Metal Attenuation Processes in the No Cash Creek Drainage

FINAL DRAFT REPORT

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1 Introduction

The No Cash Creek drainage is located on the northwest side of Galena Hill in the Keno Hill Silver District (Figure 1-1). Detailed descriptions of Keno Hill Silver District are provided in ERDC (2006) and Access (2010). The Keno Hill District contains over 65 silver ore deposits and prospects that were first mined in 1913. Most mining operations took place on the north-facing slopes of Galena Hill and also in areas to the east on Keno Hill (Figure 1-1). Both the Galena Hill and Keno Hill mines are in the watershed of the South McQueston River. Most of the major watercourses that drain Galena Hill and Keno Hill lead to the South McQueston River. Many of the smaller watercourses, including those draining the northwest side of Galena Hill, terminate in wetlands in the South McQueston River valley. Elevated metal concentrations occur in surface waters and sediments of many of the drainages associated with mining operations (Kwong et al. 1994; 1997).

No Cash Creek is a natural stream that receives water from the 500-level adit of the historic No Cash Mine in addition to flows from its watershed. The No Cash mine was mined from 1948 to 1988. Water from the 500-level adit is discharged through a culvert from the mine. The culvert passes through waste rock and enters No Cash Creek about 0.5 km downstream from the natural headwater source of No Cash Creek on Galena Hill (Figure 1-1). Water is discharged from the adit throughout the year. Measured flow rates at surveillance location KV21, where No Cash Creek passes the Silver Trail Highway, have ranged from about 3 to 15 L/s during July of 2007, 2008, and 2009 (Access, 2010).

No Cash Creek runs in a northwestern direction away from the Silver Trail Highway through boreal forest on Galena Hill and enters a poorly drained valley containing extensive areas of heavily vegetated bog/marsh. A series of other seeps and disconnected streams drain Galena Hill parallel to No Cash Creek, creating a large area of bog/marsh in the areas east and north of stream channel No Cash Creek (Figure 1-1). This area is referred to as the surrounding or nearby wetland area in this report.

No Cash Creek is not a direct tributary to any other downgradient streams but terminates in small pond in a low lying boggy area of the valley approximately 2 km south of the South McQuesten River (Figure 1-1). There is no direct connection between No Cash Creek and the South McQueston River. There are seeps along the south and east sides of the South McQueston River that are potentially downgradient of the terminus of No Cash Creek, but whether the River is gaining inflow or losing inflow to groundwater along the valley flow has not been established. Much of the area of the No Cash Creek drainage and surrounding wetland area is underlain by permafrost of variable lateral extent and thickness.

The adit water from the No Cash mine contains elevated levels of metals, namely cadmium, manganese, and zinc, as well as sulfate (Kwong et al. 1994; 1997; MERG 2000; ERDC 2006; Access, 2010). The source of these constituents is expected to be primarily oxidative dissolution of metal sulfide minerals potentially with lesser contributions from metal carbonate, and silicate minerals associated with ore deposits. The dissolved products are released to groundwater in the underground workings connected to the No Cash adit. The process of oxidative dissolution of sulfide minerals has not resulted in acid mine drainage in the No Cash adit due to high levels of carbonate (mostly calcite) in the major lithologic units that host mineralization (Kwong et al. 1994; 1997). These units include the Keno Hill quartzite (Mississippian) and Earn Group metavolcanics and metasediments (Devonian-Mississippian). Kwong et al. (1994) reports net neutralization potentials (NNP) ranging from 105 to 934 kg $CaCO_3$/tonne for these rock types indicative of a very low probability for generation of acid rock drainage except possible in localized areas of high sulfide mineral content. Adit water and No Cash Creek immediately downstream of the inflow of adit discharge typically has pH from 7 to 8.3 and alkalinity of 85 to 286 mg/L. The high alkalinities are indicative of a strong influence of carbonate mineralogy on water chemistry (Kwong et al. 1994; 1997; MERG 2000; Access 2010).

The No Cash Creek drainage was intensively sampled for water quality and sediment chemistry during the summer of 2009. Seeps along the south and east sides of the South McQueston River were also samples for water quality and sediment chemistry. More specifically, the samples included:

- Water Quality
    - Water samples were collected from the main channel of No Cash Creek from the point of discharge of water from the 500-level adit to the terminus of the Creek in the pond/wetland area in the valley
    - Water samples were collected from other surface water expressions (seeps, ponds, disconnected streams) in the wetland areas to the north and east of the main channel of No Cash Creek
    - Water samples from a series of test pits excavated in saturated soils and sediments near No Cash Creek and in the wetlands to the north
    - Water samples from a series of seeps along the south and east sides of the South McQueston River in locations potentially downgradient from the No Cash Creek drainage

- Sediment Chemistry
    - Surficial sediment samples were collected from the stream channel of No Cash Creek
    - Surficial sediment samples were collected from other surface water expressions in the wetland areas north and east of the main channel of No Cash Creek at the same locations as water samples
    - Sediment samples (surface and at depth) were collected from test pits excavated in transects perpendicular to No Cash Creek and extending north and east into the nearby wetlands. The shallow samples from the test pits may be more accurately described as soil rather than sediment.
    - Sediment samples from a series of seeps along the south and east sides of the South McQueston River at the same locations as for water quality samples

More detailed information on sample locations, sample collection methods, analyses, and data interpretation is provided below.

The purpose of this study was twofold using the analytical water quality and sediment chemistry data:

- Define the effects of discharge of metal-bearing water from the historic No Cash 500-level adit on water and sediment quality in downstream portions of No Cash Creek and the surrounding wetlands
- Determine the extent to which natural attenuation processes control the distribution and concentrations of metals in water and soils in the No Cash Creek drainage and the probable stability of those processes to continue into the future
- Evaluate whether seeps along the South McQueston River have been affected by water and/or erosional transport of sediments from the No Cash Creek drainage, assuming there may be a potential hydrologic connection

This report provides the results of the study and identifies natural attenuation processes for metals, particularly for cadmium, manganese, and zinc. Previous work by Kwong et al. (1994, 1997) has documented the effects of natural attenuation processes for limiting acid rock drainage and metal transport from mine wastes and operations in the general areas of Galena Hill and Keno Hill.

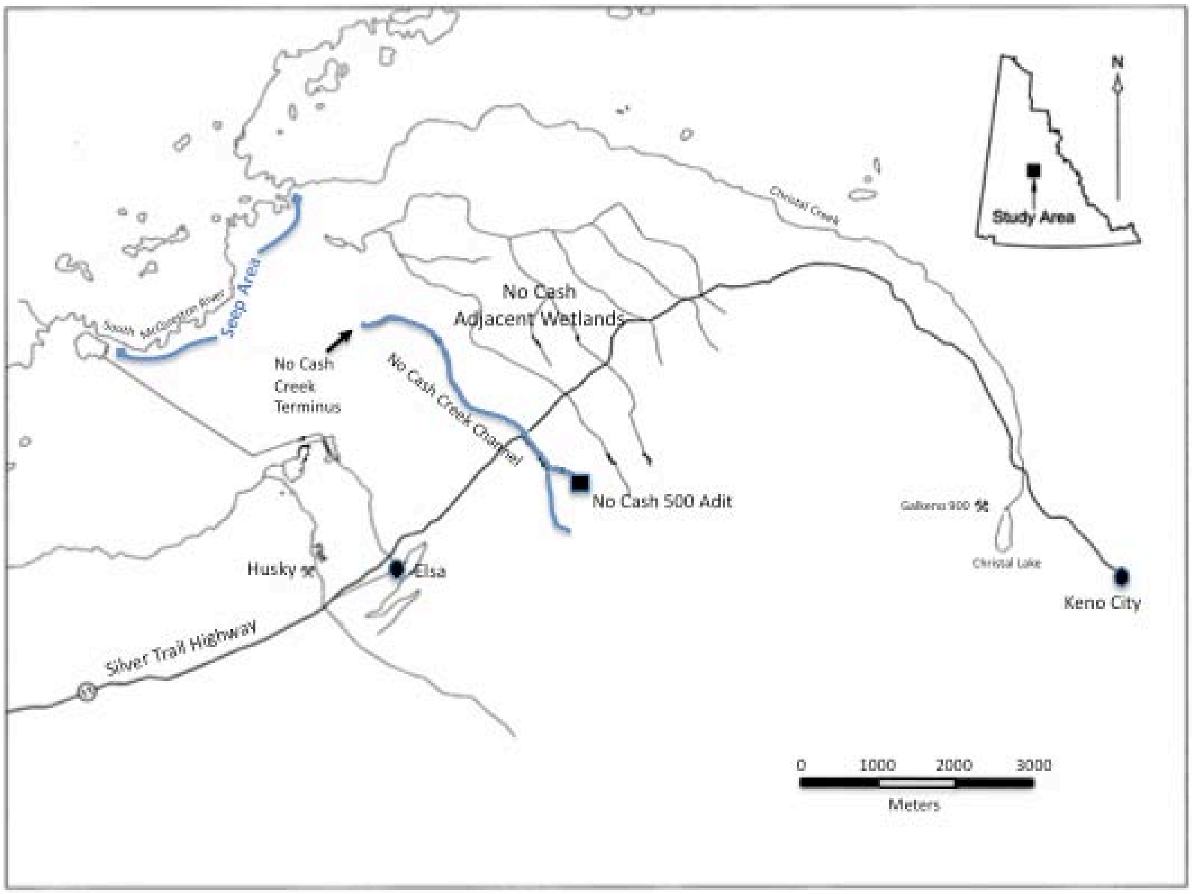

Figure 1-1 Location map for the No Cash Creek drainage

2 Sample Collection

Two sets of samples of water and sediment were collected in the No Cash Creek drainage in 2009, one in July and the second in September. The locations for sample collection are shown in Figures 2-1 and 2-2 and summarized in Table 2-1. The sample collection procedures were:

- Water Quality – Samples were collected directly from surface water expressions of No Cash Creek, seeps and disconnected rivulets in the wetlands east and north of No Cash Creek, seeps along the South McQueston River, and also from test pits that filled with seepage water. The list of analytes for water samples is given in Table 2-2. One set of water samples was filtered for analyses of dissolved metal concentrations. A second set was not filtered and used for analyses of total metal concentrations. All water samples for metals were preserved for analyses in the field following standard protocols. Field measurements of pH, temperature, and conductivity were made at the time of sample collection. Field data are given in Table 2-2.

- Sediment Chemistry– Samples were collected from the streambed of No Cash Creek at the same locations as water samples. Sediment samples were also collected from a series of test pits located along No Cash Creek and in the wetlands on both sides of No Cash Creek. Test pits were excavated either by hand or backhoe to a depth of one meter. Samples of sediment were obtained at one or two depth intervals in each pit. Test pits that filled with water from seepage were also sampled for water quality. Sediment samples were also collected from the seeps along the South McQueston River where water quality samples are also collected. The list of analytes for sediment samples is given in Table 2-2.

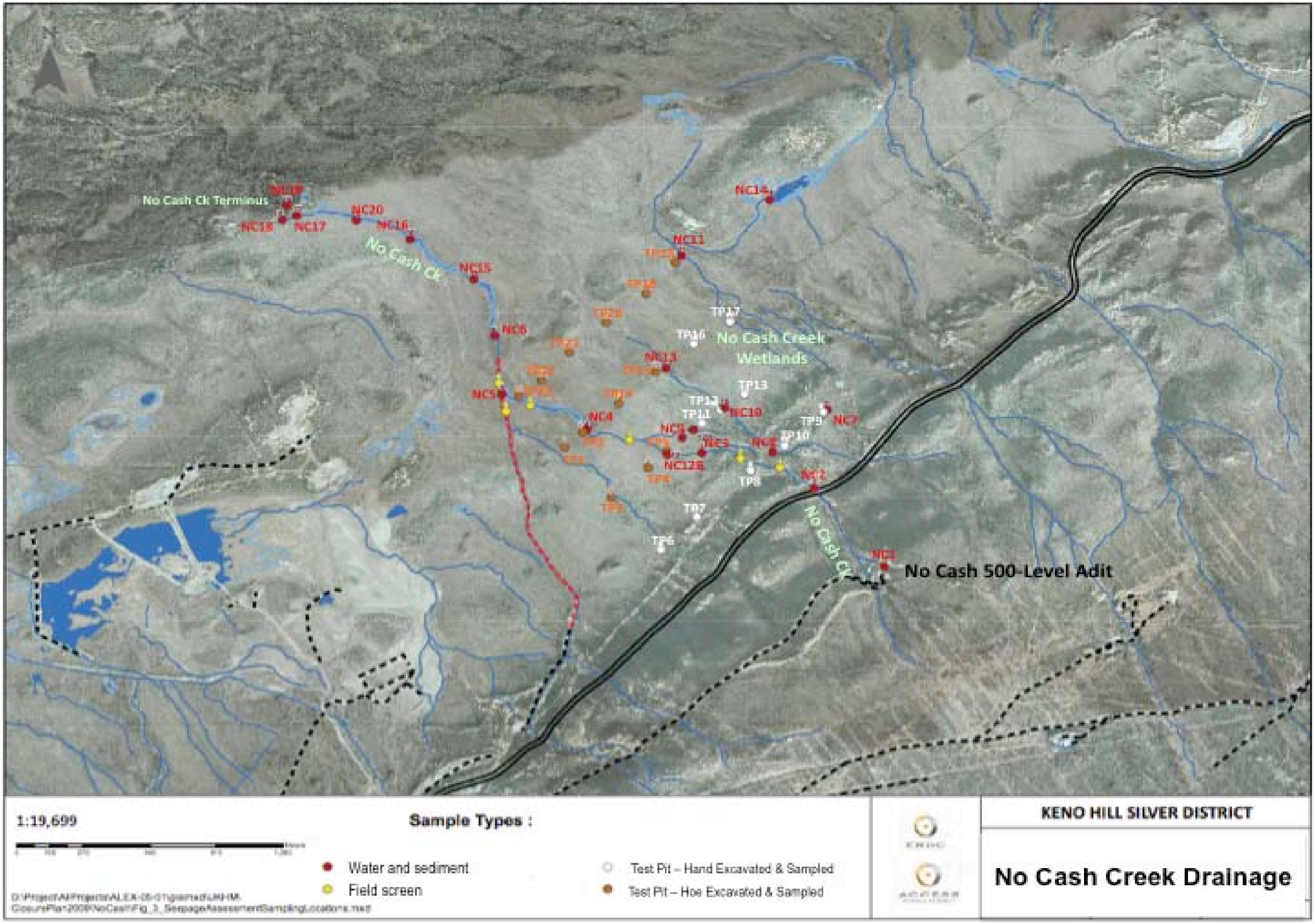

Figure 2-1 Sampling locations for water quality and sediment chemistry for the No Cash Creek drainage and nearby wetlands

