Attenuation of Metals from the No Cash 500 Mine Adit Discharge in a Natural, Cold Climate, Peat Wetland Part 2 – Hydrological and Geochemical Mechanisms.

Brent Johnson [1], L.E. Eary [2], Barbara Sherriff[3], James Harrington[4], and Scott Davidson[5]

[1]Interralogic, Inc., 913 11th Street, Golden, CO, USA, bjohnson@interralogic.com
[2]Interralogic, Inc., 4715 Innovation Drive, Suite 110, Fort Collins, CO, USA, ted.eary@interralogic.com
[3]Department of Geological Sciences, University of Manitoba, Winnipeg, MB, Canada, sherriff@cc.umanitoba.ca
[4]Alexco Environmental Group, 88 Inverness Circle East, Suite 102, Englewood, CO, USA, jimharrington@alexcoresource.com
[5]Access Consulting Group, #3-151 Industrial Road, Whitehorse, Canada, sdavidson@accessconsulting.ca

Abstract
Historical mining operations in the Keno Hill Silver District, Yukon Territory resulted in a number of mine adits that discharge water to surface streams, including the No Cash 500 adit. Discharge rates range from 3 to 15 L/s with maximums during spring freshet. Metal concentrations at the portal are: Mn (10 to 12 mg/L), Zn (13 to 19 mg/L), Cd (0.2-0.5 mg/L). Solutions are circumneutral with alkalinities from 150 to 200 mg/L and sulphate from 300 to 500 mg/L. After leaving the adit, the discharge plunges over a steep hillside aerating the water, then enters a terminal, poorly-drained peat bog. Metal concentrations rapidly decrease along the stream course; Zn decreases by 100X, Cd by 100X to 1000X, and Mn by 20X to 10,000X.

The causes of the decreases in metals in the No Cash 500 drainage are described in a two-part paper. Part 1 describes the trends in metals and develops a conceptual model. Part 2 (this paper) describes the details of hydrologic and geochemical mechanisms responsible for the observed zinc attenuation. Mineralogical data indicate zinc phases are related to successive manganese coatings with some degree of crystallinity with hydrohetaerolite ($Zn_2Mn_4O_8.H_2O$) as the dominant mineral. Other possibilities for a Mn-Zn mineral include woodruffite ($ZnMn_3O_7.2H_2O$) or Zn absorbed on birnessite ($Na_{0.3}Ca_{0.1}K_{0.1}Mn^{4+}Mn^{3+}O_4 \bullet 1.5(H_2O)$).

Key Words: natural attenuation, zinc, mineralogy, mine drainage

Introduction
The No Cash Creek (NCC) drainage is located on the northwest side of Galena Hill in the Keno Hill Silver District (District), about 350 km north of Whitehorse, Yukon Territory (Figure 1). The District contains over 65 silver ore deposits and prospects that were first mined in 1913, including the No Cash mine which was mined from 1948 to 1988. Most mining operations took place on the north-facing slopes of Galena Hill and also in areas to the east on Keno Hill (Figure 1). Elevated metal concentrations occur in surface waters and sediments of many of the drainages associated with historical mining operations (Kwong *et al*. 1994; 1997).

NCC is a natural stream that receives water from the 500-level adit of the No Cash Mine in addition to flows from its watershed (Figure 1). Water is discharged from the adit throughout the year. Measured flow rates have ranged from about 3 to 15 L/s and average about 5.5 L/s. The adit water from the No Cash Mine contains elevated concentrations of metals, namely Cd, Mn, and Zn, as well as SO_4 (Kwong *et al*. 1994; 1997; MERG 2000; ERDC 2006; Access 2010). Adit water and NCC typically have pH values from 7 to 8.3 and alkalinities of 85 to 286 mg/L.

