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Biogeochemical Selenium Sequestration in Unsaturated Coal Reject Piles

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ABSTRACT

Predicting the source and fate of selenium (Se) from mine waste requires a multi-disciplinary understanding of the biogeochemical and hydrogeological processes that can occur, as differences in rock processing, waste storage configuration and resulting hydraulic properties can lead to orders of magnitude differences in the rate of Se release.

Non-acid generating coal reject piles stored on-site at the Willow Creek Mine, north-eastern British Columbia, Canada, were identified as a Se-leaching risk during environmental assessment studies. A condition of the mine permit included moving the piles to an alternative storage location to mitigate the risk of impacts to the nearby Pine River. Rates of Se leaching assumed for environmental studies were based on laboratory and small-scale site geochemical studies, performed under aerobic conditions that were ideal for Se release. However, to date, none of the available monitoring data have shown elevated Se concentrations in groundwater surrounding the piles.

To better understand why the coal reject piles did not appear to be leaching Se at predicted rates, a multi-disciplinary characterization study of the piles was performed that included borehole instrumentation of the piles to monitor gas composition and temperature, as well as collecting solid samples for microbial characterization coupled with geochemical and physical testing results from operational sampling.

Results from the study indicated the piles were sub-oxic and support a microbial community capable of reducing selenate, nitrate and ferric iron. Despite the piles being in an unsaturated state, the small particle size of the coal rejects and high residual moisture content has likely led to the observed sub-oxic conditions that provide a mechanism for Se sequestration within the piles resulting in low to non-detectable release rates to the surrounding environment. Findings from this study suggest there is currently no need to move the piles, and raises the question of whether re-handling would perturb established Se sequestration mechanisms.

Keywords: Selenium sequestration, biogeochemistry, coal rejects, field instrumentation

INTRODUCTION

The Willow Creek Mine (WCM) is located approximately 45 kilometres west of Chetwynd, British Columbia. Metallurgical grade coal seams are recovered by open pit methods and processed on site. The most recent operational phase for the mine was between 2010 and 2014, with operations placed on care-and-maintenance in the middle of 2014 due to low coal prices.

The economic coal seams are mined from the Lower Cretaceous Gething Formation. Surrounding the coal seams are sandstones, shales, siltstones, and mudstones, which are typical of the coal-bearing strata in the Rocky Mountains of western Canada Also typical of these rock types, and notably for the coal mines in eastern BC, is the enrichment of selenium (Se) when compared to typical global values for sandstones (Price 1997) On average Se concentrations range from 2-4 mg/kg Se, but have been reported as high as 15 mg/kg (Western Coal 2010; Kennedy et al, 2012).

Unsaturated coal reject (CR) piles stored on an alluvial fan (Figure 1) at the WCM were identified as a Se leaching risk during Mines Act Permit C-153 amendment (MAPA) studies to re-open the mine in 2010 (Western Coal 2010). A condition of the Mines Act Permit included moving the piles to an alternative storage location to mitigate the potential for impacts to the nearby Pine River. Rates of Se leaching assumed for environmental studies were based on laboratory and small-scale site geochemical studies, performed under aerobic conditions that were ideal for Se release. However, none of the available monitoring data before or the year after the MAPA studies were completed showed elevated Se concentrations in groundwater surrounding the piles. As a result, in 2011 a multi-disciplinary study was initiated by SRK Consulting (Canada) Inc and Walter Energy Inc. to assess the Se leaching potential from the CR piles currently stored near the plant site and better understand the implications of moving the piles to another location as currently stipulated in the Mines Act Permit.

Conceptual model and program design

A conceptual model was used as the basis for designing the study to determine if the pile is a long term risk for Se loading to the receiving environment. The model was divided into hydrogeology and biogeochemical components. A schematic of the overall conceptual model is provided in Figure 2.