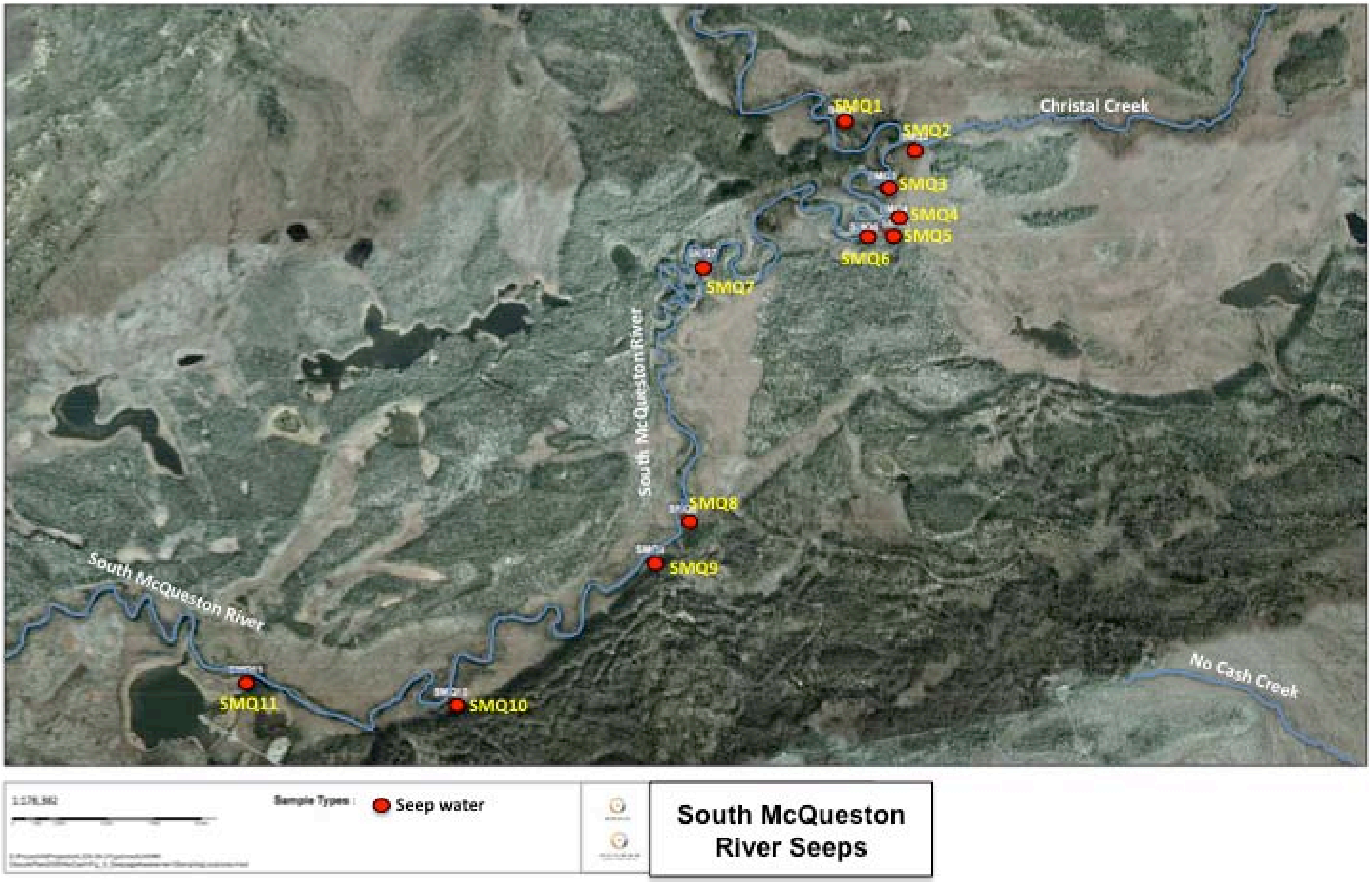

Figure 2-2 Sampling locations for water quality and sediment chemistry from seeps along the South McQueston River

Table 2-1 Summary of sampling locations and types

Sample Name	Sample Type	GPS Coordinates		July			September		
				pH	Temp (C)	EC (uS)	pH	Temp (C)	EC (uS)
No Cash Creek and surrounding areas									
NC1	Water/Sediment	no data	no data	6.81	0.7	1306	7.21	2	938
NC2	Water/Sediment	477473	7088820	8.54	2.8	1152	7.82	4.4	802
NC3	Water/Sediment	477017	7088979	7.91	1.5	1245	7.65	5	872
NC4	Water/Sediment	476550	7089080	8.28	3.5	1139	7.52	6.6	760
NC5	Water/Sediment	476206	7089239	8.08	6.8	1079	7.47	7	795
NC6	Water/Sediment	476176	7089497	8.35	6.4	1059	7.48	7.1	693
NC7	Water/Sediment	477621	7089137	7.48	1.4	1067	7.71	2.8	730
NC8	Water/Sediment	477304	7088982	7.82	0.2	689	7.77	2.6	513
NC9	Water/Sediment	476938	7089045	Dry - no sample			Dry - no sample		
NC10	Water/Sediment	no data	no data	No data			7.61	3.8	503
NC11	Water/Sediment	476978	7089844	7.33	11	491	7.51	5.7	504
NC12	Water/Sediment	476877	7088970	7.56	2.8	645	Not sampled		
NC12B	Water/Sediment	476982	7089080	Not sampled			7.18	3.8	943
NC13	Water/Sediment	476871	7089353	Not sampled			7.14	4.6	487
NC14	Water/Sediment	477292	7090102	Not sampled			6.44	8.6	130
NC15	Water/Sediment	476091	7089747	Not sampled			7.66	7.4	686
NC16	Water/Sediment	475833	7089925	Not sampled			7.41	8	671
NC17	Water/Sediment	475372	7090030	Not sampled			7.58	10.2	650
NC18	Water/Sediment	no data	no data	Not sampled			7.73	9.7	651
NC19	Water/Sediment	475332	7090074	Not sampled			7.56	10.4	653
NC20	Water/Sediment	475614	7090010	Not sampled			7.56	9	665
TP1	Test Pit - Soil/Sediment	476460	7089003	5.68	1.7	186.1	6.96	7.5	223
TP2	Test Pit - Soil/Sediment	476534	7089069	5.94	1.3	319	6.54	4.2	387
TP3	Test Pit - Soil/Sediment	476651	7088780	6.3	3	180	Not sampled		
TP4	Test Pit - Soil/Sediment	476799	7088912	6.14	1.8	81.6	6.3	6.8	160
TP5	Test Pit - Soil/Sediment	476873	7088978	6.3	0.5	284	6.04	6.2	112.5
TP6	Test Pit - Soil/Sediment	476850	7088548	6.7	0.1	258	7.32	2.2	264
TP7	Test Pit - Soil/Sediment	476996	7088693	6.88	0.1	360	6.83	3.9	465
TP8	Test Pit - Soil/Sediment	477214	7088900	Dry - no sample			Dry - no sample		
TP9	Test Pit - Soil/Sediment	477511	7089159	Dry - no sample			Dry - no sample		
TP10	Test Pit - Soil/Sediment	477352	7089009	Dry - no sample			Dry - no sample		
TP11	Test Pit - Soil/Sediment	477017	7089111	Dry - no sample			7.13	4	116.5
TP12	Test Pit - Soil/Sediment	477101	7089175	Dry - no sample			Dry - no sample		
TP13	Test Pit - Soil/Sediment	477190	7089240	Dry - no sample			6.58	4.1	104.6
TP14	Test Pit - Soil/Sediment	476678	7089197	Dry - no sample			6.66	6.8	534
TP15	Test Pit - Soil/Sediment	476831	7089337	5.87	0.8	350	6.85	3.9	420
TP16	Test Pit - Soil/Sediment	476984	7089463	Dry - no sample			6.02	6.2	120
TP17	Test Pit - Soil/Sediment	477131	7089561	6.1	1.3	169.9	6.34	2.6	124.4
TP18	Test Pit - Soil/Sediment	476790	7089685	5.2	1	206	6.76	3.7	127.5
TP19	Test Pit - Soil/Sediment	476910	7089823	6.3	4.7	541	No data		
TP20	Test Pit - Soil/Sediment	476629	7089557	6.56	0.9	521	6.31	4.4	631
TP21	Test Pit - Soil/Sediment	476479	7089424	6.15	2.9	107.9	6.01	3.7	1085
TP22	Test Pit - Soil/Sediment	476366	7089299	6.14	3.7	743	5.44	7.9	1146

				July			**September**		
Sample Name	**Sample Type**	**GPS Coordinates**		**pH**	**Temp (C)**	**EC (uS)**	**pH**	**Temp (C)**	**EC (uS)**
TP23	Test Pit - Soil/Sediment	476274	7089228	6.41	1.2	991	6.57	5.6	796
South McQueston River seeps									
SMQ1	Water/Sediment	474314	7092037	Dry - no sample			No data		
SMQ2	Water/Sediment	474571	7091938	8.2	6.2	656	No data		
SMQ3	Water/Sediment	474456	7091800	Dry - no sample			No data		
SMQ4	Water/Sediment	474498	7091680	Dry - no sample			No data		
SMQ5	Water/Sediment	474466	7091630	-	7.4	157.9	No data		
SMQ6	Water/Sediment	474391	7091617	Dry - no sample			No data		
SMQ7	Water/Sediment	473809	7091520	Dry - no sample			No data		
SMQ8	Water/Sediment	473740	7090604	Dry - no sample			No data		
SMQ9	Water/Sediment	473623	7090454	No data - broken probe			No data		
SMQ10	Water/Sediment	472906	7089943	No data - broken probe			No data		
SMQ11	Water/Sediment	472167	7090027	No data - broken probe			No data		

Table 2-2 Analytical program for water and sediment samples

Sample Type	Parameter	Method
Water	Na, K, Ca, Mg, S	EPA 200.8
	Metals (Al, Sb, As, Ba, Be, Bi, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Mo, Ni, P, Se, Ag, Sr, Tl, Sn, Ti, V, Zn, Zr	EPA 200.8
	Nitrogen (total)	SM-4500N C
	Nitrate + Nitrite (N)	EPA 353.2
	Nitrite (N)	EPA 353.2
	pH	EPA 200.2/SM-4500H+B
	Sulfate	EPA 375.4
	Total Dissolved Solids	SM 2540C
	Total Organic Carbon	SM-5310C
	Total Suspended Solids	SM-2540D
	Dissolved Organic Carbon	M 860-87T
	Chloride	EPA 325.2
	Conductance	SM-2510B
Sediment	Na, K, Ca, Mg, S	EPA 200.8
	Metals (Al, Sb, As, Ba, Be, Bi, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Mo, Ni, P, Se, Ag, Sr, Tl, Sn, Ti, V, Zn, Zr	EPA 200.8
	Moisture	Ont MOE-E 3139
	pH (2:1 DI Water Extract)	Carter, SSMA 16.2
	Sulfate (soluble)	EPA 375.4
	Sulfide	EPA 821-R01-100
	Total Organic Carbon	LECO 203-601-224

3 Results and Discussion

The effects of the discharge of water from the No Cash 500 adit on water and sediment quality are described and discussed in the following sections through evaluation of trends in concentration with distance along No Cash Creek and spatial distributions of metals (cadmium, manganese, and zinc) and other analyte concentrations throughout the study area. An evaluation of attenuation processes is provided in Section 4.c

3.1 Trends in Water Quality in No Cash Creek

The No Cash 500-level adit water contains elevated concentrations of sulfate and some metals, primarily cadmium, manganese, and zinc. The effects of the adit discharge on water quality in No Cash Creek with distance from the adit are shown in Figure 3-1 based on analytical results for samples collected down the length of No Cash Creek in order from top to bottom of NC1, NC2, NC3, NC4, NC5, NC6, NC15, NC16, NC20, and NC17:NC18:NC19 (three sampling locations at the end of No Cash Creek where it forms a wetland pond). The channel of No Cash Creek is defined in most areas but does spread and disappear into bog/marsh in some sections, reappearing again downgradient. Water samples were collected from stretches where the stream channel was reasonably well defined.

Analyses conducted for this study indicate the adit water has near neutral to slightly alkaline pH, ranging from 7.4 to 8.3 (Figure 3-1a). These circumneutral pH values are consistent with previous studies of No Cash Creek and adit discharge by Kwong et al. (1994, 1997) and MERG (2000). Sulfate concentrations range from 200 to 500 mg/L generally decreasing in concentration with distance downstream from the adit (Figure 3-1b). Sulfate concentrations measured for this study, particularly for the September 2009 samples, are generally lower than those reported in previous work by Kwong et al. (1994, 1997) and MERG (2000). Sulfate is the predominant dissolved ion; hence TDS concentrations show a similar trend as sulfate, decreasing by 20 to 30% down the length of No Cash Creek (Figure 3-1c). Total organic carbon concentrations increase with distance from the adit due to the influence of the bog/marsh areas that comprise much of the area surrounding No Cash Creek (Figure 3-1d).

The concentrations of cadmium, manganese, and zinc are elevated in the adit discharge as indicated by the highest concentrations at upstream location NC1 where the adit discharge joins No Cash Creek (Figures 3-1e-g). The metal concentrations decrease rapidly with distance downstream from the adit. The exception is iron, which shows variable concentrations in No Cash Creek. The dissolved iron concentrations are high given the neutral pH conditions, implying it is partially ferrous iron that metastably persists until the stream water becomes oxygenated. The dissolved iron concentrations are also generally lower than total iron concentrations, indicating much of the iron is transported as particulates.

Manganese shows a pattern of rapid decrease down to sampling location NC3 and then an increase at NC4 and downstream (Figure 3-1f). The initial rapid decrease is most likely due to oxidation of Mn^{2+} upon exposure to air and subsequent precipitation of manganese oxyhydroxides (Figure 3-1f). Manganous ion oxidation is relatively rapid at slightly alkaline pH particularly in the presence of iron hydroxide and manganese oxide particles as well as microbial processes, which catalyze the oxygenation reaction (Hoffman, 1990). The cause of the downstream increase in manganese is less certain. Manganese is more mobile under anoxic conditions; hence the increases are presumably due to release of manganese from sediments by reductive dissolution reactions (Burdige, 1993) occurring in bog/marsh areas high in organic carbon that are common in the lower reach of No Cash Creek where the gradient is very low.

Cadmium and zinc concentrations previously measured in No Cash Creek by Kwong et al. (1994) and MERG (2000) were generally greater than those measured in this study and showed a less rapid rate of decrease with distance downstream (Figures 3-1e,g). Cadmium concentrations are directly related to zinc in No Cash Creek water (Figure 3-2). Zinc, in turn, shows some degree of association with manganese for No Cash Creek water, but the association is less well defined than for cadmium and zinc (Figure 3-3). These associations are most likely indicative of both a common origin of the adit discharge for cadmium, manganese, and zinc and different levels of attenuation with distance down No Cash Creek.

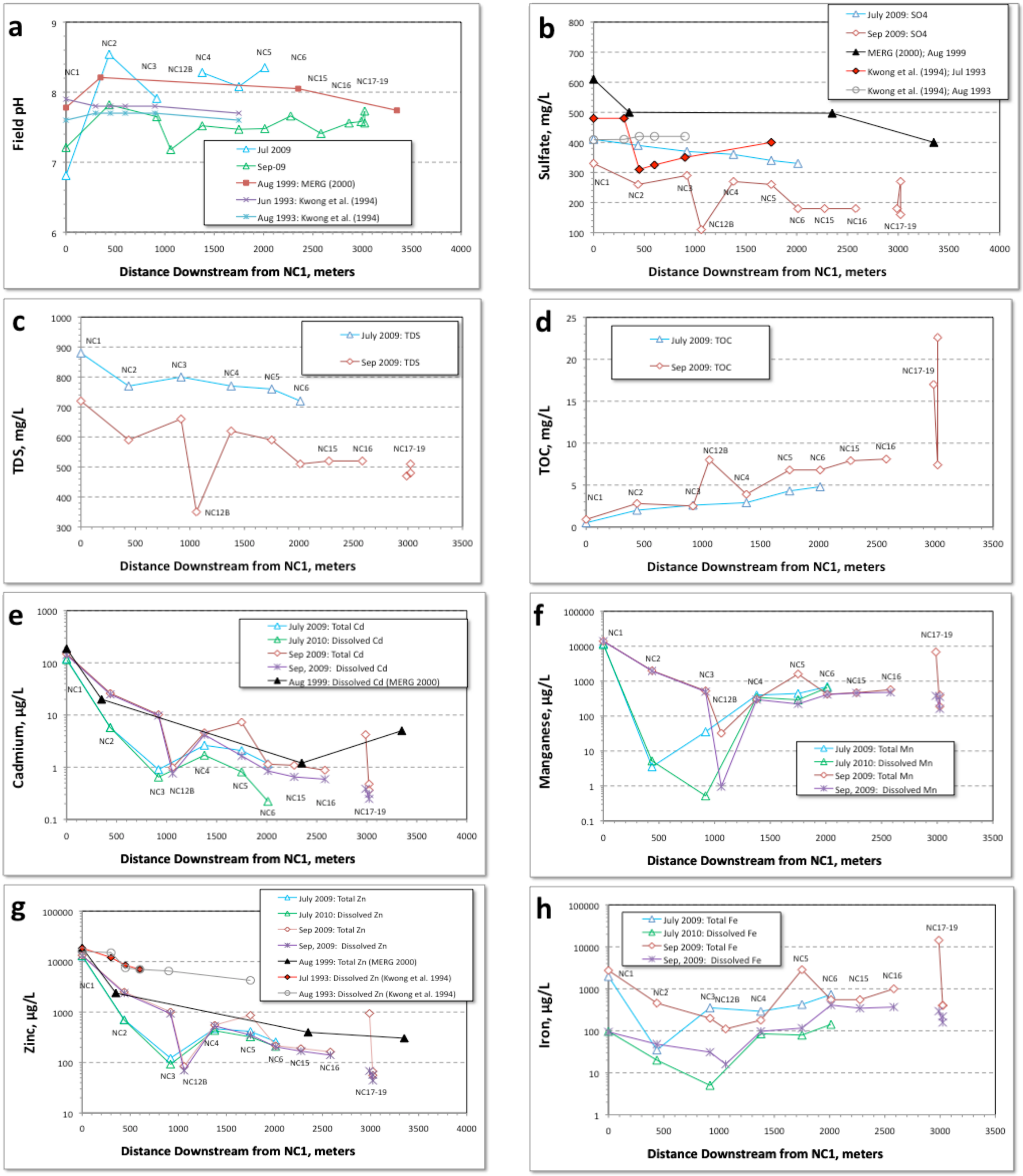

Figure 3-1 Concentration trends with distance from the No Cash 500 Adit (location NC1) in surface water of No Cash Creek