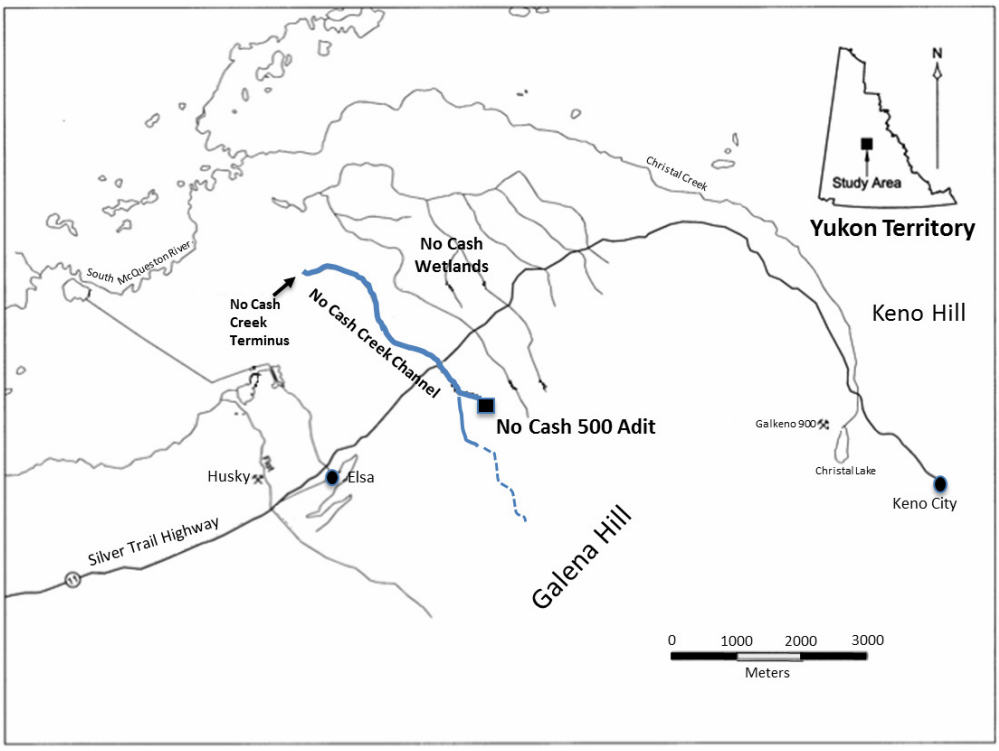

Figure 1. Location Map

It has been observed that metal concentrations decrease significantly with distance from the adit discharge point, suggesting that natural attenuation processes are effectively removing metal from solution. Kwong *et al*. (1994, 1997) have reported the effects of natural attenuation in the No Cash drainage and nearby drainages. Reclamation alternatives for mitigation of historical mining sites in the Keno Hill District are currently being evaluated. The purpose of the work described in this paper was to evaluate the efficacy of natural attenuation as a viable mitigation strategy for adit discharges for the No Cash adit discharge either as a standalone alternative or in combination with engineered systems designed to enhance and prolong the natural attenuation processes.

In Part I of this series, Eary *et al*. (2011) described the observed chemical trends along NCC and calculated potential solubility controls on these observations using geochemical modeling techniques. Figure 2 shows the decrease in Zn concentrations observed down NCC. This paper describes the hydrologic conditions and geochemical mechanisms responsible for the attenuation of zinc and other metals along NCC. Detailed mineralogical techniques were used to evaluate the mineralogy of solid samples collected at the adit and along NCC and to identify key mineral phases related to the observed zinc attenuation.

Hydrologic Conditions

The NCC drainage was inspected during the October and November 2010, March, May, August, and September 2011 field programs. There is about 260 m of relief along the drainage, most of which occurs in the first 1,000 m from the adit. Four hydrologic/geomorphic reaches have been identified on NCC based on slope, and vegetation characteristics (Figure 3). These reaches are: the adit/waste rock reach, the cascading reach, the transitional reach, and the peat bog reach. The No Cash natural attenuation system is defined as the entirety of the 3.4 km length of drainage from the adit to the "terminal pond" area.