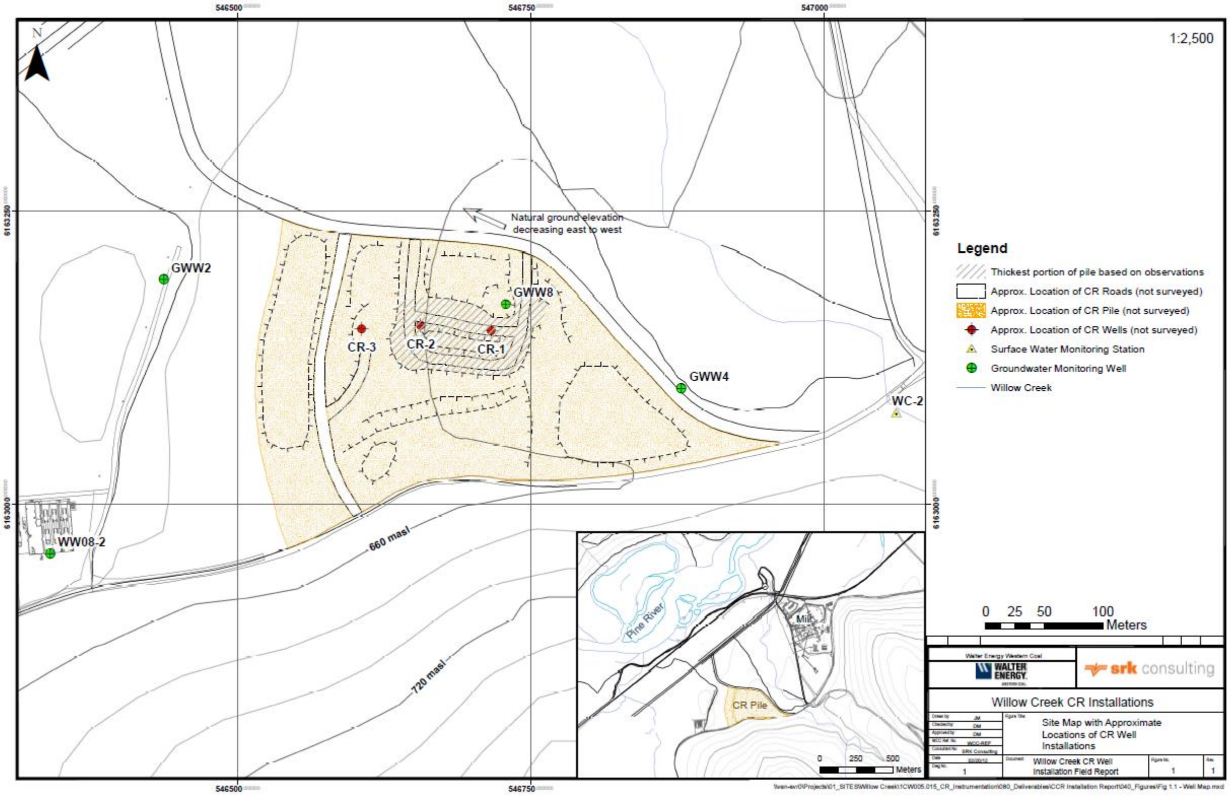

Figure 1 Location of coal reject pile on alluvial fan study site at Willow Creek Mine

Hydrogeology conceptual model

The groundwater flow system in the CR has two main components: (1) existing flow within the alluvial fan groundwater system and (2) seepage from the CR pile (Figure 2).

Groundwater is expected to move in the alluvial fan system from relatively high elevations near the apex of the fan, towards lower elevations and the Pine River. Recharge to the groundwater system comes from infiltration of direct precipitation, leakage from Willow Creek, and runoff from the mountains. Groundwater discharges to the Pine River. Seepage from the CR pile originates from precipitation infiltrating the pile and drain down of pore water within the pile when it was deposited. Precipitation on the CR pile either evaporates (or sublimates), runs off the pile, or infiltrates. The relatively fine-grained nature of the pile and presence of standing ponds indicate that infiltration is not likely to be excessive. Drain-down from within the pile itself is not likely significant.

Infiltration that does reach the base of the pile can infiltrate into the underlying substrate of the alluvial fan or run out along the ground surface and daylight as seeps at the toe of the pile. Water that does infiltrate into the alluvial fan percolates to the water table, then moves in the same direction as overall groundwater flow. There is the potential for silty interbeds to locally perch water, but all water will eventually reach the fan groundwater system.

