment may be required. A hardness of 3685 mg/L CaCO3 results in a F guideline of 1.9**		**0.4**	1	**0.4**	""	**0.4**	**0.4**	**0.4**	**0.4**	**0.2**
Nitrate (as N)	**32.8**		**0.1**	0.26	0.16	""	2.54	2.47	**0.1**	**0.1**	0.05
Nitrite (as N)	**(Cl^- < 10) NO_2^- < (CL^-)*0.03**	**(Cl^- > 10) NO_2^- < 0.60**	**0.02**	**0.05**	**0.02**	""	0.070	0.038	0.026	**0.02**	**0.01**
Sulfate (SO4)	**(Water hardness ≤ 250 mg/L). Total SO_4^{-2} = variable, maximum of 429 mg/L**	**(Water hardness > 250 mg/L). Total SO_4^{-2} may require a site-specific assessment**	803	719	175	""	319	359	554	404	476
Sulphide (as S)			0.189	0.218	4.28	""	0.81	2.05	0.62	1.58	0.82
Dissolved Organic Carbon	**Guideline a function of upstream concentrations**		583	1110	629	""	886	825	237	381	219
			000.05787								
Aluminum (Al)-Dissolved	**pH < 6.5, Al < e^[1.209 – 2.426*(pH)+0.286(pH)^2]**	**pH ≥ 6.5 Al < 0.1**	0.118	0.0929	0.0670	""	0.0345	0.0383	0.0143	0.0247	0.0175
Antimony (Sb)-Dissolved			0.0516	0.00577	0.00273	""	0.00216	0.00219	0.00356	0.00250	0.00367
Arsenic (As)-Dissolved	**Total As < 0.005**		0.0548	0.00391	0.00325	""	0.00673	0.00858	0.00668	0.00712	0.00763
Barium (Ba)-Dissolved			0.0845	0.0818	0.473	""	2.14	0.957	0.183	0.497	0.535
Beryllium (Be)-Dissolved			**0.0002**	**0.0002**	**0.0002**	""	**0.0005**	**0.001**	**0.0002**	**0.0002**	**0.0002**
Bismuth (Bi)-Dissolved			**0.001**	**0.001**	**0.001**	""	**0.0025**	**0.001**	**0.001**	**0.0001**	**0.0001**
Boron (B)-Dissolved	**Total B < 1.2**		0.533	0.555	0.446	""	0.325	0.314	0.185	0.196	0.190

Cadmium (Cd)-Dissolved	Cd < 0.001*(e^[1.03 × ln(hardness) – 5.274]), applies to water hardnesses (mg/L CaCO3) between 7 – 455 mg/L. A hardness of 455 mg/L CaCO3 results in a Cd level 0f 0.0028. Higher hardness levels require possible site-specific assessment.	0.000320	0.000055	0.000037	""	**0.00005**	**0.00010**	0.000021	0.000013	0.000014
Calcium (Ca)-Dissolved		440	542	418	""	557	633	320	376	320
Chromium (Cr)-Dissolved		0.0106	0.00564	0.00426	""	0.00316	0.0033	0.00125	0.00199	0.00154
Cobalt (Co)-Dissolved	Total Co < 0.110	0.309	0.300	0.0168	""	0.0236	0.0237	0.0129	0.00489	0.00352
Copper (Cu)-Dissolved	Total Cu < 0.001*(0.094 hardness + 2), applies to water hardnesses (mg/L CaCO3) between 13 – 400 mg/L. 400 mg/L CaCO3 of hardness corresponds to a D-Cu guideline of 0.0396 mg/L	0.00455	0.00182	0.00067	""	**0.001**	**0.001**	0.00071	**0.0005**	**0.0005**
Iron (Fe)-Dissolved	0.35	26.3	25.2	20.3	""	35.2	32.7	7.63	4.59	2.62