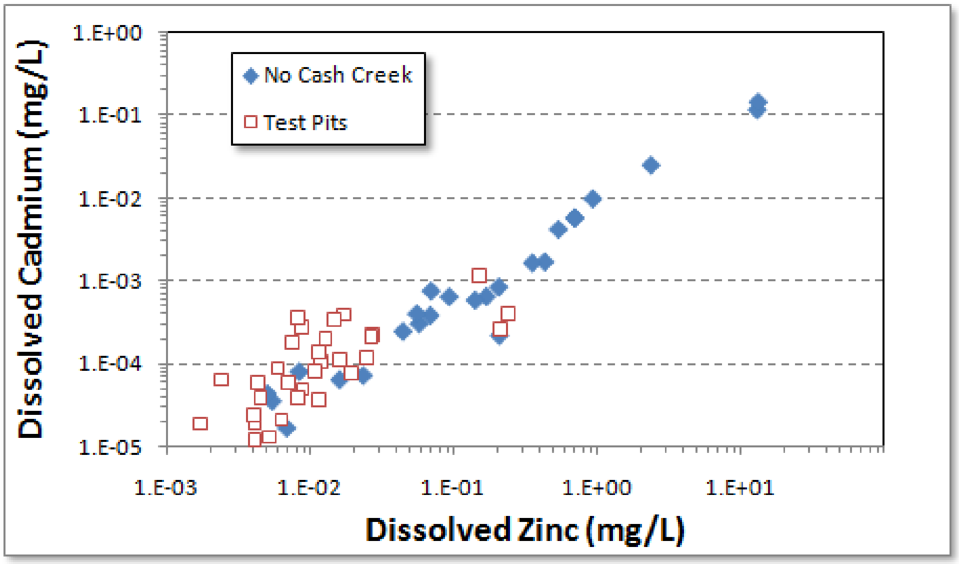

Figure 3-2 Relationship between dissolved cadmium and dissolved zinc in surface water of No Cash Creek and seepage water collected in all test pit

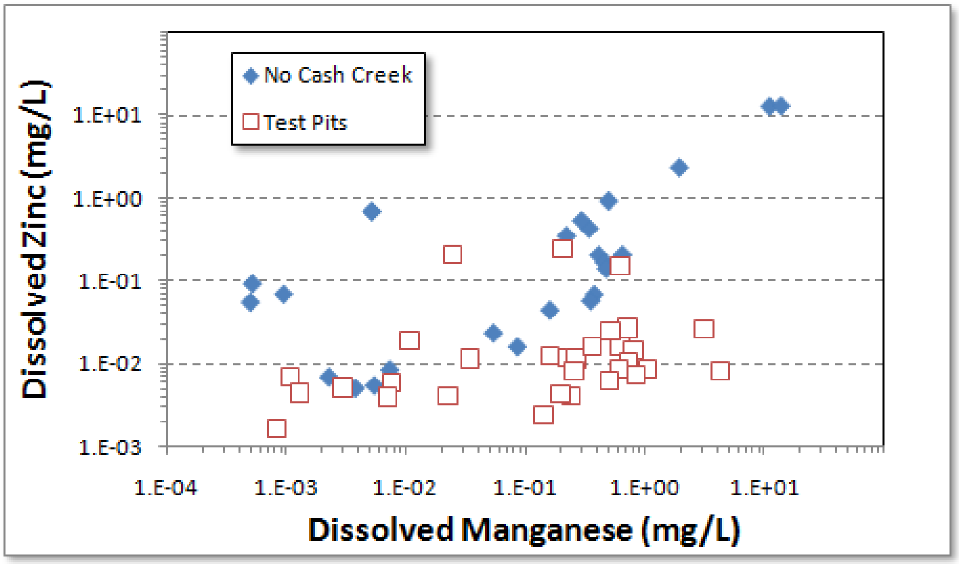

Figure 3-3 Relationship between dissolved zinc and dissolved manganese in surface water of No Cash Creek and seepage water collected in all test pits

Figure 3-4 shows the history of zinc and pH for discharge water from the No Cash 500 adit using data from Kwong et al. (1997) for 1983 to 1993, MERG (2000) for 1999, and this study for 2009. Concentrations of cadmium and zinc peaked in 1987 and have generally declined by 50 to 60% since 1987. The pH has remained stable in the range of 7 to 8 over this time period with little variation (Figure 3-4). Historical data for alkalinity given in Table 3-1 show that the adit water has substantial neutralizing capacity, which is indicative of interaction between groundwater and carbonate minerals in the flow paths leading to the adit discharge point.

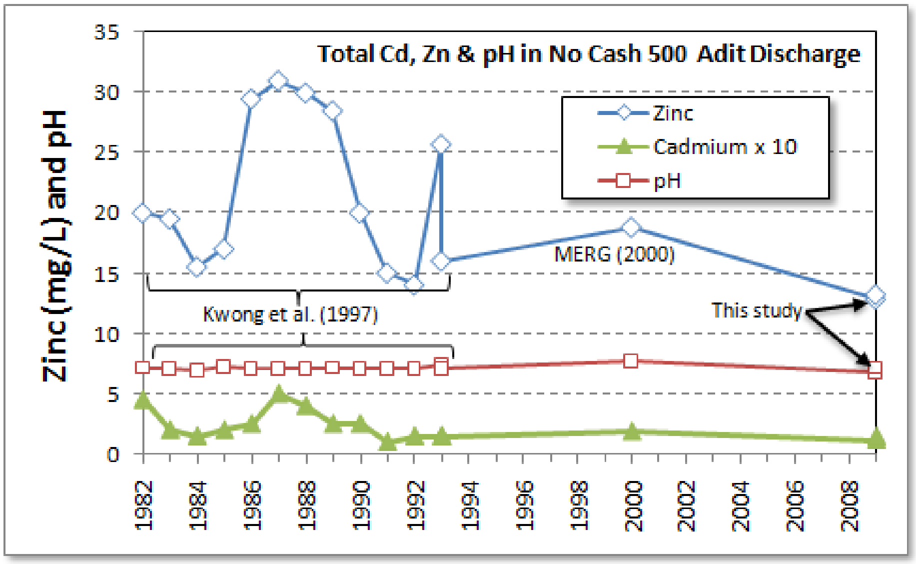

Figure 3-4 History of cadmium, zinc, and pH in the No Cash 500 adit discharge water

Table 3-1 Alkalinities reported for the No Cash 500 level discharge water

Alkalinity (mg $CaCO_3$/L)	Date	Source
70	16-Jun-93	Kwong et al. (1997)
137	11-Aug-99	MERG (2000)
154	2-Aug-2003	United Keno Hill Mines surveillance monitoring (KV-20)
122	19-Jul-2005	United Keno Hill Mines surveillance monitoring (KV-20)

Decreases in metal concentrations in No Cash Creek with distance from the 500-level adit have been previously attributed to natural attenuation processes, such as precipitation of iron hydroxides (ferrihydrite), manganese oxides (birnessite, manganite), coprecipitation with hydroxides and carbonate minerals, and adsorption (Kwong et al. 1994; 1997; MERG 2000). Kwong et al. (1994; 1997) has also reported hydroxycarbonate mineral precipitation (e.g., hydrozincite) as an important attenuation process for zinc in the nearby Onek drainage on Keno Hill where mine discharges have occurred.

The effects of attenuation processes on metals can be seen by comparison of the concentration trend with distance for sulfate, which is a relatively mobile, conservative ion[1] released in adit discharge, to trends for cadmium, manganese, and zinc, which are affected by natural attenuation processes. This comparison is shown in Figure 3-5 as ratios of concentrations in No Cash Creek to concentrations in the 500-level discharge as measured at location NC1. Sulfate concentrations show an approximate 25 to 40% decrease with distance, presumably due mostly to dilution. It is also possible that uptake and reduction of sulfate to sulfide in the organic rich soils and sediments in the boggy areas may also result in some loss of sulfate (sulfide was detected in sediments in these areas - discussed below).

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[1] Ideally, chloride would be the best conservative solute to gauge the effects of dilution. However, chloride levels are very low in the adit discharge water (<0.6 mg/L) and increase slightly with distance downstream that it is not a useful tracer for No Cash Creek. Hence, sulfate was selected as the best alternative even though it is likely subject to some degree of chemical reaction, such as reduction to sulfide in the wetland boggy areas, that slightly complicates interpretation of its concentration trends with distance down No Cash Creek.)

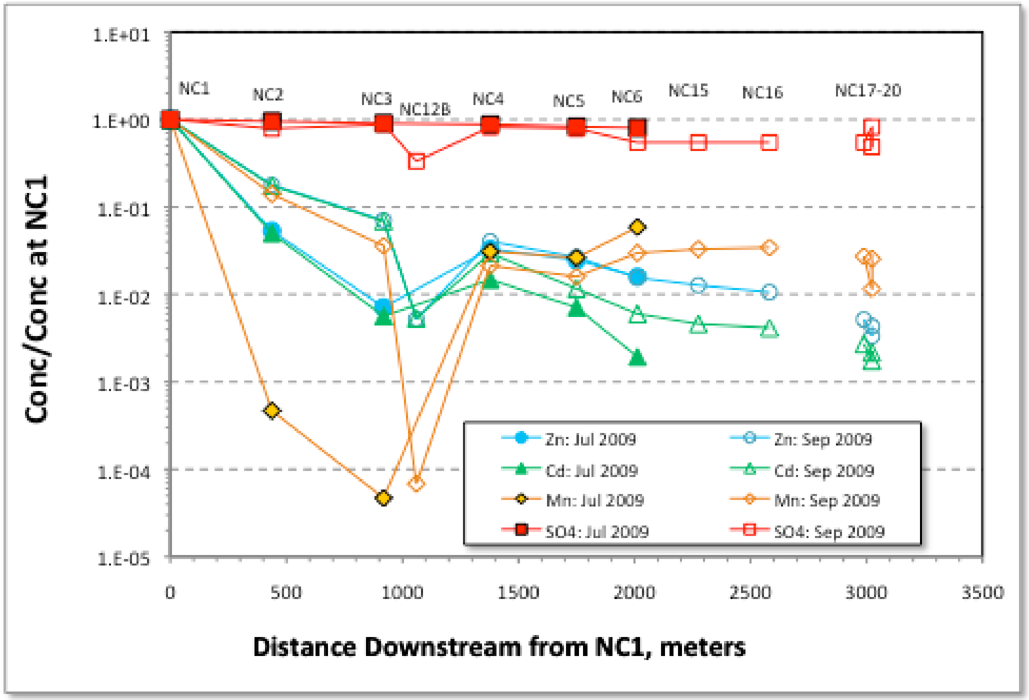

Figure 3-5 Ratios of concentrations of sulfate and metals (cadmium, manganese, and zinc) in surface water of No Cash Creek to concentrations in adit discharge measured for location NC1

Metal concentrations decrease by substantially greater proportions with distance downstream compared to sulfate (Figure 3-5). For example, zinc concentrations decrease by a factor of about 100, cadmium concentrations decrease by factors of 100 to more than 1000, and manganese decreases by factors from 20 to 10,000, depending on the location. Manganese concentrations show a very sharp drop near the adit due to oxidation immediately after exiting the adit and exposed to air, indicating that much of the discharged manganese never reaches the downstream boggy areas. The increases in manganese in the downstream portions of No Cash Creek imply there is a release of manganese from sediments in the boggy areas where oxygen deficient conditions and high organic content are conducive to manganese oxide dissolution. The distinct difference in trends between sulfate and the metals indicates that attenuation processes, including both inorganic precipitation and adsorption reactions and biologically mediated processes of oxidation are the primary mechanisms causing the sharp decreases in cadmium, manganese, and zinc concentrations rather than hydrologic processes of dilution and dispersion. Specific attenuation processes and reactions are discussed in more detail in Section 4.

Water samples were also collected from surface water locations in the wetlands in the area north of the No Cash drainage. The data for these additional surface water locations are shown spatially in Figure 3-6. The concentrations of metals at these additional locations are variable but generally tend to be lower than those observed for the lower portions of No Cash Creek (downstream of NC5) (Table 3-2). For example, the average concentrations of total zinc in the lower stretch of No Cash Creek measured at location NC5 and farther downstream are 264 µg/L (July) and 147.6 µg/L (September) compared to 12.1 µg/L (July) and 16.42 µg/L (September) for the surface water samples collected in the surrounding wetlands north and east of No Cash Creek (Figure 3-6; Table 3-2). Similarly higher concentrations for cadmium, manganese, and sulfate were observed for the water from the No Cash Creek drainage than in the nearby wetlands (Table 3-2).

Table 3-2 Metal (Cd, Mn, Zn) and sulfate concentrations in surface water samples from No Cash Creek at locations greater than 1.5 km downstream from the 500 adit discharge compared to concentrations in surface water expressions in the surrounding wetlands

	July 2009 Samples							September 2009 Samples						
No Cash Creek Drainage	Tot Cd (µg/L)	Diss Cd (µg/L)	Tot Mn (µg/L)	Diss Mn (µg/L)	Tot Zn (µg/L)	Diss Zn (µg/L)	SO4 (mg/L)	Tot Cd (µg/L)	Diss Cd (µg/L)	Tot Mn (µg/L)	Diss Mn (µg/L)	Tot Zn (µg/L)	Diss Zn (µg/L)	SO4 (mg/L)
No Cash Creek Drainage														
NC5	2.08	0.815	443	292	414	321	340	7.28	1.65	1600	222	863	351	260
NC6	1.17	0.222	692	652	258	207	330	1.14	0.848	422	413	216	205	180
NC15								1.09	0.652	466	458	190	168	180
NC16								0.877	0.589	571	477	163	140	180
NC17								4.22	0.385	6830	379	944	68.1	180
NC18								0.363	0.247	188	161	55.9	43.9	270
NC19								0.477	0.307	404	354	66.7	57.0	160
Averages	1.6	0.5	567.5	472.0	336.0	264.0	335.0	2.2	0.7	1497.3	352.0	356.9	147.6	201.4
Wetlands														
NC8	0.100		22		10.8			0.062	0.036	8.97	5.45	8.1	5.4	120
NC10	0.155	0.081	16.7	7.35	14.8	8.3	160	0.059	0.044	7.44	3.78	5.4	5.0	170
NC13								0.067	0.017	12.7	2.27	12.0	6.8	110
NC7								0.420	0.403	2.09	0.50	54.8	54.9	190
NC11	0.106	0.065	102	86.0	20.7	15.9	100	0.103	0.073	65.7	54.1	26.7	23.2	120
NC14								0.064	0.007	20.7	5.06	10.3	3.2	2.9*
Averages	0.12	0.07	46.90	46.68	15.43	12.10	130.00	0.13	0.10	19.60	11.86	19.55	16.42	142.00
*Outlier not used to calculate average.														