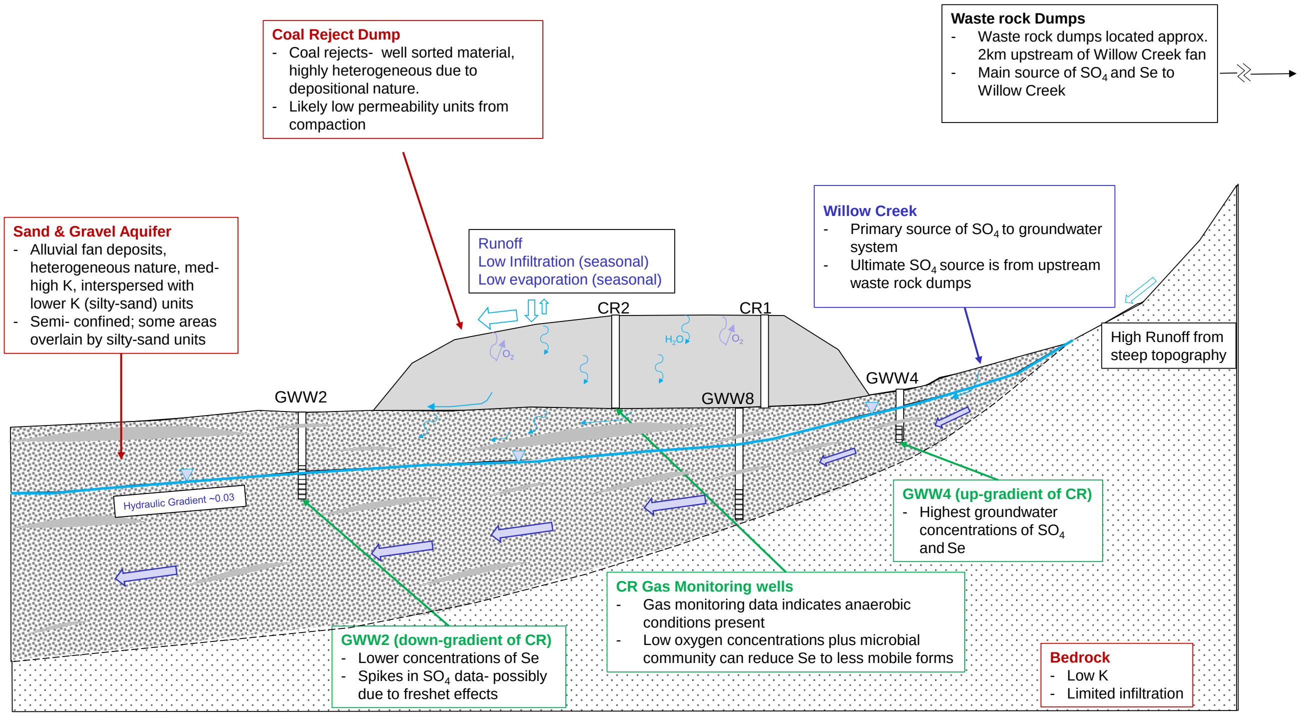

Figure 2 Conceptual model schematic for the WCM CR piles

Biogeochemical Conceptual Model

Selenium release from coal waste materials in British Columbia is generally understood to occur due to oxidative dissolution of pyrite, meaning that Se release is dependent on conditions favourable for the oxidation of sulfide minerals (Kennedy et al. 2012). Oxygen is the most likely oxidant and therefore if low level oxygen conditions are present in the CR piles, this should slow down the oxidation of sulfides and therefore Se release.

The following processes could be occurring in the CR pile:

- A thin layer on the exposed surfaces of the CR pile oxidizes producing soluble sulfate and Se, and dissolved organic carbon. Due to their concurrent release, Se and sulfate concentrations are expected to be correlated.
- Infiltrating precipitation dissolves Se, sulfate, and organic carbon.
- At depth, suboxic conditions develop and a microbial population that favours reduction becomes dominant, leading to conversion of Se to reduced states (selenite, potentially elemental Se and selenide).
- Sulfate may not undergo reduction unless anoxic conditions develop. As a result, the correlation between sulfate and Se diverge if Se is removed from solution.
- Selenium is sequestered in the pile by either selenite adsorption to reactive surfaces or by forming elemental Se and selenides (a solid phase precipitate).

Ultimately all of the above processes could result in leachate leaving the CR pile and travelling into groundwater with low Se, and relatively unchanged sulfate.