Lead (Pb)-Dissolved	Total Pb < 0.001*(e[1.273 ln (hardness*) -1.460]), applies to water hardnesses (mg/L CaCO3) between 8 – 360 mg/L. 360 mg/L CaCO3 of hardness corresponds to a T-Pb guideline of 0.0338 mg/L	0.001170	0.000140	0.000130	""	**0.000250**	**0.000100**	0.000220	**0.000100**	**0.000100**
Lithium (Li)-Dissolved		0.232	0.202	0.201	""	0.211	0.224	0.201	0.176	0.229
Magnesium (Mg)-Dissolved		104	111	90.0	""	135	129	103	113	104
Manganese (Mn)-Dissolved	Total Mn ≤ 0.01102 * hardness + 0.54, applies to water hardnesses (mg/L CaCO3) between 25-259 mg/L. 289 mg/L. Higher hardness levels require possible site-specific assessment. 289 CaCO3 of hardness corresponds to a T-Mn guideline of 3.39 mg/L	1.24	1.27	0.820	""	0.790	0.774	0.261	0.252	0.185
Molybdenum (Mo)-Dissolved	Total Mo < 2	0.0269	0.0143	0.00082	""	0.00128	0.00077	0.00499	0.00199	0.00300
Nickel (Ni)-Dissolved		1.20	1.07	0.0748	""	0.0723	0.0940	0.0958	0.0413	0.0360
Phosphorous (P)-Dissolved	Total P < 0.015	0.91	0.62	1.23	""	1.19	1.17	0.3	0.59	0.32
Potassium (K)-Dissolved		139	108	64.0	""	47.0	41.4	23.7	23.8	17.8
Selenium (Se)-Dissolved	0.002	0.0494	0.00273	0.00167	""	0.00569	0.0057	0.0187	0.00580	0.0110
Silicon (Si)-Dissolved		16.1	20.0	24.2	""	19.0	19.1	12.4	14.7	12.4
Silver (Ag)-Dissolved	Hardness > 100 mg/L T-Ag < 0.003	**0.00002**	**0.00002**	**0.00002**	""	**0.00005**	**0.00002**	**0.00002**	**0.00002**	**0.00002**
Sodium (Na)-Dissolved		131	104	98.0	""	103	112	97.7	105	98.1
Strontium (Sr)-Dissolved		0.785	0.953	0.800	""	1.20	1.15	0.580	0.612	0.553
Thallium (Tl)-Dissolved		0.000548	0.000047	**0.00002**	""	**0.00005**	**0.0002**	**0.00002**	**0.00002**	**0.00002**
Tin (Sn)-Dissolved		0.00055	0.00034	**0.0002**	""	**0.0005**	**0.0002**	**0.0002**	**0.0002**	**0.0002**
Titanium (Ti)-Dissolved		0.018	0.016	0.031	""	0.013	0.020	**0.01**	0.020	0.020
Uranium (U)-Dissolved		0.00409	0.00291	0.00229	""	0.00513	0.00503	0.0110	0.00872	0.00967
Vanadium (V)-Dissolved		0.0156	0.0106	0.0103	""	0.0061	0.0070	0.0032	**0.0050**	0.0045
Zinc (Zn)-Dissolved	Total Zn < 0.001*(33 + 0.75(hardness - 90)), applies to water hardness between 90 – 500 mg/L CaCO3, above which point a site-specific assessment may be required. A hardness of 500 mg/L CaCO3 gives a T-Zn guideline of 0.315	1.81	0.0252	0.0077	""	**0.005**	0.006	0.0062	0.003	0.0040

All results in mg/L	Column 1	Column 1	Column 1	Column 1	Column 1	Column 1	Column 1	Column 1	Column 1	Column 1	Column 1	Column 1	Column 1	Column 1	Column 1
Week	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
pH	6.54	6.46		6.67	6.45	6.40	6.51	6.67		6.56	6.86		6.61	6.81	6.59