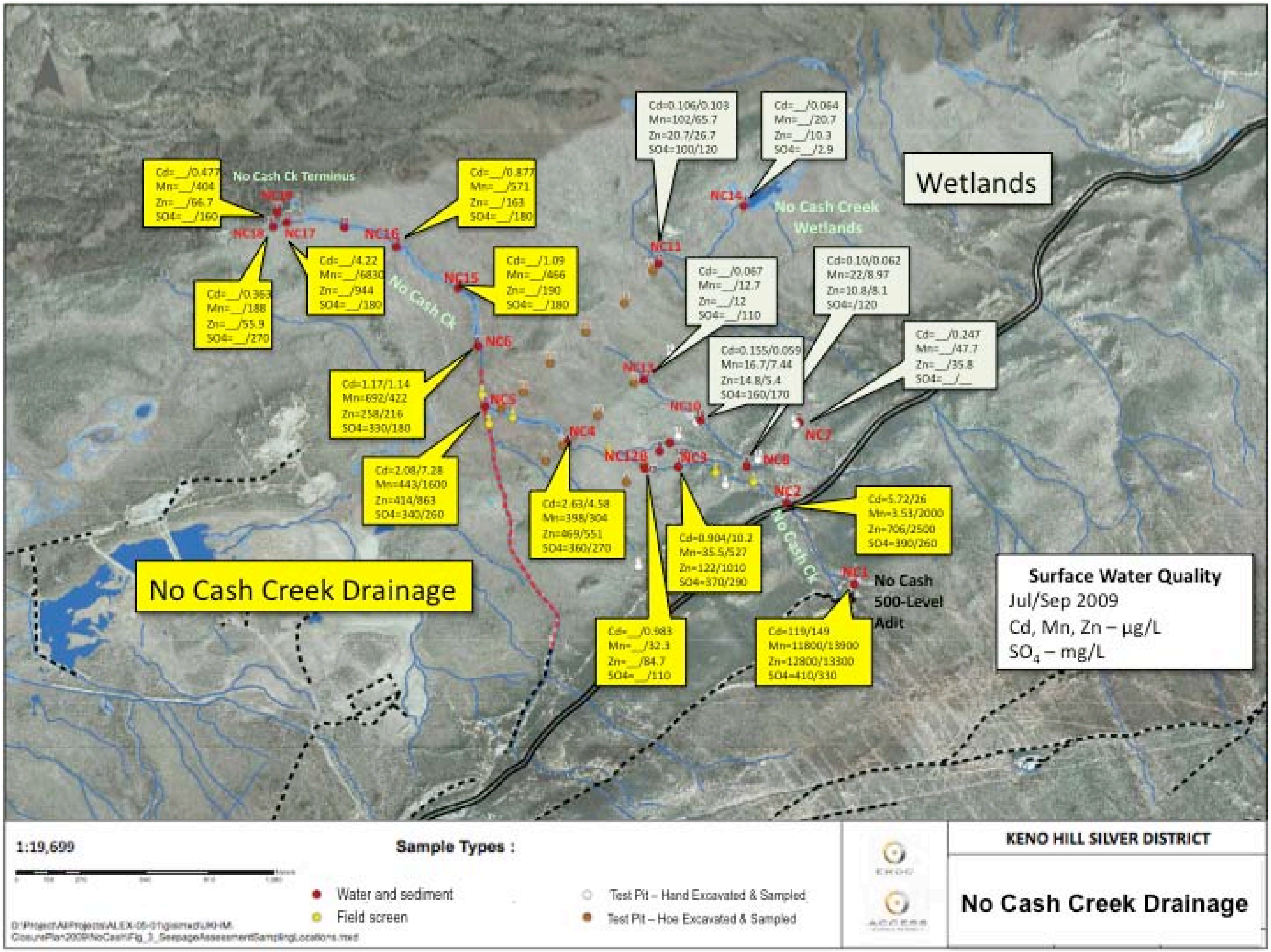

Figure 3-6 Water quality (cadmium, manganese, zinc, and sulfate) for No Cash Creek water (yellow) and surface water in the wetlands (light green)

3.2 Trends in Water Quality in Test Pits

A series of test pits were excavated on four transects positioned approximately perpendicular to No Cash Creek and extending northeast and south of No Cash Creek (Figure 3-7). These pits were excavated by backhoe or hand to about one-meter depth. They rapidly filled with seepage water. The water in the pits was collected and analyzed for chemical compositions. The results for metals (cadmium, manganese, and zinc), TOC, DOC, sulfate, and total suspended solids (TSS) are summarized in Table 3-3. The total metal concentrations in the test pit water are generally consistent with those observed in the lower No Cash Creek surface water and in other natural surface water sampling locations in the surrounding wetlands to the east and north of No Cash Creek (see Table 3-2 and Figure 3-6).

Many of the highest concentrations of metals (cadmium, manganese, and zinc) were observed for test pits located directly alongside No Cash Creek, particularly for the first set of samples collected in July shortly after the pits were dug, but elevated concentrations of cadmium and manganese also observed for the pits located in the surrounding wetlands away from No Cash Creek (Figure 3-7). This observation indicates that while No Cask Creek has historically contained and transported elevated metal concentrations, there is no clearly defined spread of metals into the neighboring shallow groundwater system. Instead, metals are relatively widespread throughout the study area with sporadic instances of high concentrations near low concentrations, that is, there is no defined plume of dissolved metals in the bog around the main channel of No Cash Creek.

The total metal concentrations in the test pit water samples are commonly significantly higher than dissolved concentrations, especially for cadmium and zinc (Table 3-3), implying the occurrence of particulates in the water samples for total metal analyses. A plot of cadmium versus TSS shows a relationship exists between metal concentrations and TSS (Figure 3-8a), confirming the presence of metal-bearing particulates at least for cadmium. These particulates may be iron and/or aluminum hydroxides or possible organic carbon. Relationships between manganese and zinc with TSS are less distinct (Figures 3-8b and 3-8c), but generally higher total manganese and zinc concentrations coincide with higher TSS concentrations. The nature of the sampling approach does not necessarily yield information about the hydrologic mobility of particulate metal forms in that an excavated pit will often contain suspended particles due to the fresh disruption in the sediment. In fact, the July test pit water samples, which were collected shortly after excavating the pits, typically had higher TSS concentration and, as a result, higher metal concentrations than water samples collected in September (Table 3-3; Figure 3-7). The extra time for settling of suspended solids resulted in lower TSS and metal concentrations for the September water samples.

Concentrations of DOC and TOC are comparatively higher in the test pit water (Table 3-3) than in No Cash Creek water (see Figure 3-1d). This result is consistent with the boggy/marshy, heavily vegetated environment of the areas where the test pits were located. Concentrations of sulfate in test pits are generally lower than those observed for samples taken directly from No Cash Creek.

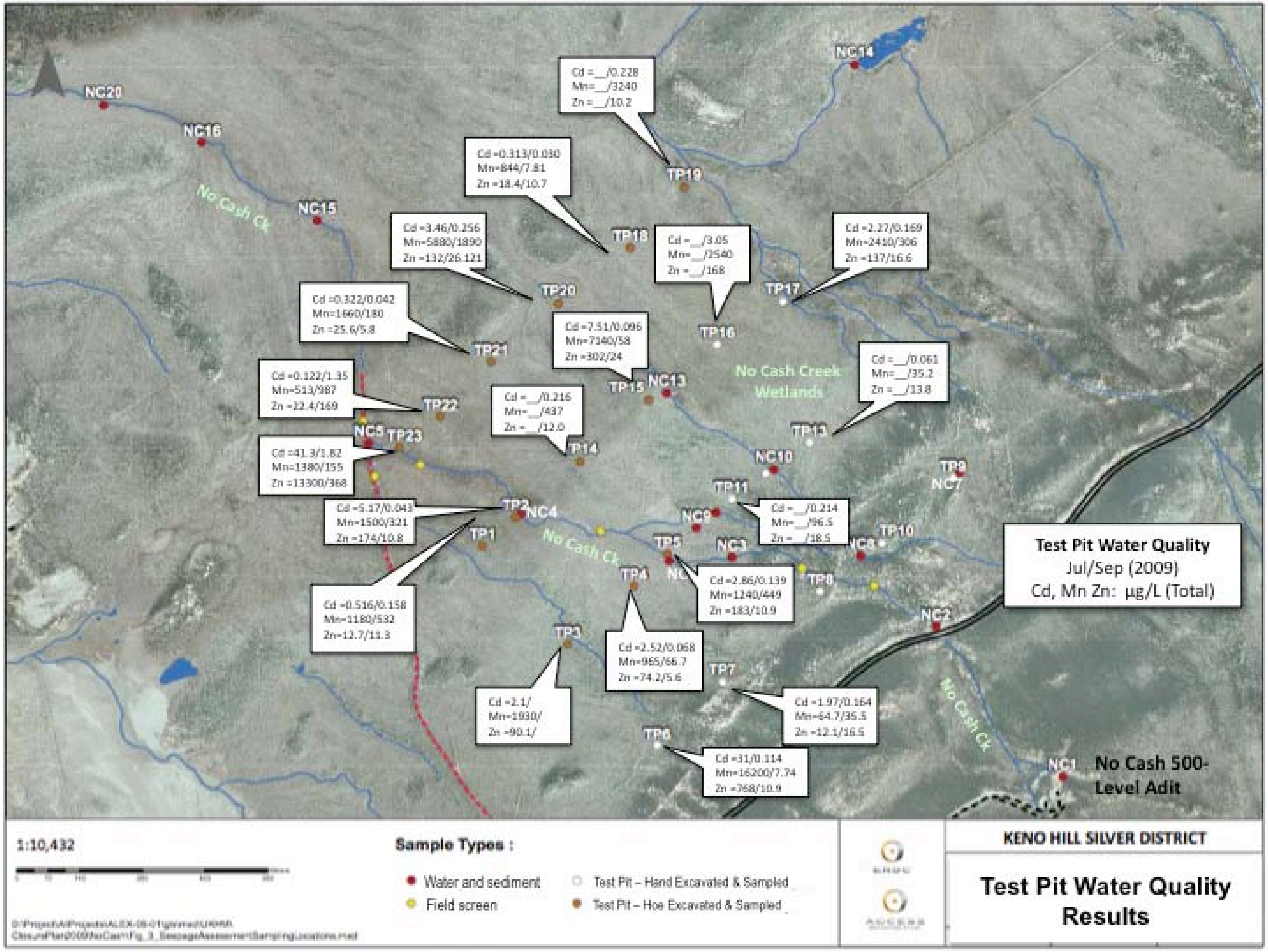

Figure 3-7 Water quality (cadmium, manganese, and zinc) in water collected in test pits

Table 3-3 Summary of metal concentrations (cadmium, manganese, and zinc), DOC, TOC, sulfate, and TSS in test pit water

	Cd (µg/L)		Mn (µg/L)		Zn (µg/L)					
Jul-09	Total	Dissolved	Total	Dissolved	Total	Dissolved	DOC (mg/L)	TOC (mg/L)	SO4 (mg/L)	TSS (mg/L)
TP1	0.516	0.271	1180	1070	12.7	8.7	44	54	<5*	360
TP2	5.17	0.383	1500	624	174	16.9	15.2	24	79	1800
TP3	2.1	0.334	1930	805	90.1	14.5	72	96	<5*	1400
TP4	2.52	0.201	965	165	74.2	12.7	38.8	55	<0.5	19000
TP5	2.86	0.221	1240	722	183	27.1	19.8	24	53	190
TP6	31	0.065	16200	10.8	768	7.2				
TP7	1.97	0.087	64.7	7.65	12.1	5.9	19.5	51	79	17000
TP15	7.51	0.209	7140	3160	302	26.6	15.0	56	120	2400
TP17	2.27	0.105	2410	232	137	11.8	25.3	46	32	21000
TP18	0.313	0.080	844	741	18.4	10.7	20.8	22.8	38	56
TP20	3.46	0.357	5880	4290	132	8.2	14.1	25	110	2300
TP21	0.322	0.049	1660	611	25.6	8.8	25.1	31	<0.5	97
TP22	0.122	0.021	513	516	22.4	6.3	10.6	11.9	270	3600
TP23	41.3	0.388	1380	206	13300	240	7.0	31	340	3500
Averages	7.25	0.20	3064.76	940.03	1089.39	28.96	25.17	40.59	124.56	5593
Sep-09										
TP1	0.158	0.019	532	243	4.1	11.3	18.2	19.6	18	14
TP2	0.043	0.012	321	22.7	4.1	10.8	13.2	14.0	30	<1
TP4	0.068	0.060	66.7	199	4.3	5.6	24.3	28.3	2.1	52
TP5	0.139	0.118	449	519	24.8	23.5	18.8	18.2	6.9	6
TP6	0.114	0.019	7.74	0.85	1.7	10.9	21.1	21.4	23	3
TP7	0.164	0.059	35.5	1.09	7.0	16.5	12.4	13.5	83	57
TP11	0.214	0.039	96.5	1.32	4.5	18.5	25.9	26.7	16	11
TP13	0.061	0.013	35.2	2.99	5.2	13.8	27.3	27.3	<0.5	8
TP14	0.216	0.064	437	143	2.4	12.0	14.6	15.2	18	3
TP15	0.096	0.078	58.0	10.9	19.4	24.0	11.5	14.2	140	11
TP16	3.05	0.136	2540	267	11.5	168		62	1.1	14000
TP17	0.169	0.024	306	7.07	4.0	16.6	23.7	24.4	23	140
TP18	0.030	0.036	7.81	34.6	11.5	10.7	22.8	23.0	0.7	<1
TP19	0.228	0.179	3240	849	7.4	10.2	46	45.4	<0.5	88
TP20	0.256	0.111	1890	367	16.2	26.1	12.2	17.6	71	4
TP21	0.042	0.039	180	257	8.1	5.8	24.7	24.6	14	5
TP22	1.35	1.14	987	627	152	169	8.6	9.6	500	31
TP23	1.82	0.254	155	24.9	210	368	4.4	6.5	230	13
Averages	0.46	0.13	630.25	198.75	27.68	51.18	19.39	22.86	73.55	903

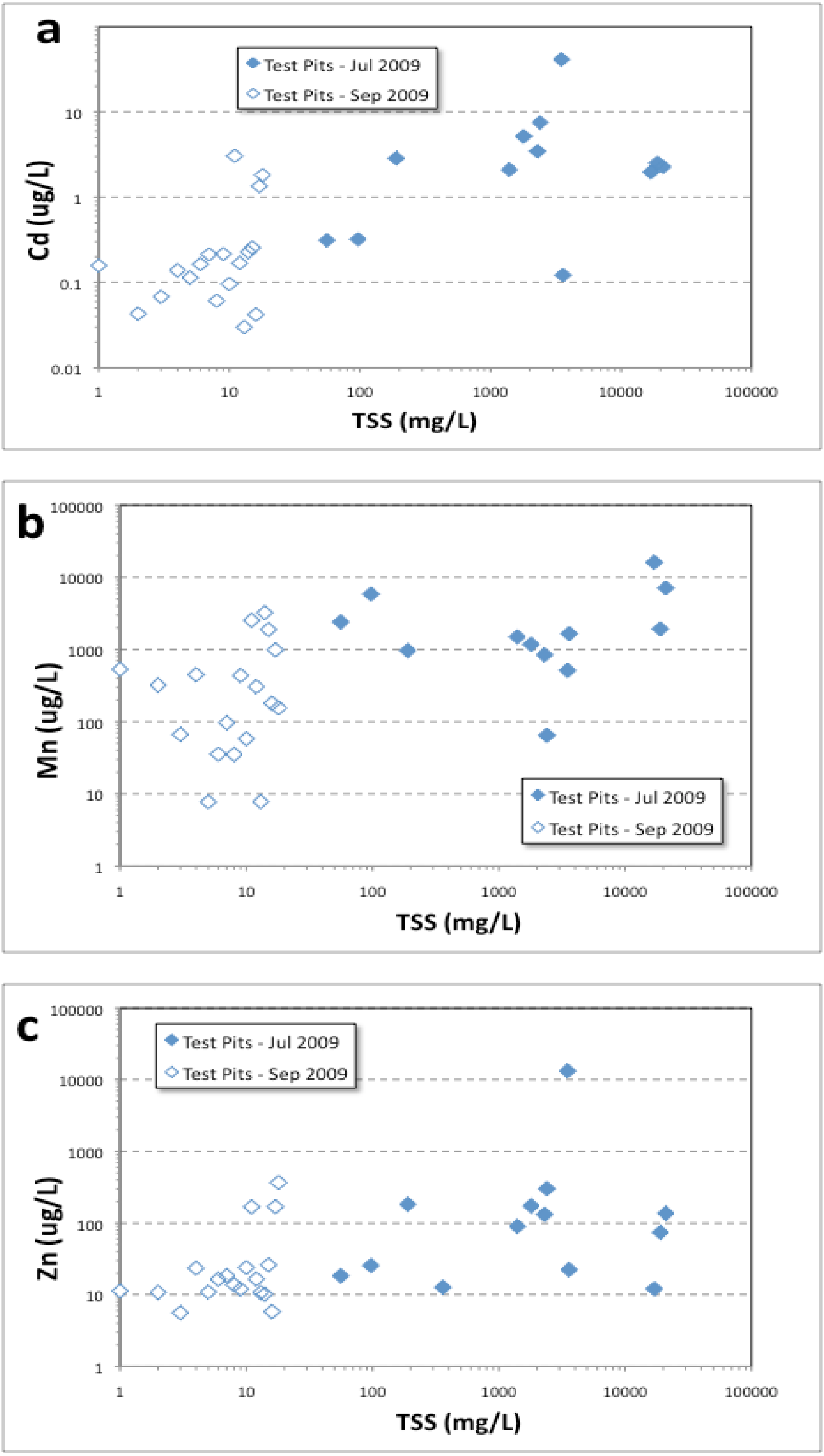

Figure 3-8 Relationships between total metal concentrations and TSS in test pit water for a) cadmium, b) manganese, and c) zinc

3.3 Trends in Water Quality in South McQueston Seeps

The concentrations of dissolved and total cadmium, manganese, zinc, and sulfate in water samples collected from the seeps along the South McQueston River are shown in Figure 3-9. The range of concentrations is generally lower than what was measured for the surface water locations in the lower portions of No Cash Creek and in the wetlands located east and north of No Cash Creek (Figure 3-6). However, the metal concentrations for the seeps are variable from one location to the next with no discernable pattern. Higher metal concentrations in seeps nearest the terminus of No Cash Creek are not necessarily higher than concentrations at more distant seeps.