METHODOLOGY

In order to further understand the processes occurring in the CR piles, a multi-disciplinary characterization study of the piles was performed that included borehole instrumentation of the piles to monitor gas composition and temperature, as well as collecting solid samples for microbial characterization coupled with geochemical and physical testing results from operational sampling. The details of each component are provided below.

CR pile instrumentation and monitoring

Three monitoring boreholes were installed in 2012 using air rotary drilling into the CR piles. Each hole had thermistor strings installed and Solinst continuous multilevel tubing (CMT) with multi-level gas monitoring systems. Locations of these wells (CR-1, CR-2 and CR-3) are shown on Figure 1.

Monitoring of the gas wells included carbon dioxide and oxygen concentrations using an RKI Eagle multi-parameter gas sampling probe. Temperature was monitored by a multimeter capable of measuring the resistance in the thermistor strings.

Solids chemistry and reactivity assessment

Geochemical characterization of the CRs was based on previous studies from the MAPA study (Western Coal 2010) and supplemented by additional grab samples in 2010 and 2011 by WCM staff. The MAPA study included analysis of 44 operational samples from 2005 and 2006 and another 69 samples from operations after the mine re-started.

Analytical testing of all samples included acid-base accounting (Sobek et al. 1978) and element composition by aqua-regia digestion and ICP-MS. Neutralization potential (NP) is site specific at the WCM as defined in permit C-153 where NP for CR is calculated as Sobek NP (in kg $CaCO_3$/t) multiplied by 0.8 plus 0.71. Acid potential (AP) for all rock types is calculated from sulfur concentrations determined by ICP-MS following aqua-regia digestion. Mineralogy of CR was characterized by semi-quantitative XRD and optical petrography descriptions.

Weathering kinetics were assessed using a humidity cell test (referred to as the "CCR H Cell" in the MAPA study), a 200 to 300 kg field barrel test and meteoric water mobility procedure (MWMP, NDEP 1990) tests on weathered samples collected in 2005 and 2006.

Microbial characterization

Grab samples were recovered aseptically from each borehole and shipped to the Microbial Geochemistry Laboratory at the University of Toronto, Ontario, for microbial analysis. A cultivation presence/absence approach was selected due to difficulties recovering DNA from the surface of the coal, which was found to be somewhat hydrophobic.

Media for anaerobic cultivation were prepared by mixing an artificial groundwater solution with solutions to support one of: nitrate; selenate; iron; or sulfate reduction. Lactate, acetate and pyruvate were used as the carbon sources. All solutions were sterilized (i.e. autoclaved) prior to inoculating with CR sediment. Sand and silt sized particles of CR were transferred into cultivation vials in an anaerobic chamber and stored at room temperature for 5 weeks. Successful cultivation was indicated by biofilm accumulation on the vial walls for the nitrate and iron reducing media and by the presence of pink precipitates in the Se media.

Groundwater and surface water chemistry

In 2005, eight groundwater monitoring wells were installed in the Willow Creek Fan and the Pine River floodplain. The purpose of these wells was to assess groundwater quality and to develop a hydrogeological conceptual model for the fan in preparation for construction of the CR pile (Western Coal 2010). Five of the eight monitoring wells are located in the fan itself, although only GWW2, GWW4, and GWW8 are used in this study (Figure 1). Groundwater sampling data were available from late 2005 to 2013, with analyses including pH, sulfate, alkalinity, chloride, fluoride, nitrogen species, phosphorus species, dissolved organic carbon, and a 32 element scan by ICP MS for dissolved ions.

The spatial context of the fan monitoring locations (Figure 1) and context for interpreting water quality data are as follows:

- WC-2 represents upstream surface water that carries sulfate and Se from the up-land waste rock dumps at WCM.
- Groundwater generally follows topography, flowing from higher elevation portions of the fan towards the Pine River (i.e. GWW4 towards GWW2, passing GWW8), a distance of approximately 600 m horizontally from the toe of the CR pile.
- GWW4 is located upgradient of the CR pile and will not be impacted by the pile. The monitoring screen in GWW4 is within sandy gravel materials at a depth of 10 to 13 m below ground surface. The water table is about 7 m below ground surface at this location.
- GWW8 is screened below the CR pile footprint and has the potential to be impacted by the CR pile. The monitoring screen in GWW8 is within silty sand and gravel materials at a depth of 19 to 28 m below ground surface. The water table is about 9 m below ground surface at this location.
- GWW2 is located about 90 m down gradient of the CR piles and has the potential to be impacted by the CR piles. The monitoring screen in GWW2 is within sand and gravel materials at a depth of 10 to 16 m below ground surface. The water table is about 9 m below ground surface.