Dissolved Oxygen		2.613333333		1.326666667	0.466666667	1.6975	1.515	0.97		2.53			1.33	2.846666667	2.436666667
Hardness (as CaCO3)	""	1090	964	932	996	1010	""	908	971	974	1010	""	1060	1040	1010
Alkalinity Total (as CaCO3)	""	861	770	554	787	839	641	880	767	728	692	""	666	674	467
Ammonia, Total (as N)	""	0.0544	0.0085	0.0168	0.0189	0.0102	0.0153	0.0107	0.0643	0.0093	0.0690	""	0.0686	0.0107	**0.005**
Bromide (Br)	""	**1**	**1**	**0.5**	**0.5**	**1**	**0.5**	**0.5**	**0.5**	**0.5**	**0.5**	""	**0.25**	**0.5**	0.5
Chloride (Cl)	""	**10.0**	**10.0**	10.2	10.4	**10.0**	**10.0**	**10.0**	10.1	**10.0**	9.9	""	9.6	10.2	**10.0**
Fluoride (F)	""	**0.4**	**0.4**	0.26	0.30	**0.4**	0.26	0.28	0.26	0.27	0.22	""	0.31	0.28	0.2
Nitrate (as N)	""	**0.1**	**0.1**	**0.05**	**0.05**	**0.1**	**0.05**	**0.05**	1.61	0.05	0.490	""	0.652	1.60	22.6
Nitrite (as N)	""	**0.02**	**0.02**	**0.01**	**0.01**	**0.02**	0.030	0.022	0.219	0.046	0.176	""	0.0679	0.013	0.117
Sulfate (SO4)	""	456	583	517	548	509	476	553	546	487	532	""	573	611	706
Sulphide (as S)	""	1.09	0.031	0.26	0.173	0.215	1.01	0.57	6.7	5.2	3.42	""	5.5	1.32	0.206
Dissolved Organic Carbon	""	112	""	29.1	38.9	39.1	48.3	33.6	36.8	50.3	4.39	""	33.3	""	""
Aluminum (Al)-Dissolved	""	0.0155	""	0.0103	0.0140	0.0147	0.0174	0.0155	0.0125	0.0145	0.0138	""	0.0186	0.0156	0.0073
Antimony (Sb)-Dissolved	""	0.00426	""	0.00474	0.00523	0.00369	0.00293	0.00340	0.00265	0.00288	0.00304	""	0.00233	0.00222	0.00444
Arsenic (As)-Dissolved	""	0.00866	""	0.00793	0.00865	0.00790	0.00955	0.0106	0.00817	0.00965	0.00811	""	0.00912	0.00697	0.00566
Barium (Ba)-Dissolved	""	0.552	""	0.415	0.405	0.368	0.304	0.339	0.176	0.378	0.260	""	0.381	0.265	0.111
Beryllium (Be)-Dissolved	""	**0.0001**	""	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	""	**0.0001**	**0.0001**	**0.0001**
Bismuth (Bi)-Dissolved	""	**0.00005**	""	**0.00005**	**0.00005**	**0.00005**	**0.00005**	**0.00005**	**0.00005**	**0.00005**	**0.00005**	""	**0.00005**	**0.00005**	0.00005
Boron (B)-Dissolved	""	0.162	""	0.119	0.170	0.143	0.148	0.145	0.142	0.161	0.154	""	0.147	0.160	0.138

Cadmium (Cd)-Dissolved	""	0.0000113	""	0.0000113	0.0000143	0.0000094	0.0000118	0.0000064	**0.000005**	**0.000005**	0.0000131	""	0.0000092	0.0000056	**0.000005**
Calcium (Ca)-Dissolved	""	279	""	233	242	243	201	225	218	231	228	""	254	249	238
Chromium (Cr)-Dissolved	""	0.00139	""	0.00120	0.00132	0.00142	0.00140	0.00132	0.00116	0.00144	0.00116	""	0.00142	0.00124	0.00042
Cobalt (Co)-Dissolved	""	0.00246	""	0.00293	0.00342	0.00173	0.00069	0.00067	0.00032	0.00040	0.00042	""	0.00039	0.00038	0.00076