It is not clear there is a hydrologic connection between No Cash Creek and the South McQueston River or whether the River segment shown in Figure 3-9 is a gaining or losing stretch. The patterns for metal concentration data, sulfate and other solutes do not provide definitive clues about the hydrologic flow paths. It is not possible to make a reasonable determination about whether metal loads in No Cash Creek have affected water quality in seeps along the South McQueston River through consideration of only the seep water quality for metals and sulfate. Sediment chemistry data discussed in Section 3-6 provide more informative information than the water quality data.

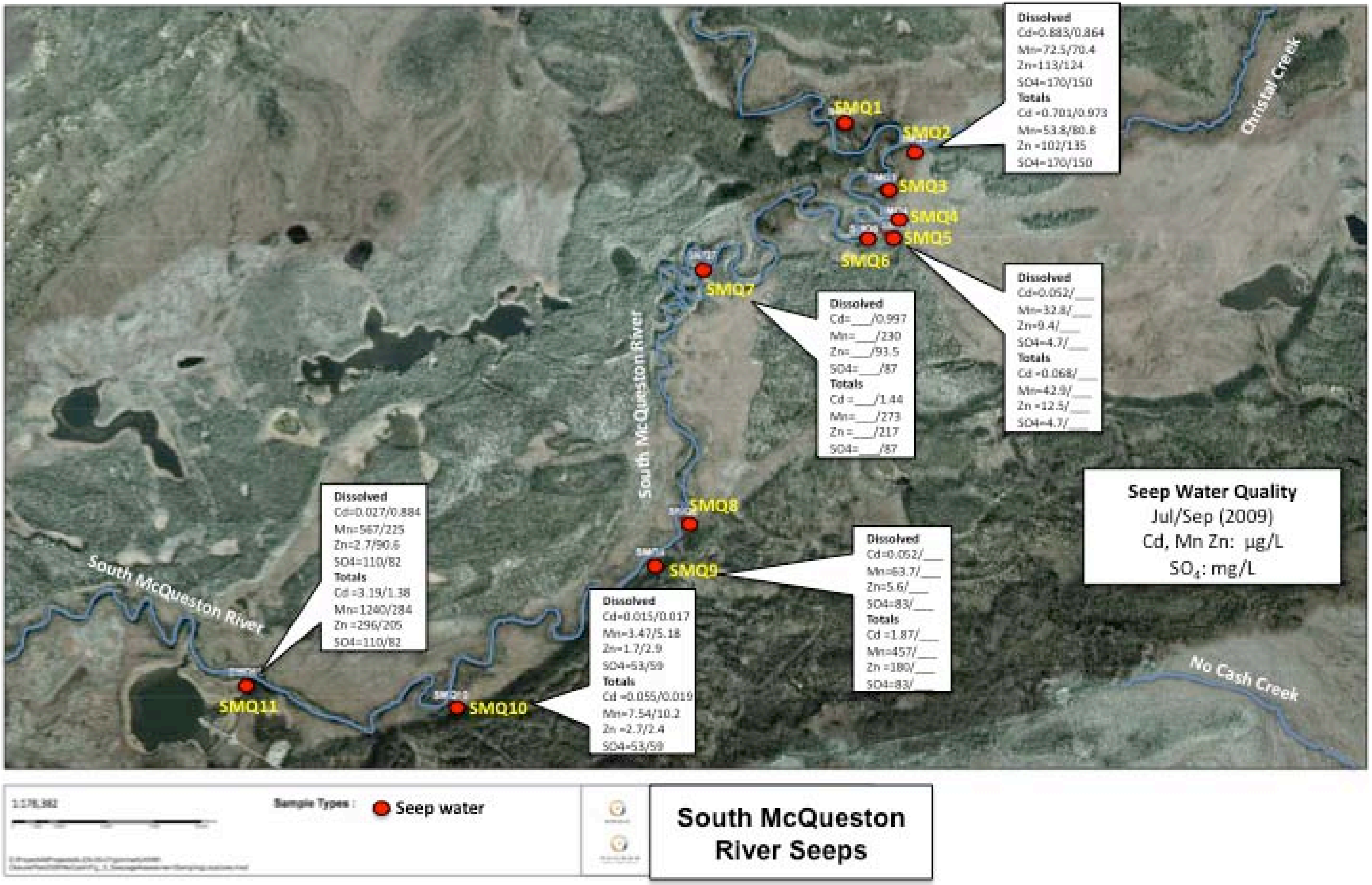

Figure 3-9 Concentrations of dissolved and total metal (cadmium, manganese, zinc) and sulfate in South McQueston seeps

3.4 Trends in Stream Channel Sediment Chemistry on No Cash Creek

Concentrations of metals, sulfate, and sulfide in stream channel sediments from No Cash Creek are shown in Figures 3-10 (July 2009 data) and 3-11 (September 2009 data) with distance from the 500-level adit discharge at location NC1. The areal distribution and metal data for the sediment samples collected from the No Cash Creek stream channel and at locations of other surface water expressions in the surrounding wetlands and data are shown in Figure 3-12.

Both sets of stream channel data from July and September 2009 show similar trends of decreasing concentrations of cadmium, manganese, and zinc with distance downstream. Metal concentrations in sediments collected from the stream channel of No Cash Creek are generally greater than those in sediments collected from the surrounding wetlands north and east of No Cash Creek. The trends are indicative of metal enrichment in sediments nearer to the adit discharge due natural attenuation processes, particularly in the upper part of No Cash Creek.

The sediment samples were also analyzed for soluble sulfate and sulfide. Concentrations of soluble sulfate in sediments show relatively constant concentrations with distance, whereas sulfide shows a marked increase with distance downstream in the September data, which includes samples all the way to the end of No Cash Creek (Figure 3-11). The trends for metals and sulfate in sediments are generally consistent with those for water concentrations discussed above.

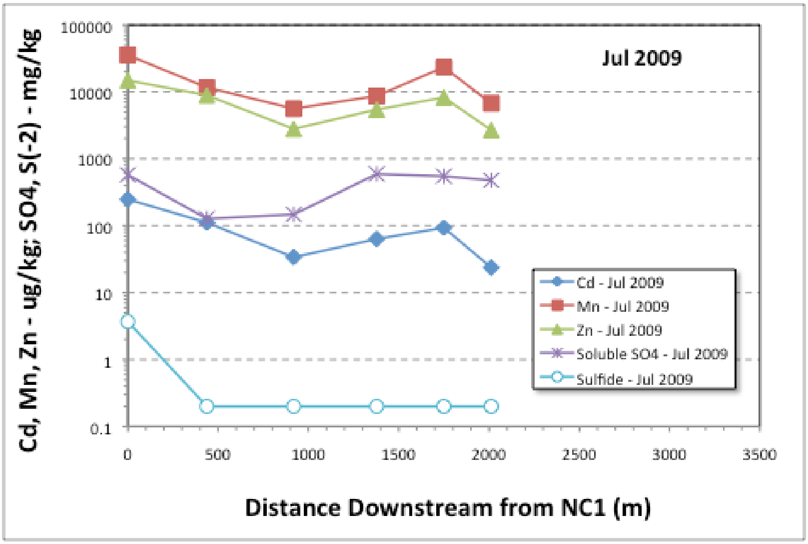

Figure 3-10 Concentrations of metals (Cd, Mn, and Zn) and soluble sulfate in stream channel sediments of No Cash Creek with distance from the 500-level adit discharge (July 2009 data)

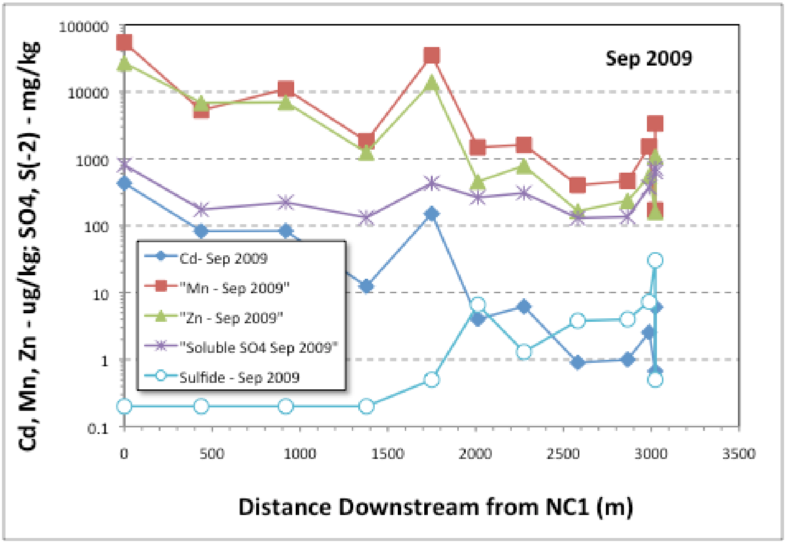

Figure 3-11 Concentrations of metals (Cd, Mn, and Zn) and soluble sulfate in stream channel sediments of No Cash Creek with distance from the 500-level adit discharge at location NC1 (September 2009 data)

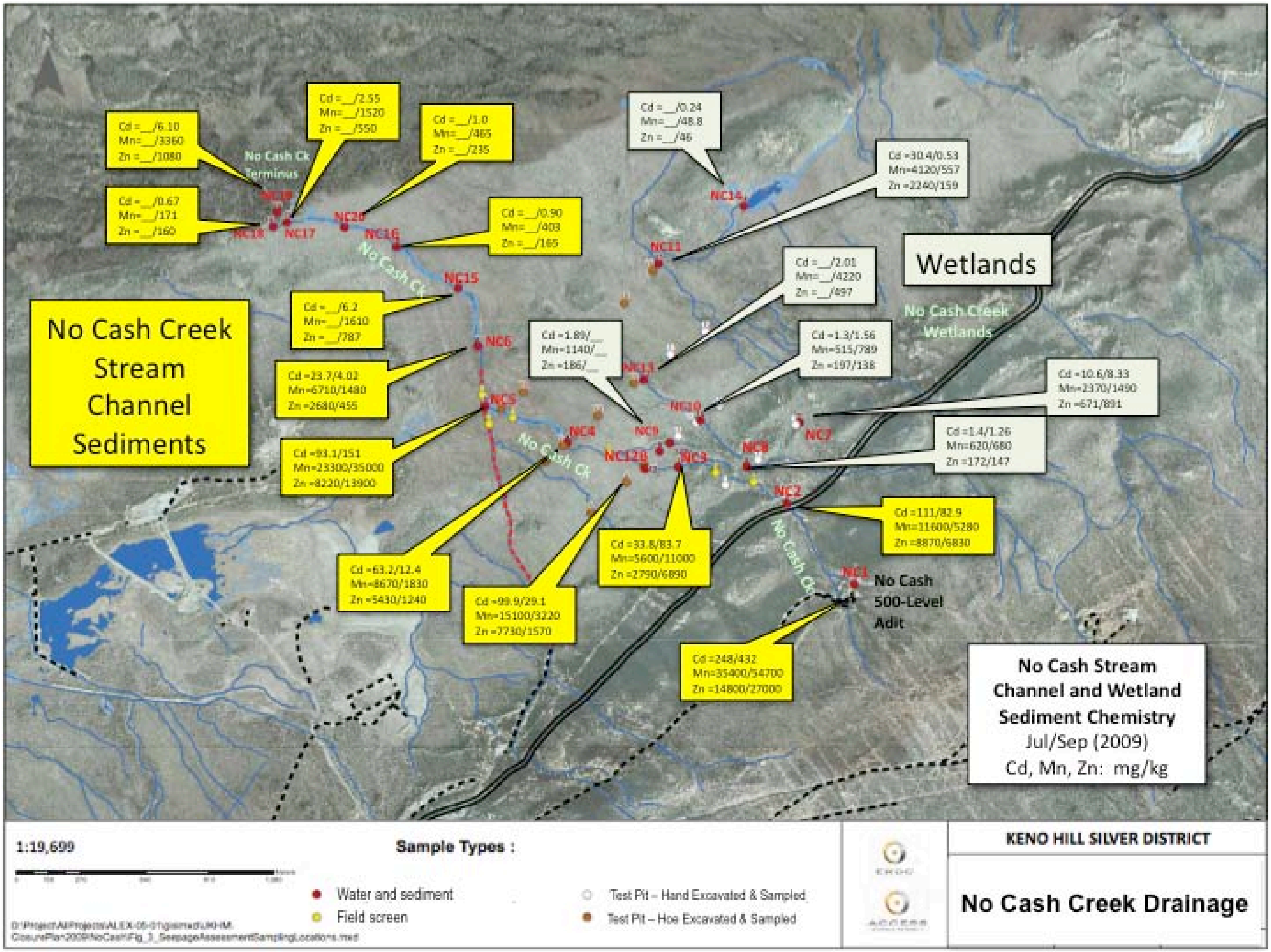

Figure 3-12 Metal concentrations (cadmium, manganese, and zinc) in sediment samples from No Cash Creek stream channel and other surface water expressions in the wetlands north and east of No Cash Creek

3.5 Trends in Sediment Chemistry in Test Pits

The areal distribution and metal concentrations for the test pit locations are shown in Figure 3-13. The sediment samples from the test pits were collected from depth intervals of 0 to 0.2-0.35 m (top sample) and 0.2-0.35 to 0.7 m (bottom sample). Metal concentrations in sediments samples directly along or close to No Cash Creek are generally greater than those in sediments in the surrounding wetlands north and east from No Cash Creek, although there are many exceptions to this generalization. Metal concentrations are also generally greater in the surface samples (0 to 0.2-0.35 m) than deeper samples especially for manganese for all locations.

The concentrations of metals in test pit sediments from the lower portions (location NC5 and downstream) of the No Cash Creek stream channel are greater than those observed in test pit sediments in the surrounding wetlands (Table 3-4). For example, the average concentration of zinc in No Cash Creek test pit sediments is 2823 mg/kg compared to 516 mg/kg for test pit sediments in the surrounding wetlands east and north of the main channel of No Cash Creek. The concentrations of cadmium, manganese, and soluble sulfate show a similar difference between the No Cash Creek sediments and surrounding wetland sediments (Table 3-4).

The sediments from both the stream channel of No Cash Creek (Figure 3-12) and test pits in the surrounding wetlands were also found to contain low concentrations of sulfide-sulfur. The data form two populations: one for the No Cash stream channel sediments; and a second for the Test Pits, which were located on transects perpendicular to the Creek through the surrounding wetlands (Figure 3-14). The Test Pit samples generally contain higher TOC levels because they represent boggy, highly vegetated areas. For both populations, sulfide concentrations tend to be greatest in sediments with the highest TOC levels (Figure 3-14). The increase in sulfide content with distance downstream in the September stream channel data (Figure 3-11) is likely a result of sample collection from lower energy deposition/higher vegetation areas near the terminus of No Cash Creek where it ponds in a bog/marsh. The increase in sulfide with TOC is probably more consistent with in situ production of sulfide from biologically mediated decay of organic material rather than indicative of deposition of primary sulfide minerals due to erosion of mineralized surface outcrops. The presence of sulfate-reducing bacteria has been documented in sediments from a constructed wetland at Galkeno and a natural wetland on the South McQueston River (MERG, 2000). The presence of sulfide in the sediments provides the potential for the precipitation of metal sulfide minerals, which may provide for additional attenuation of metals in the saturated sediments where anoxic conditions may prevail due to biological activity associated with high levels of organic carbon.