RESULTS AND DISCUSSION

Gas composition and temperature of the coal reject pile

Gas composition changes quickly over the first two metres below the surface with oxygen dropping below 4% and concentrations near detection at 8 metes below the surface. Carbon dioxide concentration shows an opposite trend in that it immediately increases below the surface to 3% and is relatively stable thereafter to the base of the pile.

Temperatures also appear to be higher inside the pile than regional ambient conditions during parts of the year, notably winter. Temperature monitoring of ambient conditions of the CR piles was not performed, although the average temperature during winter (November to March) in Chetwynd, British Columbia, ranges between -10°C and -5°C.

Geochemical characteristics

The CRs were characterized by relatively low sulfide sulfur (average of 0.16% interpreted from ICP aqua regia results) and levels of Se (average of 2.6 mg/kg) typical of coal waste material in eastern British Columbia. A statistical summary of the 69 grab samples that were analysed since the MAPA is provided in Table 1. When compared to the 2005 and 2006 operational samples (Western Coal 2010), sulfide sulfur and NP were somewhat lower in the grab samples. However, the overall difference between the acid-base account (NP divided by AP) of the two samples sets was small with averages for both around 3.0. Selenium concentrations were very similar between the two sample sets, with the average Se concentration in the 2005 and 2006 samples approximately 3 mg/kg.

The main sulfide mineral identified was pyrite, with possible pyrrhotite and trace levels of sphalerite and chalcopyrite also noted. X-ray diffraction determined that calcite, dolomite/ankerite and siderite were the main carbonates present.

The previous assessment of the CR piles by SRK (2007) and Western Coal (2010) indicated that the ARD potential was low. Grab sample results provided by WCM since the 2007 assessment support the original finding when an NP/AP criterion of 2 is used to delineate between PAG and non-PAG. While some of the samples have produced some acidity (as interpreted from a negative NP), water quality results from around the pile (Western Coal 2010) support that the piles overall are not a source of acidity despite being allowed to weather for several years.

Table 1 Summary of geochemical characteristics for operational coal reject samples

Statistic	**Sulfide %S**	**AP kg $CaCO_3$/t**	**NP(Sobek) kg $CaCO_3$/t**	**NP/AP**	**Se mg/kg**
Minimum	0.030	0.94	-3.3	-1.0	0.05
5th Percentile	0.040	1.3	3.4	0.64	0.94
25th Percentile	0.08	2.5	7.1	1.5	1.5
Mean	0.16	4.9	16	3.2	2.6
75th Percentile	0.21	6.6	18	5.0	3.2
95th Percentile	0.35	11	39	14	6.1
Maximum	0.61	19	108	43	8.9

Concentrations of Se and sulfide sulfur were compared in this study to confirm previous findings from other coal mines in British Columbia that Se was likely associated with sulfide (Kennedy et al. 2012). Selenium substitutes for sulfur and is often present as an accessory element in pyrite. The correlation coefficient for total sulfur (which will include any organic sulfur and sulfate sulfur) and Se was poor (r = 0.26, 99% confidence = 0.31), but improved when sulfide sulfur and Se were correlated (r = 0.45). Figure 3 compares of sulfide sulfur and Se in the CR samples.