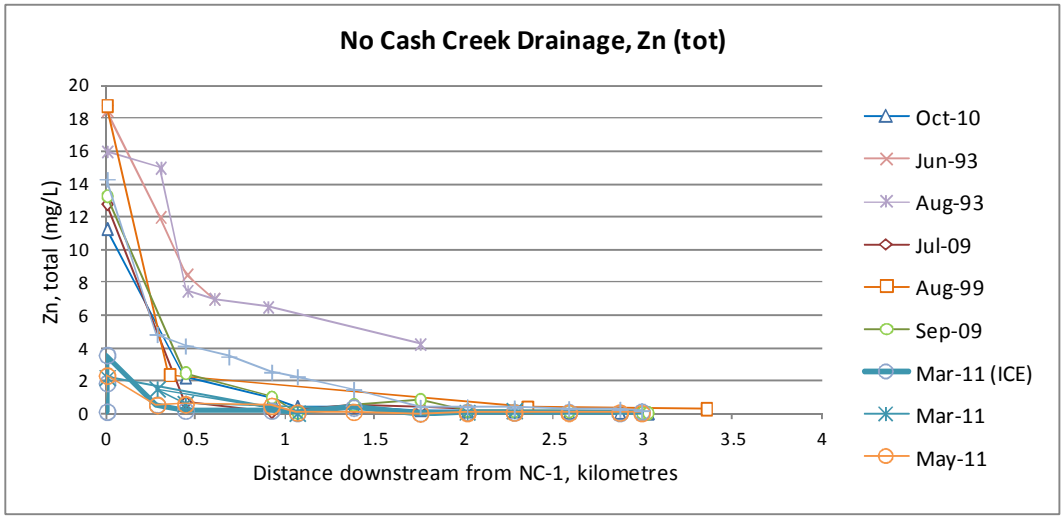

Figure 2. Zinc concentrations down No Cash Creek

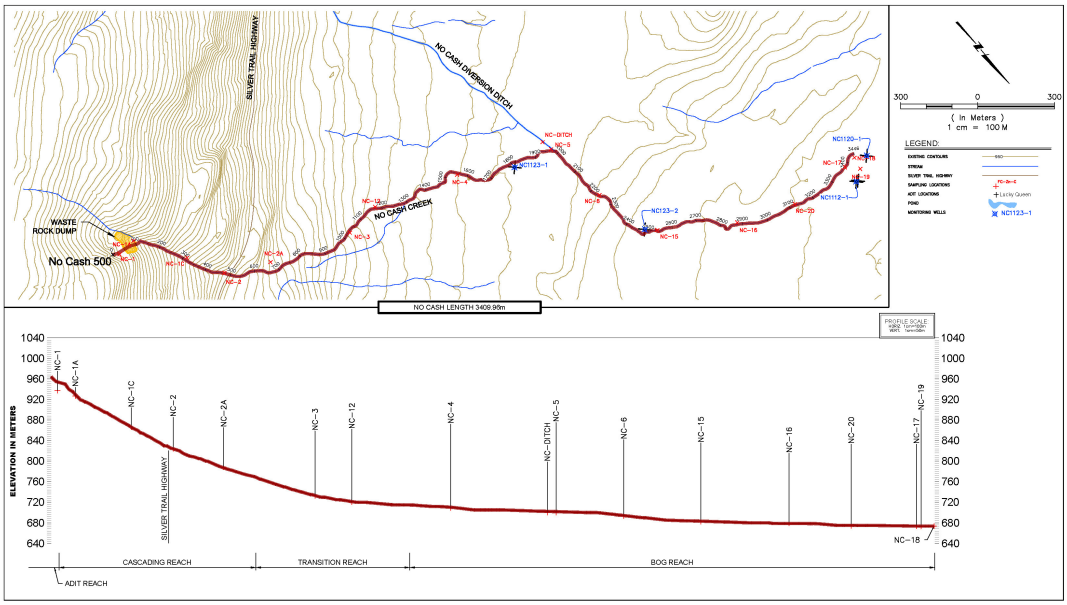

Figure 3. No Cash Creek Location and Profile

The adit/waste rock reach consists of the adit structure, the drain pipe from which the water flows and the immediate receiving area. This reach includes a waste rock pile at angle of repose, comprising two lifts. Discharge from the adit flows directly onto and across the top of the waste rock for about 10 m, cascades off the top waste rock bench approximately 30 m onto the lower bench of waste rock. It then flows across the bench spilling another few meters into a steep, forested area where it joins NCC. A minor amount of water (less than 0.3 L/s) flows from a drain pipe that protrudes from the upper waste rock pile during non-winter months.

There is significant aeration of the water within the adit as it discharges from the adit structure, through the pipe, and down the waste rock face. Significant amounts of reddish and brownish precipitate composed of Fe and Mn oxyhydroxides with elevated Zn and other metals are present in the discharge area. Additional mineralogical data are presented later in this paper.

The cascading reach runs for approximately 750 m from the base of the waste rock dump, which includes flowing through a culvert under the Silver Trail Highway. This reach is characterized by a steep (about 20 percent slope) stream channel with cobbles and boulders. There are abundant trees and pockets of dense vegetation. The upper section of this reach shows some reddish precipitate similar to that found in the adit/waste rock reach.

The transition reach is not as steep as the cascading reach and has fewer cascading areas. Boulders and cobbles are the dominant substrate in this reach. The slope in this section decreases to about 12% and the stream begins to show signs of meandering and braiding as the slope becomes less steep. Abundant trees and undergrowth are present in the upper section of this reach; some peat is present in the lower section. Occasional areas of reddish stream sediment were observed in this reach.

The peat bog reach is flat and irregular, with willows and sparse tree growth. The slope decreases to about 10%. The few black spruce trees present appear to be stressed or dead. The stream branches numerous times, and the main channel is often not clearly identifiable, with multiple parallel/braided stream channels of similar size present in the same section/reach. The channels are commonly 1 to 2 m across and about 0.5 m deep. A surface water diversion that collects water from Galena Hill, south of the Valley Tailings Facility, intersects NCC approximately 1.75 km from the adit. The peat bog-reach ends where a small ephemeral pond has developed with no apparent surficial outlet. Occasional reddish, muddy, sediment was observed in this reach, including near the sample location NC-5, below the confluence with the diversion ditch.

During the winter survey in early March 2011, surface flows were either not observed or very low compared to non-winter months. In the adit reach, no water was flowing from the adit portal either at the surface or below the ice. In addition, the pipe, which flowed during the non-winter months, was completely frozen and no flow was present. A small flow of liquid water was located about 10 m southeast of the pipe outlet beneath the snow and ice sheet on the slope of the waste rock pile. So while flow had apparently ceased from the adit through "normal" non-winter pathways, flow continued to exit the mine through alternative pathways, daylighting at the face of the waste rock beneath the snowpack.

In the cascading reach, liquid water was heard and/or directly observed flowing beneath the ice along most of this reach during the winter sampling round. Ice varied from between a few centimeters to over a meter in some areas. In the transition reach liquid water was encountered sporadically in the main channel; however, it was common to dig "dry" holes (holes with no liquid water) before excavating one that was capable of being sampled. In the bog reach, liquid water was not encountered at most of the sampling locations. Multiple holes were dug at each location through the ice until either water or soil was encountered.

In the transition and bog reaches, ice damming was observed whereby complete freezing of the main channel occurred, occluding liquid water and forcing it to alternative flow paths. Figure 4 shows a schematic of flow through the channel under different seasonal conditions. Summer flows are largely confined to the main channel. Except for responses to summer storms, creek flows gradually decline through summer reaching a low just before freeze-up occurs in October (Figure 4 – summer section). The peat bog gradually dries out through the summer months as water from snow melt and freshet inundation evapotranspirates and drains into peat crevices and ultimately into main channels.

October flows tend to be low and confined to the main channels where the depth of water is generally less than 20 to 30 cm. Colder temperatures begin freezing the water in the main channels from the top down, initially leaving flowing water beneath the ice. As winter temperatures decline, the channel continues to freeze downward, in some areas completely freezing and damming the main channels.