Table 3-4 Metal, sulfate, sulfide, and TOC concentrations in stream channel sediments from No Cash Creek and nearby wetlands

	Cd (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Soluble (5:1) Sulfate (SO4) (mg/kg)		Sulfide (µg/g)	Moisture (%)	Organic Carbon (TOC) (g/kg)
No Cash Creek Drainage Jul 2009								
NC5	93.1	23300	8220	549	<	0.2	70	88
NC6	23.7	6710	2680	477	<	0.2	67	49
No Cash Creek Drainage Sep 2009								
NC5	151	35000	13900	432		0.5	65	54
NC6	4.02	1480	455	264		6.6	41	45
NC15	6.20	1610	787	308		1.3	40	27
NC16	0.90	403	165	130		3.8	54	63
NC20	1.00	465	235	136		4.0	43	99
NC17	2.55	1520	550	373		7.3	61	110
NC18	0.67	171	160	634		30.4	78	230
NC19	6.10	3360	1080	720		0.5	77	170
Averages	28.9	7401.9	2823.2	402.3		5.5	59.6	93.5
Surrounding Wetlands Jul 2009								
NC7	10.6	2370	671	316	<	0.2	64	63
NC8	1.40	620	172	139	<	0.2	53	94
NC10	1.30	515	197	181		0.3	55	110
NC11	30.4	4120	2240	136		0.2	31	40
Surrounding Wetlands Sep 2009								
NC7	8.33	1490	891	133		0.4	60	76
NC8	1.26	680	147	145		0.4	58	120
NC10	1.56	789	138	380		1	63	33
NC11	0.53	557	159	150		0.5	27	21
NC13	2.01	4220	497	638		0.4	79	110
NC14	0.24	48.8	46	928		7.8	89	390
Averages	5.8	1541.0	515.8	314.6		1.1	57.9	105.7

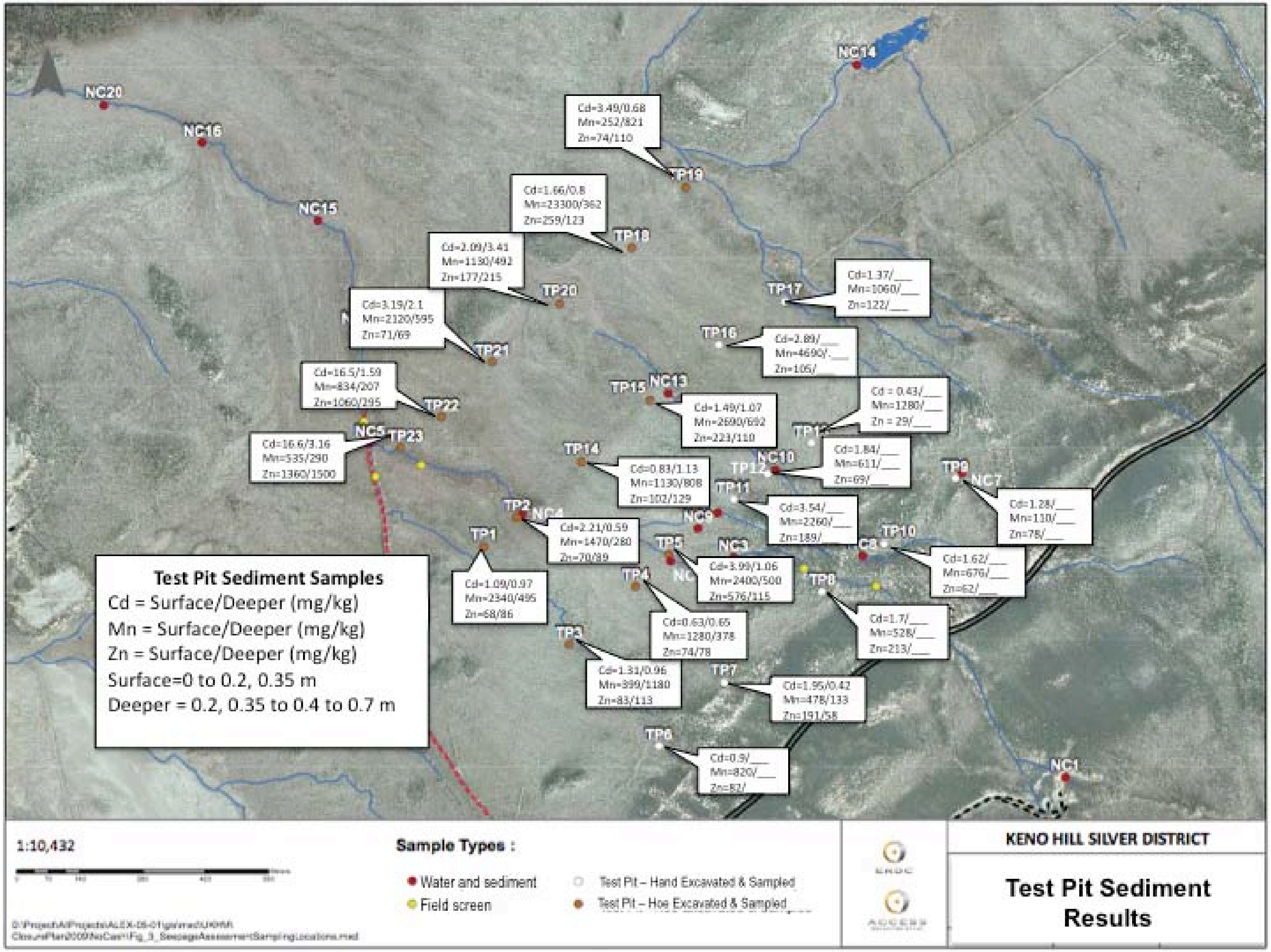

Figure 3-13 Metal (cadmium, manganese, and zinc) concentrations in sediment samples from Test Pit location

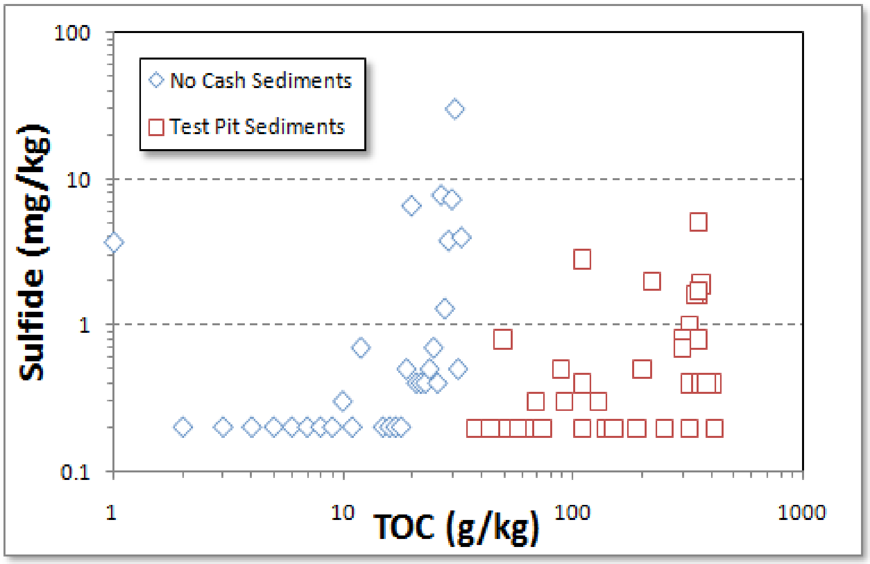

Figure 3-14 Relationship between sulfide and TOC concentrations in No Cash Creek stream channel sediments and Test Pit sediments

3.6 Trends in Sediment Chemistry for the South McQueston Seeps

Concentrations of metals in sediments collected at the locations of seeps along the South McQueston River are shown in Figure 3-15. The metal concentrations are variable for the seep sediments and are generally higher than those measured in sediments from the lower portions of No Cash Creek (Figure 3-12) and in test pits in the No Cash Creek drainage and nearby wetlands (Figure 3-13).

The higher concentrations in the South McQueston seeps can be seen in a comparison of sediment metal concentrations in Table 3-5. Table 3-5 gives the individual and average metal concentrations for the seep sediments. Table 3-5 also gives the individual and average metal concentrations for sediment samples collected at the terminus of No Cash Creek where the stream ends in a pond and bog area. The terminus of No Cash Creek is the area closest to the South McQueston seeps and is most downstream location for metal transport and deposition for No Cash Creek. The average cadmium concentration in the South McQueston seep sediments of 14.07 mg/kg is about 6 times greater than in the No Cash Creek sediments (2.24 mg/kg). Likewise, the average manganese and zinc concentrations in the seep sediments are over 3 times greater than those in No Cash Creek (Table 3-5). Average soluble sulfate concentrations are comparatively greater in the No Cash Creek sediments, whereas average sulfide contents are greater in the seep sediments (Table 3-5).

The metal concentrations observed in sediments in the No Cash Creek drainage are the result of a history of attenuation of metals discharged from the 500-level adit. The attenuation processes result in decreases in metal concentrations in both water and sediments with distance from the adit. Given the history of adit discharge and presence of elevated metal loads in No Cash Creek, there is a question whether these metals could have also affected water and sediment chemistry in the South McQueston River. The South McQueston River and seeps is topographically downgradient from the terminus of No Cash Creek (although whether the No Cash Creek terminus is also hydrologically downgradient has not been established). The trends in water quality for the seeps do not indicate an influence of increased metal loadings from No Cash Creek nor do they indicate no effects (Section 3-3). However, the sediment chemistry data are more definitive. They indicate metal concentrations in the No Cash Creek drainage are substantially lower than those in the South McQueston seep sediments, making it very unlikely that No Cash Creek could be the primary source of metals in the seeps. Instead, there must be another source of metals either upgradient on the South McQueston River or the metal levels observed in the seeps are typical and characteristic of the valley seeps and sediments along the River.

Table 3-5 Comparison of concentrations of metals (cadmium, manganese, and zinc), sulfate, and sulfide in South McQueston seep samples to samples from the terminus area of No Cash Creek

Sample	Sample Date (2009)	Cd (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Soluble SO_4 (mg/kg)	Sulfide (µg/g)
South McQueston Seeps						
SMQ1	July	13.4	5210	1700	136	<0.2
SMQ2	July	30.3	3360	2280	114	9.1
SMQ3	July	8.19	5390	966	70	193
SMQ4	July	11.4	5170	1250	167	3.5
SMQ5	July	8.62	4860	654	136	6.1
SMQ6	July	7.59	4740	1080	58	0.6
SMQ7	July	11.8	5460	1360	154	0.6
SMQ8	July	19.4	4180	1590	53	1.5
SMQ9	July	13.4	5500	1380	65	3.2
SMQ10	July	14.7	4830	1070	128	1.5
SMQ11	July	17	4680	1400	132	5.5
SMQ2	September	28.5	5980	2370	50	0.2
SMQ3	September	10.1	1380	1480	132	14
SMQ4	September	8.83	1950	1260	172	0.7
SMQ5	September	7.74	1420	1130	203	4
SMQ7	September	11.1	2450	1460	144	0.8
SMQ8	September	18.5	8490	1750	50	1
SMQ10	September	10.4	1230	765	144	9
SMQ11	September	16.4	3290	1730	316	2.1
	Averages	**14.07**	**4188**	**1404**	**128**	**14.2**
No Cash Creek						
NC16	September	0.9	403	165	130	3.8
NC17	September	2.55	1520	550	373	7.3
NC18	September	0.67	171	160	634	30.4
NC19	September	6.1	3360	1080	720	0.5
NC20	September	1	465	235	136	4
	Averages	**2.24**	**1184**	**438**	**399**	**9.2**

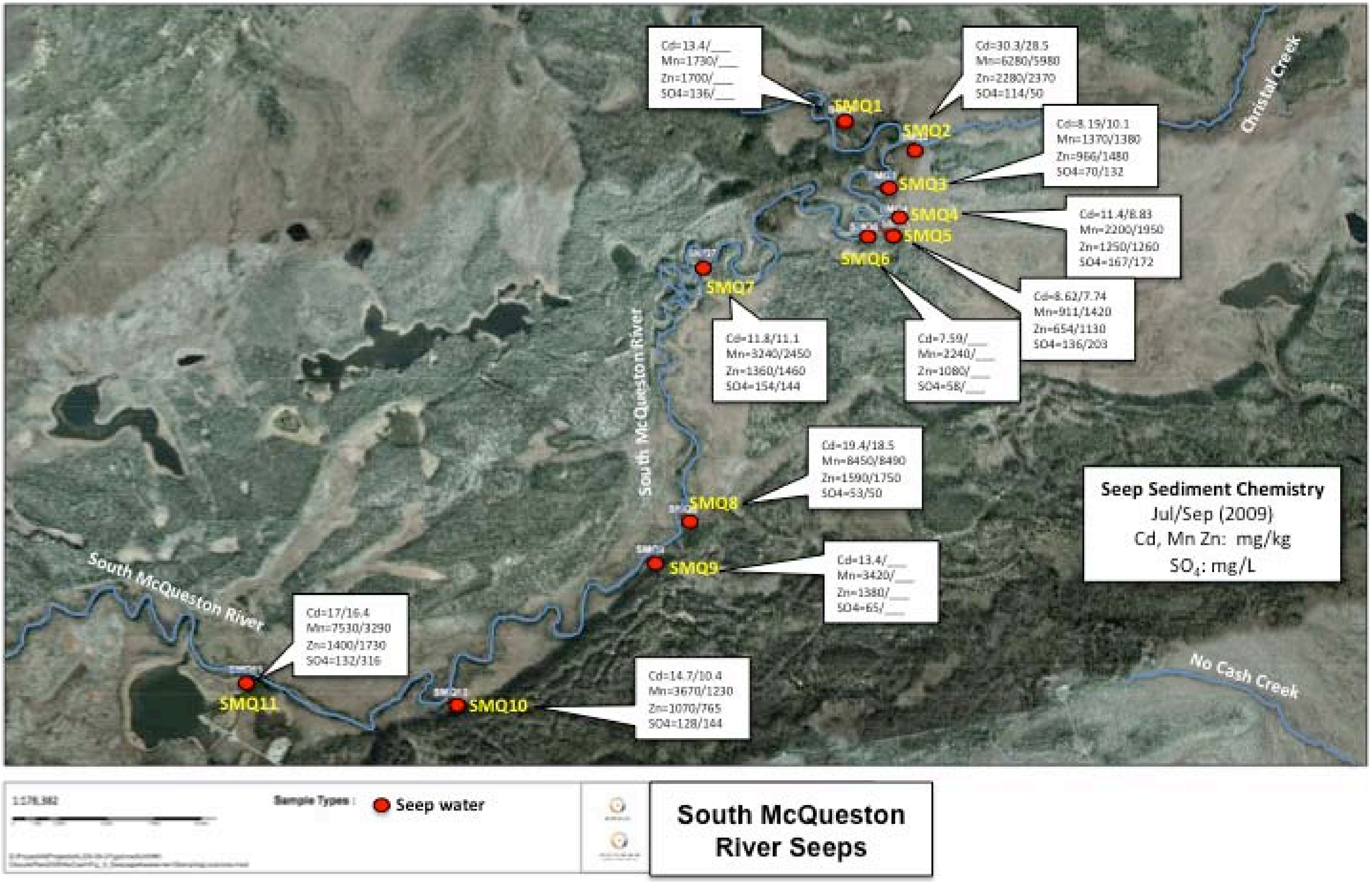

Figure 3-15 Metal and sulfate concentrations in sediment samples collected at seep locations along the South McQueston River

4 Attenuation Processes

The data collected in this study show that natural attenuation processes cause decreases in metal concentrations in the No Cash Creek drainages. This conclusion is consistent with previous work by Kwong et al. (1994, 1997) and MERG (2000). Geochemical modeling was conducted to define the specific chemical processes and reactions causing attenuation.