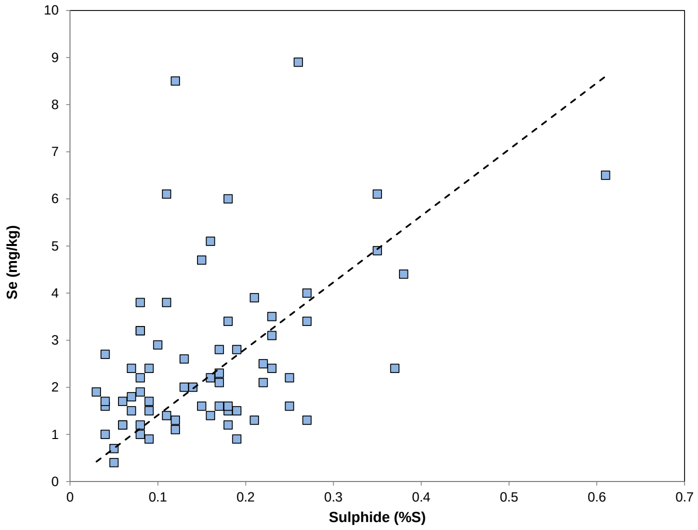

Figure 3 Comparison of Se and sulfide sulfur in WCM CR samples

Based on the results presented in Figure 3 and experience at other coal sites in British Columbia (e.g. Kennedy et al, 2012), Se leaching is expected to result from sulfide oxidation and generally at elevated levels compared to background levels (e.g., greater than 0.1 mg/L).

The field barrel test produced leachate pHs between 7.7 and 8.1, sulfate concentrations ranging from 283 to 2300 mg/L, and Se concentrations between 0.18 to 0.49 mg/L. Results from the MWMP tests confirmed these findings, as did the humidity cell tests, albeit at lower concentrations owing to the higher dilution in the humidity cell test (Western Coal 2010).

Microbial characterization

Results of microbial cultivation analysis demonstrated the viability of nitrate-, selenate- and iron-reducing communities of bacteria. Sulfate-reducing bacteria do not appear to be viable based on the cultivation tests.

The microbial communities identified are consistent with the low oxygen conditions present in at least portions of the CR piles. Bacteria respiring on selenate for electron transfer results in the formation of the more reduced forms of Se, such as selenite and elemental Se (Oremland 1994). These more reduced forms are readily removed from the soluble phase in groundwater by either adsorption or precipitation (selenite will adsorb, elemental Se will precipitate) (Neal & Sposito, 1989; Ralston, Unrine & Wallschläger, 2008). Nitrate and selenate are reduced at very similar oxidation potentials, while iron reduction requires more reducing conditions. Finding all three communities is a good indication that conditions are ideal to support suboxic to anoxic microbial communities and also that other requirements for survival are available, such as dissolved organic carbon and trace nutrients.

Based on the microbial characterization results, it is likely that a microbial community capable of converting selenate to more insoluble forms (e.g. selenite and elemental Se) will persist in the CR piles so long as suboxic conditions are maintained. It is likely a microbial communtiy is able to inhibit elevated concentrations of Se entering the receiving environment that was predicted by MAPA studies based on reactivity of the CRs under aerobic laboratory and field testing conditions.

Groundwater and surface water chemistry

Concentrations of sulfate and Se in groundwater and surface water are compared to infer the potential reactions occurring within the CR piles. This is because field and laboratory leach tests from previous studies indicated that pyrite in the CR oxidizes to release sulfate and if no other processes were occurring within the CR piles, a plume of sulfate and Se would be expected in the groundwater below and down gradient of the CR pile.

At the upstream surface water monitoring station WC-2 (Figure 4), sulfate concentrations are highest compared to all other monitoring stations, with seasonal spikes typically around 100 mg/L over the last four years. Sulfate concentrations in the groundwater wells typically decreases in a downstream direction. Monitoring well GWW2 shows moderate (~60 mg/L) seasonal spikes in sulfate concentrations, potentially indicating that this location is impacted more by surface water than GWW8 during certain times of the year. There are gaps in the record for GWW4, so it is not possible to confirm if seasonal spikes also occur at this location, but it is considered likely based on historic comparison of GWW4 and WC-2. Monitoring well GWW8 has shown a slow increase in sulfate concentration over time, roughly intermediate between GWW4 and GWW2 on an average annual basis.

Selenium concentrations were highest at WC 2 and GWW4 (Figure 4) at around 0.005 and 0.003 mg/L. Concentrations downstream the CR piles (i.e., GWW8) are near analytical detection limits (0.0005 mg/L) (Figure 5) and an order of magnitude lower than WC2 and GWW4 (i.e. than upstream of the pile). The step change in Se concentrations in 2010 is likely a function of changing detection limits in the analytical laboratory, although this has not been confirmed.