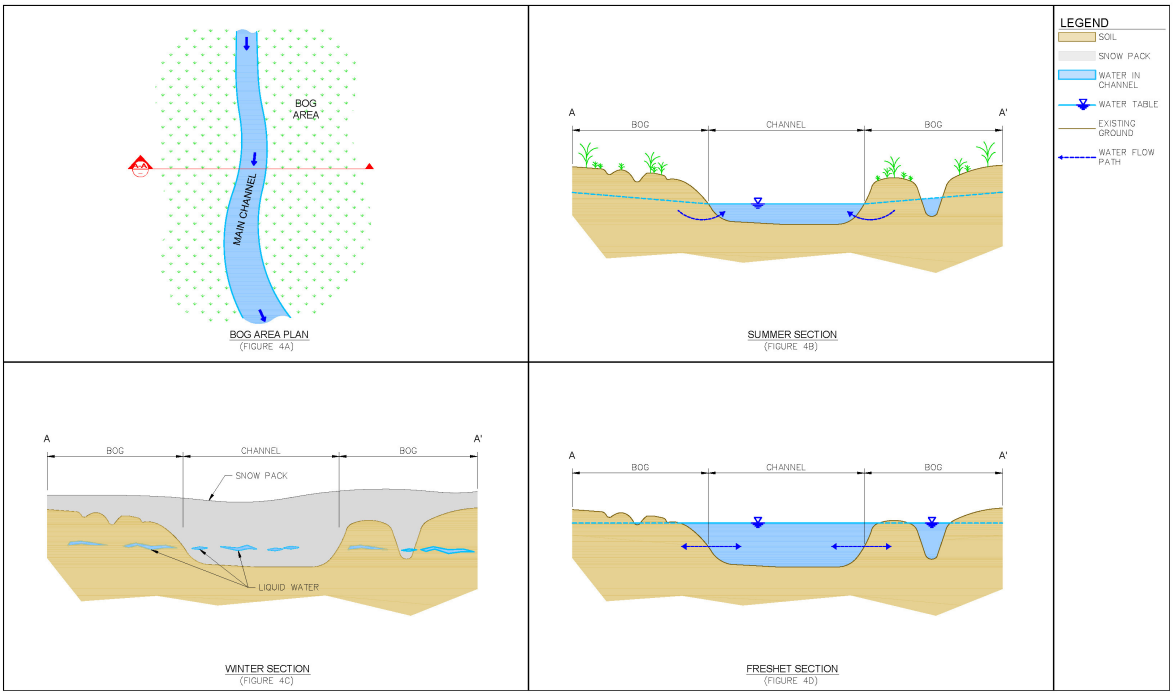

Figure 4. Seasonal Hydrologic Conditions in the NCC Bog

Liquid water, trapped between permafrost below and icing up from above, is forced through alternative pathways either within or outside of the main channels (Figure 4-winter section). Observations during winter sampling of NCC in the bog reach indicated liquid water was only sporadically present within the main channel.

The ice pack begins melting at the surface as air temperatures rise through April and May and sometimes into June; initially with daily thawing and re-freezing at night. The thawing process proceeds from lower to higher elevations resulting in water flowing across underlying ice pack. Overland flow dominates in the cascading and transition reaches where steep slopes direct water into the main channels which generally contain these high flows. In the lower transition and bog reaches, water inundates large areas outside the main channels (Figure 4-freshet section) reaching maximum extent in early summer, which is generally in early to mid-June in the Galena Hill area.

The effects of seasonal changes in flow conditions on Zn attenuation are minimal. Observed Zn concentrations along the NCC are similar in all seasons and flow conditions except that in the winter and freshet, the concentration of Zn is markedly lower than other seasons (Figure 2). A key result of the seasonal changes in flow is that additional flow paths develop outside the main channel during freshet and during winter months. During freshet, water overtops the main channel in the transition and bog reaches and water flows readily over and through the peat bog outside of the channel. This process increases the surface area of the water promoting oxidized conditions at the top of the stream surface while also increasing contact with organic-rich bog soils where adsorption reactions enhance metals attenuation.

During winter months, the low flow of water flowing through the channel is forced out of the channel into adjacent sediments. This causes slower movement of water (compared to channel flow) and increased physical contact with sediments and increased time for reaction and formation of Mn precipitates on sediment grains, which also serve to remove Zn by adsorption and co-precipitation.

In summary, observations indicate that there is no increase in Zn in the creek water due to winter or freshet hydrologic conditions. The cascading reach of the NCC maintains the aerated oxidizing conditions required for efficient precipitation of Mn oxides and associated Zn. The high flows during freshet and the low flows during winter have lower concentrations of Zn compared to summer conditions, suggesting that, despite low temperatures, natural attenuation in the winter and freshet months is enhanced.