4.1 Geochemical Modeling Approach

The PHREEQC model (version 15, Parkhurst and Appelo, 1999) was used to perform calculations of aqueous speciation and mineral solubility for the purpose of identifying attenuation mechanisms for cadmium, manganese, and zinc. The wateq4f.dat thermodynamic database was used with PHREEQC with the following modifications.

The solubilities and enthalpies of reaction for hydrozincite and smithsonite were updated according to data from Preis and Gamsjäger (2001), which is also in good agreement with Mercy et al. (1998), for hydrozincite and smithsonite, as follows:

Hydrozincite: $Zn_5(OH)_6(CO_3)_2 + 8\ H^+ = 2\ HCO_3^- + 5\ Zn^{2+} + 6\ H_2O$: $\log K_{25°C}=29.45$, $\Delta H_{rxn}=-67.4$ kcal/mol

Smithsonite: $ZnCO_3 = Zn^{2+} + CO_3^{2-}$: $\log K_{25°C} = -10.9$, $\Delta H_{rxn} = -2.53$ kcal/mol

The solubilities for greenockite, amorphous CdS, and bisulfide complexes of dissolved cadmium were updated with data from the minteq.v4.dat thermodynamic database. These data are derived from Daskalakis and Helz (1992).

Greenockite: $CdS + H^+ = Cd^{2+} + HS^-$: $\log K_{25°C} = -14.36$, $\Delta H_{rxn} = 16.36$ kcal/mol

Amorphous CdS: $CdS + H^+ = Cd^{2+} + HS^-$: $\log K_{25°C} = -12.4$, $\Delta H_{rxn} = 16.36$ kcal/mol

(The log K value for amorphous CdS is estimated at two orders of magnitude greater than greenockite due to small particle size and amorphous crystal structure, Daskalakis and Helz, 1992).

Aqueous species: $Cd^{2+} + HS^- = CdHS^+$: $\log K_{25°C} = -8.008$
$Cd^{2+} + 2\ HS^- = Cd(HS)_2^0$: $\log K_{25°C} = -15.212$
$Cd^{2+} + 3\ HS^- = Cd(HS)_3^-$: $\log K_{25°C} = -17.112$
$Cd^{2+} + 4\ HS^- = Cd(HS)_4^{2-}$: $\log K_{25°C} = -19.308$

Forward geochemical modeling was conducted to compare metal concentrations in No Cash Creek to mineral solubilities. Oxidizing conditions were assumed to be representative of No Cash Creek and other surface water sampling locations. Additional modeling calculations were made to compare metal concentrations in test pit water to the solubilities of metal sulfide minerals. Reducing conditions were assumed for these calculations based on the observed presence of sulfide-sulfur and high organic carbon contents in Test Pit sediments.

Alkalinities were not determined for water samples. Hence, alkalinities were calculated from charge balance using PHREEQC. The computed alkalinities for No Cash Creek water are shown in Figure 4-1. They are in reasonably good agreement with the range of alkalinities measured in previous monitoring studies of No Cash Creek at monitoring points KV-20 and KV-21 (Figure 4-1). These two points are the approximately the same as sampling locations NC1 and NC2. No comparable alkalinity data for the Test Pits are available from previous studies, so the computed alkalinities from charge balance were assumed to be representative.

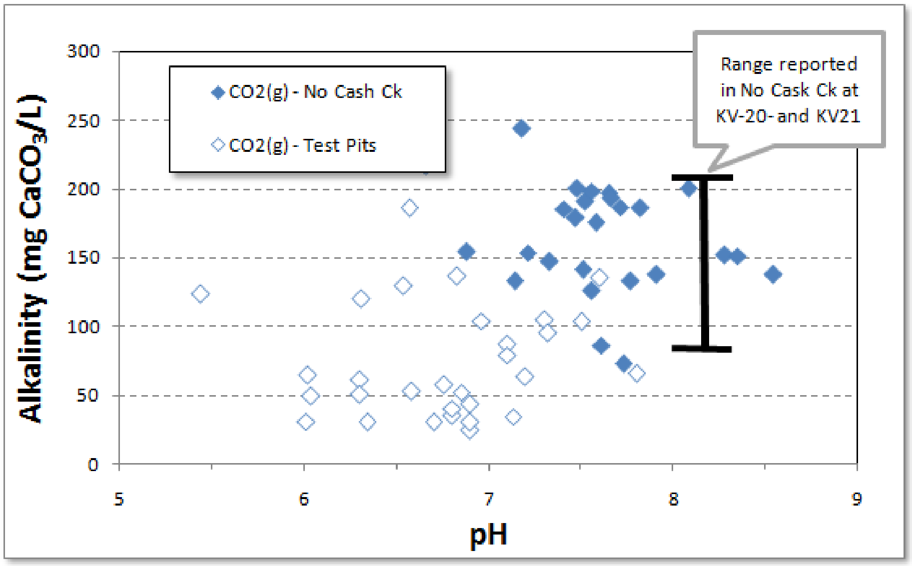

Figure 4-1 Alkalinities calculated with PHREEQC from charge balance compared to the range reported for surveillance monitoring points KV-20 and KV-21 (1994-2005 data)

4.2 Geochemical Modeling Results

Calculated partial pressures for $CO_{2(g)}$ [$pCO_{2(g)}$] as a function of pH are shown in Figure 4-2 for No Cash Creek and the Test Pit water. The ranges in $pCO_{2(g)}$ for No Cash Creek are consistent with levels reported for mine discharge water from carbonate-bearing host rocks in other mining districts (Carroll et al. 1998). The Test Pit water generally has lower pH and higher $pCO_{2(g)}$ compared to the No Cash Creek water and also water from other surface water sampling locations in the wetlands east and north of No Cash Creek (Figure 4-2). The Test Pit water is comprised of seepage from boggy/marshy areas. The organic acids and degradation of organic carbon likely both contribute to the lower pH values and higher $pCO_{2(g)}$ levels in the Test Pit water than in the surface water samples.

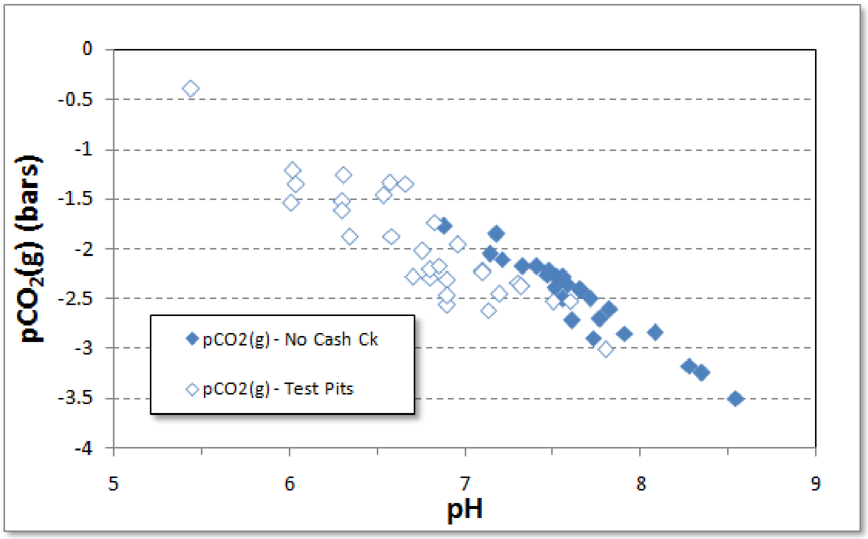

Figure 4-2 Calculated $pCO_{2(g)}$ for surface water in No Cash Creek and surface water sampling locations in the nearby wetlands and Test Pit water

The No Cash 500-level adit collects groundwater from the hydrologic system in Galena Hill and discharges it to No Cash Creek. The discharged water is subjected to decreased $pCO_{2(g)}$ and increased $pO_{2(g)}$ upon exposure to ambient atmospheric conditions compared to the subsurface. The change in conditions results in both a degassing of CO_2(g) and oxidation reactions. The effect of CO_2(g) degassing would be an increase in pH, which generally leads to lower solubilities for carbonates and some oxyhydroxides minerals, depending on the final pH. The effect of oxidation would be conversion of ferrous and manganous ions to less soluble oxide and hydroxide mineral forms. These oxidation reactions are rapid under slightly alkaline conditions and can be expected to occur immediately downgradient from the discharge from the 500-level adit.

The effects of degassing, oxidation, and mineral precipitation are seen in comparisons of No Cash Creek and Test Pit water to mineral solubilities in Figures 4-3 to 4-6 (discussed below). The y-axis in these figures is the saturation index. The calculation of saturation index is done with geochemical models using the analytical data for solution composition and thermodynamic data for all dissolved solutions and mineral forms potentially present in any given system. The saturation index is defined by SI=log (IAP/Ksp), where IAP is the ion activity product of the constituents involved in a solubility reaction for a specific mineral and Ksp is the solubility product for the dissolved solutes involved in the reaction (Langmuir, 1997). A saturation index greater than zero indicates oversaturation under which a specific mineral can precipitate from solution but cannot dissolve. Conversely, a saturation index less than zero indicates undersaturation under which a specific mineral can dissolve but not precipitate from solution. A saturation index of zero, which is rarely observed, indicates exact solubility equilibrium for a specific mineral.

The No Cash Creek water and Test Pit water are both oversaturated with ferrihydrite [$Fe(OH)_3$] solubility (Figure 4-3). Oversaturation with ferrihydrite is common in mine water (Nordstrom and Alpers, 1999) due to a number of factors, such as persistence of dissolved ferrous iron and slow ferrihydrite precipitation kinetics, presence of small particulates that pass through filters during sampling, and substitution of ions in ferric hydroxide to create non-stoichiometric precipitates. The No Cash Creek water is also oversaturated with gibbsite [$AlOH)_3$] and close to saturation with amorphous $Al(OH)_3$ at least for the test pits (Figure 4-3). The upper portions of No Cash Creek have been observed to have coatings of reddish ferric iron precipitates (Kwong et al. 1994, 1997). This observation is consistent with the solubility calculations of oversaturation with ferrihydrite.

The No Cash Creek and test pits are also substantially oversaturated with manganese oxide minerals, such as manganite [MnOOH] and birnessite [MnO_2] (Figure 4-4). Manganese is less rapidly oxidized than ferrous ion at neutral pH (Eary and Schramke, 1990; Hem, 1989). Although manganese oxides are common precipitates observed in mine water (Nordstrom and Alpers, 1999; Tan et al. 2010), incomplete precipitation and oxidation kinetics commonly result in conditions oversaturation mine waters (Eary, 1999). The No Cash Creek and test pits with highest manganese concentrations are consistent with rhodochrosite [$MnCO_3$] solubility (Figure 4-4). This observation is most likely indicative of rhodochrosite precipitation in the workings of the No Cash mine and potentially in No Cash Creek due to the effects of degassing of CO_2(g) from the adit water.

Cadmium and zinc show similar behavior to manganese in that the highest concentrations are bounded by the solubilities of carbonates, such as otavite [$CdCO_3$], hydrozincite [$Zn_5(OH)_6(CO_3)_2$], smithsonite, and $ZnCO_3 \cdot H_2O$ (Figures 4-5 and 4-6). The No Cash Creek water is also very close to solubility equilibrium with calcite [$CaCO_3$] (Figure 4-5). Calcite is present in the major lithologic units that host mineralization in the area (Kwong et al. 1994; 1997).