Copper (Cu)-Dissolved	""	**0.0005**	""	0.00068	**0.0005**	**0.0005**	**0.0005**	**0.0005**	**0.0005**	**0.0005**	**0.0005**	""	**0.0005**	**0.0005**	**0.0005**
Iron (Fe)-Dissolved	""	1.80	""	1.54	1.16	0.626	0.355	0.343	0.162	0.239	0.149	""	0.055	0.063	0.835
Lead (Pb)-Dissolved	""	0.000100	""	0.000099	**0.000050**	**0.000050**	0.000053	**0.000050**	**0.000050**	**0.000050**	**0.000050**	""	**0.000050**	**0.000050**	0.000057
Lithium (Li)-Dissolved	""	0.194	""	0.147	0.211	0.195	0.206	0.212	0.184	0.196	0.205	""	0.202	0.209	0.205
Magnesium (Mg)-Dissolved	""	95.2	""	85.4	95.1	98.4	109	91.3	103	96.2	108	""	103	102	102
Manganese (Mn)-Dissolved	""	0.121	""	0.0801	0.0847	0.0877	0.0848	0.0852	0.0840	0.0851	0.0905	""	0.107	0.122	0.115
Molybdenum (Mo)-Dissolved	""	0.00316	""	0.00433	0.00498	0.00273	0.00151	0.00189	0.000888	0.000779	0.00135	""	0.000818	0.000905	0.00295
Nickel (Ni)-Dissolved	""	0.0265	""	0.0356	0.0368	0.0285	0.0187	0.0144	0.0114	0.0117	0.0117	""	0.00829	0.00698	0.0103
Phosphorous (P)-Dissolved	""	**0.3**	""	**0.3**	**0.3**	**0.3**	0.34	0.34	**0.3**	**0.3**	**0.3**	""	**0.3**	**0.3**	**0.3**
Potassium (K)-Dissolved	""	15.8	""	12.0	12.2	11.6	10.2	10.7	9.0	9.6	9.0	""	12.4	10.1	6.9
Selenium (Se)-Dissolved	""	0.0115	""	0.0172	0.0114	0.0110	0.00661	0.0134	0.00859	0.00905	0.0167	""	0.0177	0.0128	0.0319
Silicon (Si)-Dissolved	""	12.9	""	10.6	11.4	11.8	10.9	11.0	9.59	10.9	9.62	""	12.7	10.2	6.45
Silver (Ag)-Dissolved	""	**0.00001**	""	**0.00001**	**0.00001**	**0.00001**	**0.00001**	**0.00001**	**0.00001**	**0.00001**	**0.00001**	""	**0.00001**	**0.00001**	**0.00001**
Sodium (Na)-Dissolved	""	101	""	92.0	97.9	99.3	95.2	97.6	99.6	97.7	99.1	""	104	97.9	97.4
Strontium (Sr)-Dissolved	""	0.517	""	0.449	0.458	0.415	0.406	0.418	0.385	0.395	0.406	""	0.432	0.445	0.419
Thallium (Tl)-Dissolved	""	**0.00001**	""	**0.00001**	**0.00001**	**0.00001**	**0.00001**	**0.00001**	**0.00001**	**0.00001**	**0.00001**	""	**0.00001**	**0.00001**	**0.00001**
Tin (Sn)-Dissolved	""	**0.0001**	""	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.0001**	""	**0.0001**	**0.0001**	**0.0001**
Titanium (Ti)-Dissolved	""	0.016	""	**0.01**	0.013	0.013	**0.01**	**0.01**	**0.01**	**0.01**	**0.01**	""	**0.01**	**0.01**	**0.01**
Uranium (U)-Dissolved	""	0.00939	""	0.0156	0.0123	0.0102	0.0112	0.00878	0.00895	0.00616	0.00917	""	0.00285	0.00654	0.0107
Vanadium (V)-Dissolved	""	0.00463	""	0.00355	0.00417	0.00433	0.00479	0.00430	0.00412	0.00449	0.00422	""	0.00478	0.00405	0.00204
Zinc (Zn)-Dissolved	""	0.0054	""	0.0053	0.0034	0.0063	0.0031	0.0031	0.003	0.003	0.003	""	0.003	0.0055	0.0032