Geochemical Conditions

Sphalerite is an abundant mineral in all mineralized areas of the District; belonging to the siderite stage, and less often, the galena stage of mineralization. Sphalerite is generally of hypogene origin with some occurrences of supergene sphalerite along fractures. The sphalerite consists predominantly of ZnS with accessory metals Fe (0.6 to 11.5 percent), Cd (0.7 to 1.2 percent) and Mn (0.005 to 0.20 percent) (Boyle and Jambor, 1962). The Mn content generally increases with Fe content. Siderite is also present in the Galena Hill deposits as the primary gangue mineral (Watson 1985) and commonly contains significant amounts of Mn (Access 2009). The sphalerite, siderite, and other ore and gangue minerals associated with the Pb-Zn-Ag mineralization (e.g., galena, freibergite, pyrite, chalcopyrite) (Gleason and Boyle, 1980) and their oxidation products exert primary control on the chemistry of water flowing from the adits. Water-rock interaction in mined and unmined ore bodies dissolves metals resulting in water characteristics reflecting the chemistry of the mineralized zones. The elevated concentrations of Zn, Cd, Fe, and Mn in waters flowing from adits in the district reflect the overall mineralized nature of the district but subtle differences in dissolved metals content also reflects the individual character of different ore bodies. These characteristics and distinctions are described more fully in the following sections, specifically in context with the geochemical mechanisms resulting in precipitation of metal phases as water flows from the chemically reducing conditions of the subsurface, out of the adits, and onto ground surface.

Of particular significance to the No Cash natural attenuation area described in this paper is the equilibrium chemistry of Fe, Zn and Mn, which are key components of water discharging from the No Cash and other adits located nearby. The equilibrium behavior of Fe and Mn is in some ways similar and strongly influenced by redox and pH conditions of the water. Aqueous Fe and Mn are typically present in their reduced forms (Fe^{+2} and Mn^{+2}) in natural subsurface waters and under reducing conditions can be present in elevated concentrations. However, as waters become more oxidized, the Fe^{+2} and Mn^{+3} oxidize to Fe^{+3} and Mn^{+3}/Mn^{+4} and rapidly precipitate out as oxyhydroxide phases. This behavior is particularly relevant to the flowing adits (and natural attenuation) area where reduced Fe and Mn dissolve within the mined and unmined mineralized deposits, which then oxidize as the water flows from the adit and downslope. The Fe and Mn rapidly precipitate out of solution and form Fe/Mn-rich mats, flocs, and stream sediment, reducing the concentration of Fe and Mn in the resulting downstream water.

Zinc is present at only a single oxidation state (+2) in natural waters (Hem, 1992) and is not directly affected by changes in redox. Solubility of Zn in natural waters, in the absence of other metals, is generally controlled by hydroxide and/or carbonate phases. However, in the presence of high concentrations of Fe and Mn, co-precipitation and sorption of Zn is a key solubility control (Lee, 1975). Numerous investigators have observed a correlation between Zn and Mn in precipitated solids (e.g., Angino, *et al*., 1974, Fuller and Harvey, 2000). This pattern has been observed in the District also as MacGregor (2002) found a strong correlation between Mn and Zn in the Galkeno 300 mine adit discharge precipitate in soils downhill of the adit as well as in laboratory testing. We have observed a strong relationship between Zn and Mn in precipitants in the NCC attenuation area, including evidence of co-precipitation in a crystalline phase, which is consistent with observations of previous workers.

Geochemical Mechanisms – Methods

Samples of sediment were selected from various depths and distances along the NCC drainage area. Polished thin sections were examined optically to determine overall composition and delineate areas of interest. Selected areas of 30 thin sections were imaged on the Electron Microprobe (EMP) at the University of Manitoba using Back Scattered Electrons (BSE) and mapped for Mn, Fe, S, Zn, and sometimes Si. Element scans were made across selected coatings on lithic grains and plant fragments. Several hundred points on the coatings were the quantitatively analyzed.

The EMP was operated at an acceleration potential of 15 kV and a beam current of 3 nA measured on the Faraday cup, with a 1 μm diameter beam. The standards for the quantitative analysis were albite (Na), olivine (Mg), andalusite (Al), diopside (Si, Ca), pyrite (S , Fe), orthopyroxene (K), sphene (Ti), spessartine (Mn), pentlandite (Ni), chalcopyrite (Cu), Gahnite (Zn), cobaltite (As), barite (Ba), chromite (Cr), and galena (Pb). The results of quantitative point analyses are given in wt. % elements with oxygen added to balance the cations.

The mean and standard deviations of the quantitative analytical data for each sample were calculated and then molar ratios were calculated for Mn:Zn. Full details of the analyses are available in Interralogic (2011) with just the mean values for Mn, Zn and Fe being presented in this paper.

Geochemical Mechanisms – Results and Discussion

Optical microscopy of the NCC sediments showed lithic grains, as well as individual grains of quartz and calcite (Figure 5A). Samples that were collected in more boggy areas contained more plant fragments than lithic and mineral grains (Figure 5B).