Sulfate and Se concentrations at WC-2 were well correlated (r = 0.85, 99% confidence = 0.2) whereas at GWW8 they were not (r = -0.3) (Figure 5). The divergence at GWW8 is likely evidence of conditions in the sub-surface supporting reduction of selenate to selenite and possible elemental Se. While redox was not measured in the wells, using the concentration of redox sensitive elements and compounds under alkaline conditions (pH of about 8), the redox level of the groundwater is estimated to be approximately 400 mV, which is near the redox potential required to reduce selenate to selenite (Ralston, Unrine & Wallschläger, 2008). This is interpreted from the concentrations of nitrate and nitrite at GWW8 (0.1 and 0.01 mg/L, respectively) and also from dissolved iron concentrations. Iron occasionally spikes in GWW8 (up to 0.11 mgFe/L), which could simply be a result of poor filtering (i.e. partiulcate iron oxide contamination), or indicate times when redox conditions are closer to 0 mV and favour the formation of elemental Se. Under alkaline pH conditions, iron is only soluble when it is present in the reduced form as ferrous iron.

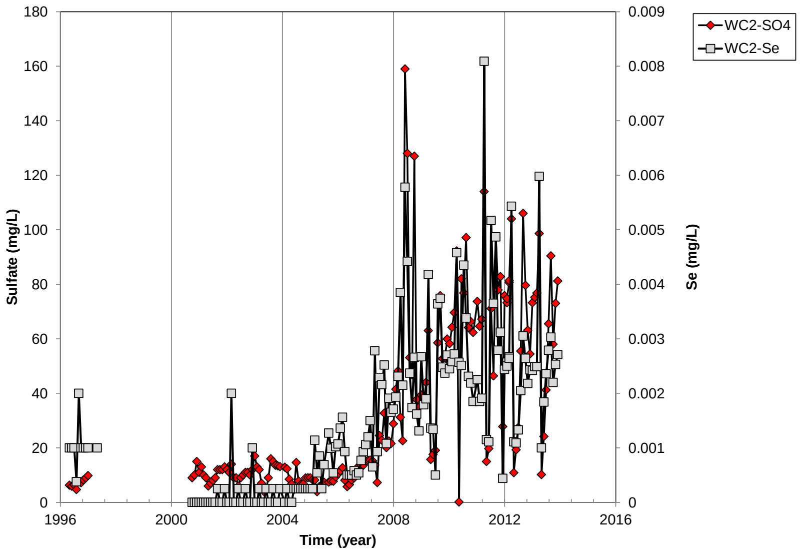

Figure 4 Sulfate and Se concentrations at surface water station WC2

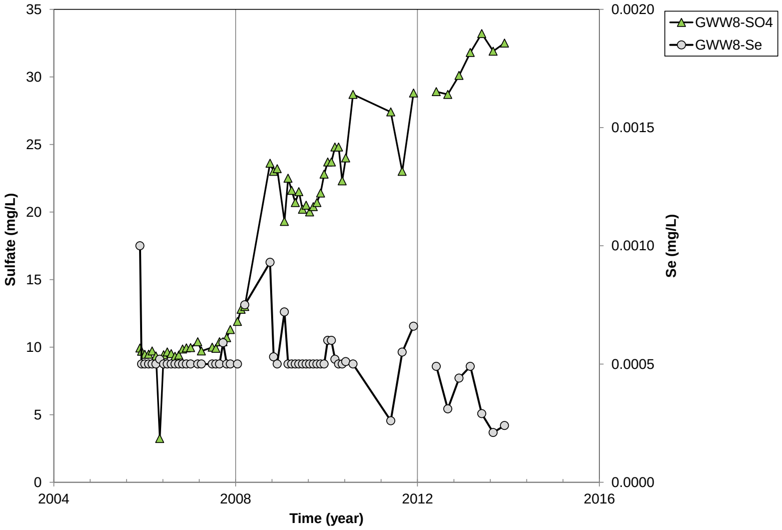

Figure 5 Sulfate and Se concentrations at groundwater monitoring station GWW8

CONCLUSION

A multi-disciplinary characterization approach was used to assess the Se leaching potential from the CR piles at the WCM. Based on the results of this study, the piles appear to be sub-oxic and support a microbial community capable of reducing selenate. Despite the piles being in an unsaturated state, the conditions within the CR piles provide a suitable environment for selenate reduction and therefore Se sequestration to occur resulting in low to non-detectable release rates to the surrounding environment. Findings from this study suggest there is currently no need to move the piles, and raises the question of whether re-handling would perturb established Se sequestration mechanisms.

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