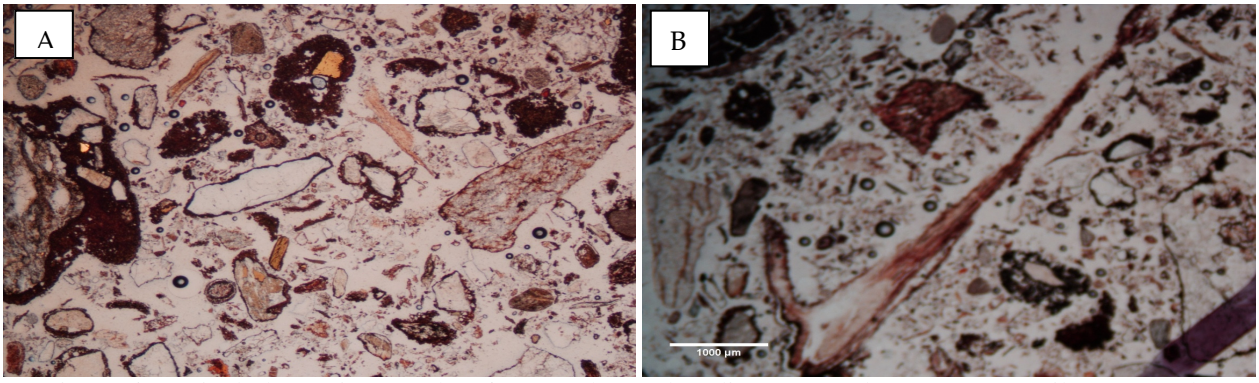

Figure 5. Optical photomicrographs of No Cash Creek sediment sample #38 NC12 Soil 8" Note the brown line around the lithic grain in A and around the plant fragment in B

Electron back-scattered images of coatings surrounding lithic grains showed that the coatings consisted of successive botryoidal layers. Element scans across the coatings indicated that the bright layers on the BSE image consisted mainly of Mn and Zn with a close relationship between concentrations of Mn and Zn (Figure 6 Table 1). The coatings around the plant fragments were similar in appearance but have much lower concentrations of Mn and Zn and a lower Mn:Zn ratio (Figure 7 and Table 1).

Samples were selected for microscopic analyses to represent different depths and distances along NCC to see whether there was a systematic change in Mn, Zn and Fe content or Mn:Zn ratio with distance downstream, with depth or with type of lithic. The mean concentrations of lithic and plant coatings for each sample are given in Table 1.

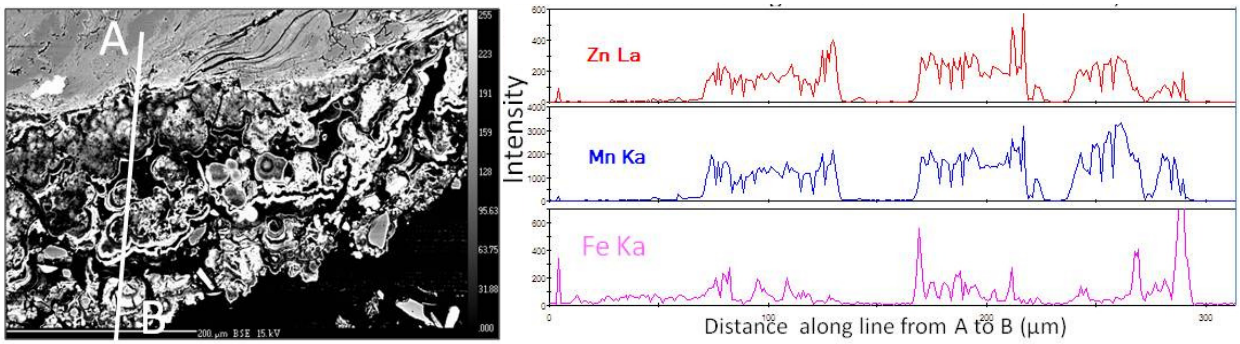

Figure 6. Back-scattered electron image of the coating around a lithic grain and Zn, Mn and Fe element scans across the coating

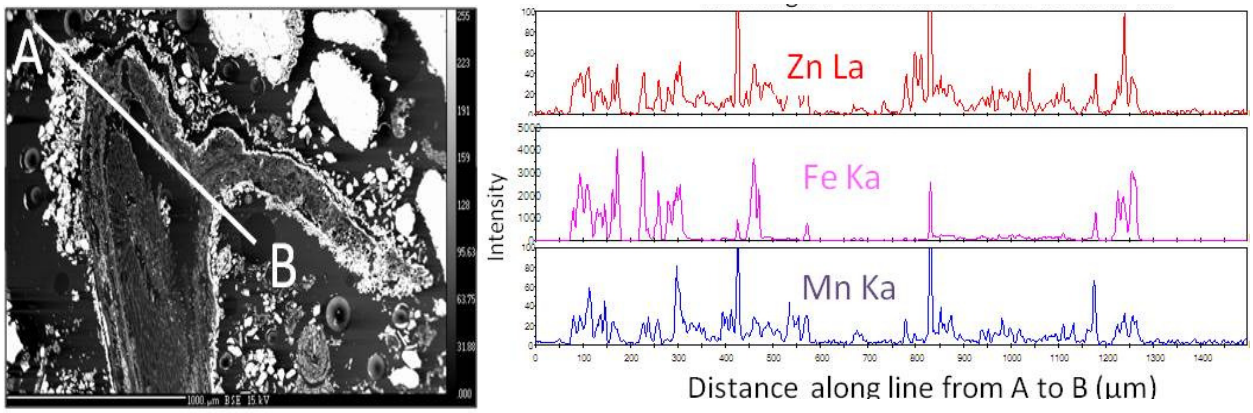

Figure 7. A back-scattered electron image of a typical plant coating with Zn, Mn and Fe element scans along the line AB

The samples from NC1 contained mostly lithic fragments whereas the samples from further down the creek had more plant material. From Table 1, it can be seen that coatings on plants have much lower Mn and Zn and higher Fe than the lithic coatings. The concentration of Zn and Mn tend to decrease downstream from NC 1 to NC 16 but there does not seem to be a systematic variation in composition of the coatings with depth.

Although there are considerable variations between the concentrations of Mn, Zn and Fe for both lithic grain and plant fragment coatings, the molar ratio of Mn:Zn is relatively consistent at 1.1 to 4.1 for lithic coatings and 0.3 to 1.1 for coatings around plant material. This observation indicates there are commonly crystallographic controls on the composition of the coatings

The relationship between Mn and Zn was clarified by examining the composition of the individual layers of a coating on one lithic grain. The comparison of the mean concentrations of Mn, Zn and Fe of the Mn-Zn rich coating of one grain in sample NC adit 18" depth (Figure 8, Table 2) shows the variation in concentration across a single coating but the similarity in molar ratios of Mn:Zn. A comparison of these values with other samples from sites close to the No Cash adit (Table 2) shows the variation in mean Mn, Zn and Fe concentration but again a narrow range of Mn:Zn molar ratio from 1.2 to 2.6 with a mean value of 2.0.

Table 1. Mean Zn, Mn and Fe concentrations (wt.%) and Mn:Zn molar ratios of lithic and plant coatings along NCC.

Location	Depth	Description of grain	Zn	Mn	Fe	Molar Mn:Zn
NC adit	18”	lithic coating	7.9	19.8	5.5	2.2
NC1	6"	lithic coating	8.6	16.6	9.9	8.3
NC1	6"	plant coating	0.7	0.9	3.2	2.7
NC1a	12"	lithic coating	9.0	15.7	5.0	4.2
NC1a	12"	sandstone coating	8.1	15.3	3.5	2.9
NC1a	12"	pyrite coating	5.5	23.2	20.7	17.4
NC1a	12"	metamorphic coating	11.0	18.8	3.0	2.5
NC1a	12"	sphalerite coating	3.9	8.9	12.6	10.6
NC1a	12"	quartzite coating	9.6	13.2	14.5	12.2
NC-1s	surface	lithic coatings	5.8	18.1	0.10	0.1
NC-12	8"	Lithic coating	5.4	18.2	0.26	0.2
NC-12	8"	plant coating	1.5	0.8	30.1	25.3
NC4	stream	plant coating	3.1	6.9	20.4	17.2
NC4	stream	lithic coating	4.1	19.9	3.5	2.9
NC4	8"	Lithic coating	8.2	25.0	2.7	2.2
NC4	8"	plant coating	0.5	0.2	5.5	4.6
NC4	8"	plant coating	0.3	0.1	4.8	4.0
NC16	stream	plant coating	0.0	0.1	2.3	2.0
NC16	3"	plant coatings	0.1	0.1	5.0	4.2
NC17	3"	plant coating	0.3	0.04	2.1	1.7

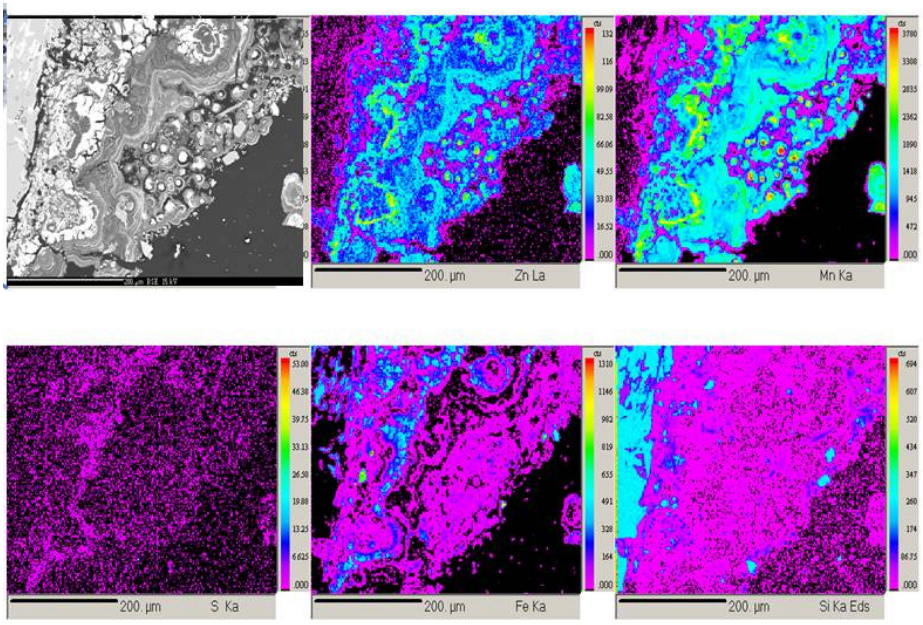

Figure 8. BSE image (top left) and element maps (element noted in the legends) of area 1A of the Mn-Zn rich coating on grain number 1 from sample NC adit 18”. Note the bright Mn and Zn rich band close to the lithic grain and the appearance of small nodules which could be spores or cysts.

Table 2. Summary of the mean values (wt %) and molar Mn:Zn ratios for Mn-Zn rich coatings on lithic grains from NC1

Sample	Mn	Fe	Zn	Molar Mn/Zn
NC adit 18" 1A1 bright band	20.8	9.7	9.1	2.1
NC adit 18" 1A2 nodule centre	26.9	2.4	9.8	2.3
NC adit 18" 1A2 nodule edge	15.3	3.8	6.2	2.2
NC adit 18" 1C	19.8	5.9	7.7	2.1
NC adit 18" grain 3	22.6	8.1	6.9	2.4
NC1 surface	18.1	0.0	5.8	2.6
#41-1 NC1 6"	16.6	9.9	8.6	1.6
#45-1 NC1a 12"	15.7	5.0	9.0	1.5
#45-2 NC1a 12"	18.8	3.0	11.0	1.4
#45-4 NC1a 12"	13.2	14.5	9.6	1.2
Mean	18.9	6.2	8.3	2.0

Our results for the Mn-Zn coatings from NCC indicate they are comprised of a mixture of poorly crystalline oxide forms. The most likely mineral form is hydrohetaerolite ($Zn_2Mn_4O_8 \bullet H_2O$) based on the Mn:Zn molar ratios observed in our samples. However, the observed ratios span a range of values, indication the probable presence of other similar minerals, such as pyrochroite ($Mn(OH)_2$) and woodruffite ($ZnMn_3O_7 \bullet 2H_2O$). In addition, there may be a considerable amount of Zn that is adsorbed on birnessite.

These results are consistent with those observed in the District and in other areas with mine affected water. In particular, in their study of Keno Hill samples of NCC sediment/precipitate, Gault and Jamieson (2011) used a combination of scanning electron microscopy (SEM), associated energy dispersive X-ray (EDX) spectroscopy, synchrotron-based micro-X-ray fluorescence (μ-XRF) mapping and micro-X-ray diffraction (μ-XRD) measurements to examine the mineralogy of one Mn-Zn-rich lithic coating. Gault and Jamieson (2011) identified a strong oxygen Kα peak in their EDX of the Mn coating indicating the coatings are primarily comprised of oxides. Multiple μ-XRD spot (5 x 9 μm) analyses indicated the Mn-Zn rich rims are primarily composed of hydrohetaerolite ($Zn_2Mn_4O_8 \bullet H_2O$) and possibly pyrochroite ($Mn(OH)_2$) or woodruffite ($ZnMn_3O_7 \bullet 2H_2O$). They found Mn:Zn molar ratios in the range 0.8 – 1.5, less than the stoichiometric Mn/Zn molar ratio of 2 in hydrohetaerolite.

Also, Mn oxides can be biologically formed by both bacteria and by algae. Robbins *et al*. (1999) found that 12 different biochemical mechanisms for the removal of Mn by oxidation from coal mine water. These involved a consortium of bacteria, cyanobacteria, diatoms, green algae and fungi. The dominant method that they found was coating of holdfasts by an Fe oxidizing bacterium (*Leptothrix discophora*) and by a green algae (*Ulothrix sp*). They also found that bacteria were more efficient in the spring and the green algae in the summer. A similar variety of biological mechanisms and seasonal variation could explain the variations in thickness and composition for Mn-Zn coatings found in the NCC sediments. Bargar *et al*. (2009), in a detailed study of Mn coatings in a contaminated stream in Arizona, found poorly crystalline birnessite formed by a freshwater bacterium *Pseudomonas putida* in biofilms. They also studies the stability of Mn^{+3} and Mn^{+4} species and found that the Mn^{+3} oxy-hydroxides were stable over the 5 month period of the experiment. Yu *et al*. (2011) found that Zn adsorbed on poorly crystallized birnessite ($Na_{0.3}Ca_{0.1}K_{0.1}Mn^{4+}Mn^{3+}O_4 \bullet 1.5(H_2O)$) in a laboratory study of the removal of Zn from Mn rich mine water by *Paraconiothyrium* Fungus.

Conclusions

In summary, the NCC hydrology is conducive to oxidized conditions that are responsible for the rapid precipitation of Fe/Mn/Zn phases and that winter and freshet temperatures and flow rates accentuate the Zn attenuation processes. In addition, Zn is rapidly precipitated with Mn oxyhydroxides as coatings on lithic fragments and as Fe oxyhydroxide coatings on plant fragments in NCC. Formation of the oxyhydroxide coatings occurs by a combination of inorganic (aeration) and biologically mediated processes (precipitation and adsorption). These processes are responsible for the high degree of natural attenuation that occurs as adit water flows down NCC. Mineralogical investigations indicate that the most likely mineral form for the oxyhydroxide coatings is hydrohetaerolite ($Zn_2Mn_4O_8 \bullet H_2O$), although there is variation in the composition both within and between coatings based on the observed range of Mn:Zn molar ratios from 0.8 to 3.0.Other potential mineralogical forms are pyrochroite and woodruffite. The consistent detection of the nanocrystalline Mn-Zn-bearing oxide minerals in our work as well as that of others indicates that the bulk of Zn is structurally sequestered rather than solely adsorbed to surfaces and therefore resistant to remobilization. Other evidence indicating a lack of remobilization and high capacity for attenuation is that attenuation is observed to occur during all seasons of the year and has been occurring consistently since 1982 (Eary *et al*. 2011).

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Acronyms

NCC	No Cash Creek
EMP	Electron microprobe
BSE	Back-scatter electron
XRD	X-ray diffraction
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray
μ-XRD	Micro-X-ray diffraction
μ-XRF	Micro-X-ray fluorescence