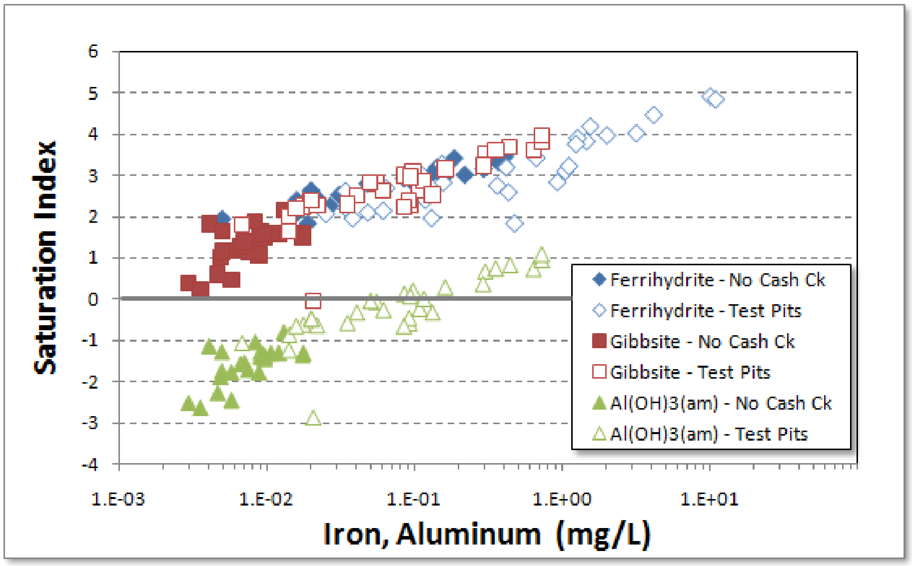

Figure 4-3 Saturation indices for iron and aluminum minerals

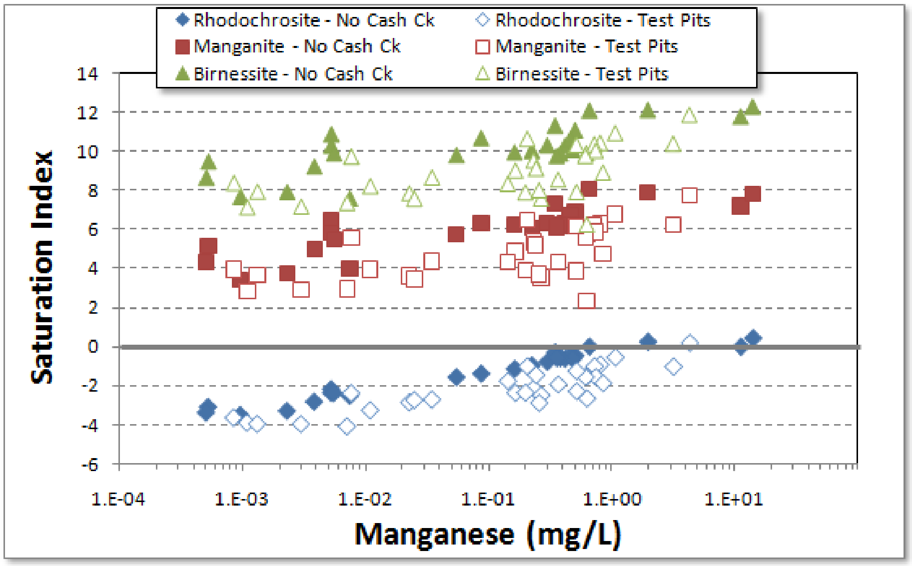

Figure 4-4 Saturation indices for manganese minerals

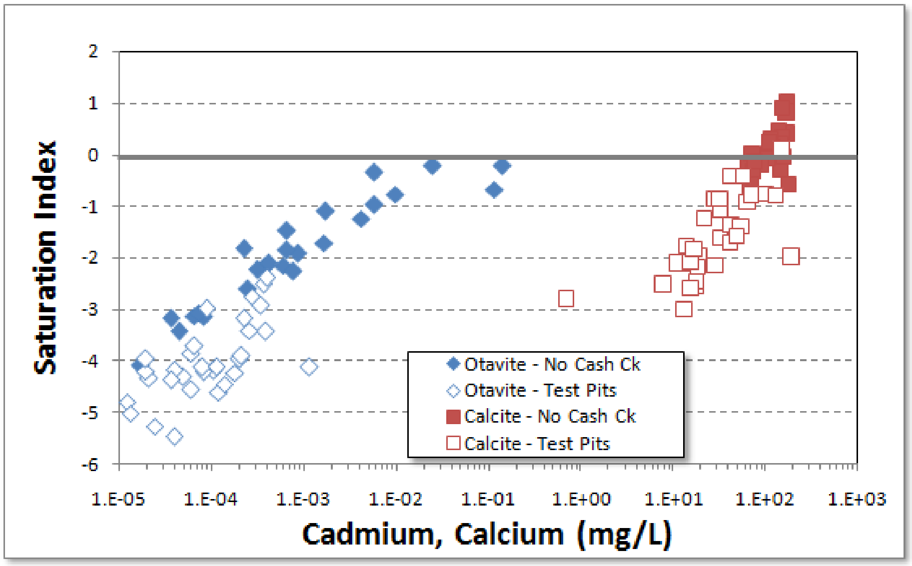

Figure 4-5 Saturation indices for cadmium minerals

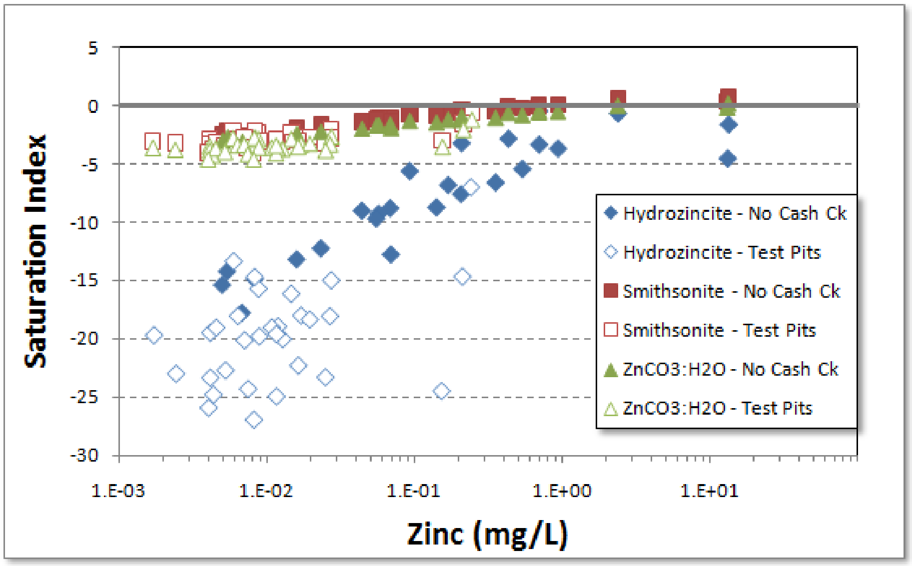

Figure 4-6 Saturation indices for zinc minerals

The geochemical model calculations indicate conditions exist for precipitation of hydroxide and carbonate minerals forms of aluminum, iron, cadmium, manganese, and zinc. Precipitation of iron and manganese hydroxides provides abundant adsorbent surfaces for the uptake of other metals, including zinc and cadmium. The solubilities of the carbonates appear to limit the maximum concentrations of cadmium, manganese, and zinc. This observation is most likely indicative of a combined process where metal sulfide ore minerals, such as sphalerite [(Zn,Cd)S], pyrite [FeS_2], galena [PbS], oxidize and dissolve where they are exposed to air and water in underground workings of the No Cash Mine followed by reaction with calcite [$CaCO_3$] to produce a circumneutral pH with positive alkalinity and elevated metal concentrations. Precipitation of metal carbonate minerals (e.g., hydrozincite, rhodochrosite, smithsonite, calcite) occurs as a result of the reactions with calcite and the effect of degassing of CO_2(g) from the adit water, which shifts pH upwards to conditions of lower solubility for carbonate minerals. The degassing of

CO_2(g) has been identified a key factor controlling cadmium and zinc concentrations in other mine water systems (Carroll et al. 1998).

The solubility controls identified by the geochemical modeling are consistent with the results of sequential extractions and mineralogical analyses conducted on sediments in the area in previous studies. For example, Kwong et al. (1994, 1997) determined that about 40% of the cadmium content existed in the form of adsorbed species based on sequential extractions of nine samples of sediments from the Keno Hill mining district. Kwong et al. (1994, 1997) also observed that 42% of zinc was associated with carbonate mineral forms and 30% with iron and manganese oxhydroxides. MERG (2000) reported that most cadmium and zinc was associated with iron and manganese oxyhydroxides in sediments from a constructed wetland at the nearby Galkeno mine based on sequential extraction tests. MERG (2000) also reported that a substantial fraction of cadmium was present in sulfide mineral forms and zinc was present in both sulfide and iron-manganese oxyhydroxides in sediments from the No Cash Creek drainage.

Kwong et al. (1994, 1997) identified hydrozincite and poorly crystalline iron hydroxide in sediments in the Onek drainage, which is another nearby mine-affected drainage in the District. Podda et al. (2000) also reported the importance of hydrozincite as a natural attenuation process for zinc and other divalent metals (lead, cadmium, nickel, and copper) in mine waste water. The geochemical modeling calculations described here are consistent with the observations of Kwong et al. (1994, 1997), MERG (2000), and Podda et al. (2000) that precipitation of metal hydroxides and carbonates are important attenuation processes for cadmium, manganese, and zinc in the No Cash Creek drainage.

While the solubility controls identified above provide reasonably good bounds on maximum concentrations of cadmium and zinc especially for the oxidizing conditions of surface water in the upper portions of No Cash Creek immediately below the adit, they do not explain the low concentrations observed in the Test Pit water. The Test Pits were excavated in boggy areas of water-saturated sediments where vegetation is thick and organic carbon concentrations are high. These conditions promote reducing conditions, which was confirmed by the detection of sulfide in sediment samples from the test pits and elevated concentrations of manganese relative to surface water. The data in Figure 3-11 show that sulfide concentrations tend to increase with increase in organic carbon as would be expected from the actions of sulfate-reducing bacteria in an anoxic environment, such as the boggy areas surrounding the lower portions of the No Cash Creek drainage. Sulfate is present in the No Cash Creek water as a result of adit discharge, providing an energy source for sulfate-reducing bacteria in the associated sediments. MERG (2000) has documented the presence of sulfate-reducing bacteria in sediments from nearby areas.

The presence of sulfide in the sediments indicates that metal sulfide precipitation is another important attenuation process for metals in the sediments of the No Cash Creek drainage and surrounding wetlands. Metal sulfides are generally sparingly soluble. The solubilities of cadmium sulfides for levels of total dissolved sulfide of 1×10^{-5} and 1×10^{-4} m (0.32 to 3.2 mg/L S^{2-}) are compared to measured dissolved cadmium concentrations in the Test Pit water samples in Figure 4-7. The measured cadmium concentrations are substantially greater than the solubility of greenockite (crystalline CdS) and are roughly consistent with the solubility of amorphous CdS. MERG (2000) observed that most cadmium in sediment samples from No Cash Creek drainage was present in sulfide mineral forms based on sequential extraction testing.

A similar comparison is shown Figure 4-8 for dissolved zinc in the test pits and the solubilities of sphalerite (crystalline ZnS) and amorphous ZnS. The measured zinc concentrations are roughly similar to the solubility of amorphous ZnS for the sulfide range of 1×10^{-6} m to 1×10^{-5} m (0.032 to 0.32 mg/L S^{-2}). The importance of ZnS precipitation for controlling zinc concentrations in systems containing sulfide has been reported by Labrenz et al (2000), who showed that very fine-grained ZnS (sphalerite) can be produced in biofilms by sulfate-reducing bacteria. Labrenz et al. (2000) reported that precipitation of ZnS resulting in zinc attenuation from liquid to solid phase by a factor of 10^6. Lau et al. (2008) have also reported the importance of ZnS to remove zinc in sulfidic systems particularly in systems containing natural dissolved organic compounds that stabilize ZnS against oxidation. MERG (2000) observed that zinc was equally distributed between sulfides and oxides in sediments from No Cash Creek drainage based on sequential extraction testing, providing evidence that metal sulfide precipitation is an ongoing attenuation process in sediments.

Manganese sulfides, such as alabandite (MnS) and amorphous MnS, are much more soluble than other metal sulfides and also more soluble than manganese oxides and carbonates (Figure 4-9). Hence, it is less likely that sulfide mineral precipitation is a key attenuation process for manganese. The low concentrations of dissolved manganese are more likely attributable to the precipitation of manganese oxides and carbonates in oxic portions of No Cash Creek and uppermost sediment profile in the surrounding wetlands. Both No Cash Creek and test pit water are substantially oversaturated with most manganese oxides, indicating that conditions are conducive to their formation.

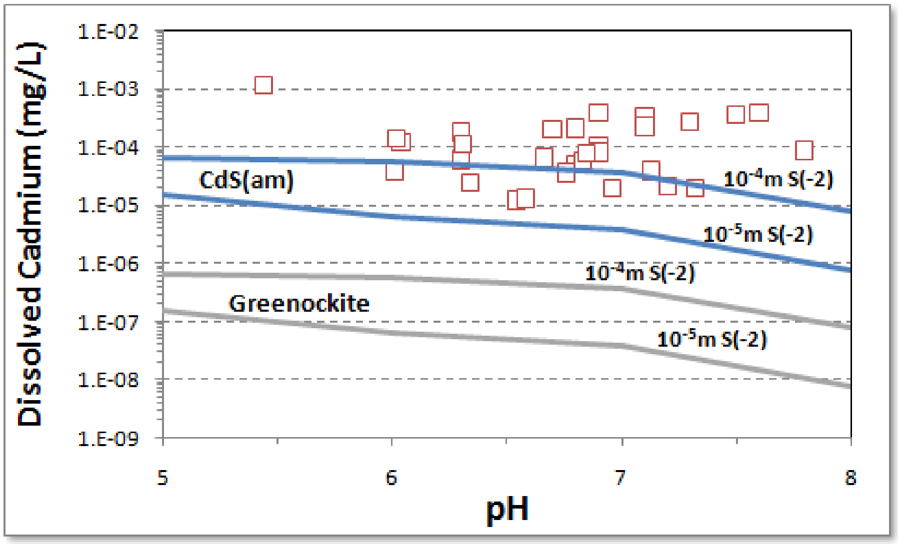

Figure 4-7 Comparisons of dissolved cadmium concentrations in test pits to cadmium sulfide mineral solubilities

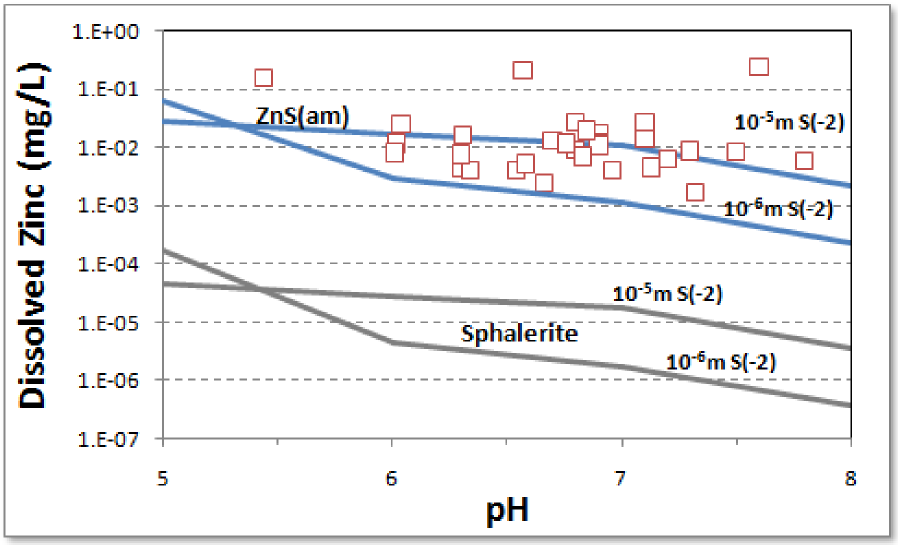

Figure 4-8 Comparisons of dissolved zinc concentrations in test pits to zinc sulfide mineral solubilities

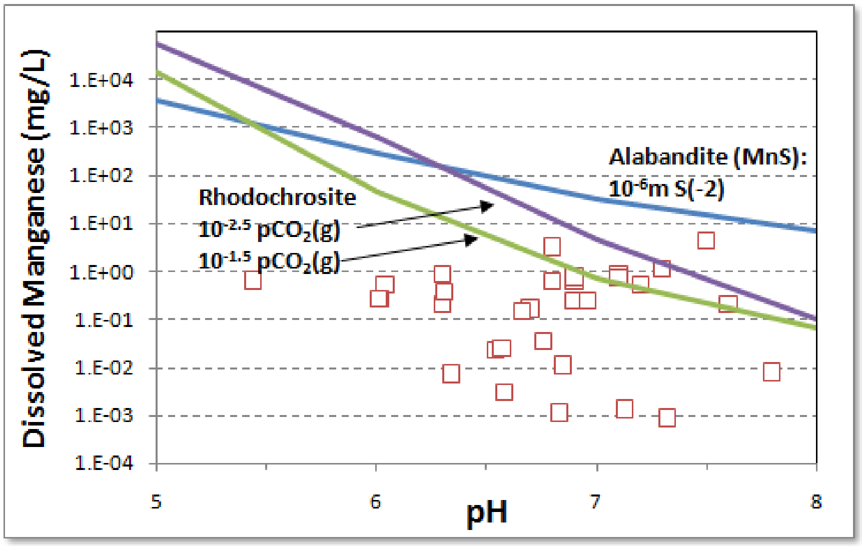

Figure 4-9 Comparisons of dissolved manganese concentrations in test pits to manganese sulfide and manganese carbonate mineral solubilities

5 Conclusions

An extensive study of metals in water and sediments was conducted in the No Cash Creek drainage and seeps along the South McQueston River in the summer of 2009 for the purpose of identifying attenuation mechanisms and their effectiveness for permanently reducing metal concentrations. No Cash Creek receives water directly discharged from the historical No Cash 500-level adit. The adit discharge water is groundwater that is drained from underground mine workings in Galena Hill. The adit discharge water contains elevated concentrations of metals, particularly cadmium, manganese, and zinc. The original source of these metals is likely to be oxidation of metal sulfide minerals associated with ore mineralization that was exploited in the underground mines located in Galena Hill.

The following conclusions are made from the results of the study with emphasis on attenuation mechanisms for cadmium, manganese, and zinc.

- The pH of the 500-level discharge has remained stable since 1982 and zinc and cadmium concentrations have decreased by more than one half since a high point in 1987.

- The concentrations of metals decrease rapidly downstream in No Cash Creek water with distance from the discharge point of the No Cash 500-level adit. Zinc concentrations decrease by a factor of about 100, cadmium concentrations decrease by factors of 100 to more than 1000, and manganese decreases by factors from 20 to 100. The decreases in metal concentrations are substantially greater than those observed for sulfate, which shows a reduction of 25 to 40%. The decrease in sulfate is probably due to dilution from water sources other than adit discharge, such as watershed runoff, and possibly biologically mediated reduction to sulfide in stagnant pools and sediments. The proportionately much larger decreases in metals require processes other than simple dilution. Natural attenuation processes are responsible for the large reductions in metal concentrations.

- Metal concentrations in water samples collected in test pits are generally higher in pits located nearest the No Cash Creek drainage. A similar pattern is observed for metal concentrations in sediments, although there is variability in results from location to location and for different metals.

These results imply that metal attenuation occurs primarily in areas nearest No Cash Creek with little spread of metals into surrounding wetlands in dissolved form. Some amount of movement and redistribution of metal bearing sediments by physical processes, such as stream meandering and flood events, has likely occurred over time. The entire valley area has received deposition of metal-bearing sediments from historical mining operations and natural erosion of near-surface mineralization; hence, precise delineation of the specific contributions of the No Cash 500-level adit is probably not possible.

- Water quality samples from seeps located along the South McQueston River show variable concentrations of cadmium, manganese, zinc, and sulfate in ranges that approximate those measured in the lower stretch of No Cash Creek and in surface water expressions in the wetland area east and north of No Cash Creek. The water quality data are not indicative of an influence of No Cash Creek water on the seeps nor are they indicative of no effect. Sediment chemistry data are more definitive. Metal concentrations in sediments from the terminus of No Cash Creek, where it ponds and disappears into a wetland, are compared to concentrations in sediments from the South McQueston seeps. This comparison shows that concentrations of cadmium, manganese, and zinc in the No Cash Creek sediments are substantially lower than those in the South McQueston seep sediments. Based on this comparison, it is reasonable to conclude that No Cash Creek is not the primary source of metals for either the seep water or sediments. Instead, there must be another source of metals either upgradient on the South McQueston River or the metal levels observed in the seeps are typical and characteristic of the valley seeps and sediments along the River.

- Geochemical modeling indicates that a number of attenuation processes are occurring that result in the removal of metals from No Cash Creek. These are:

    - Oxidation reactions occur as the discharge from the 500-level adit exits the subsurface and is exposed to surface conditions. These reactions result in the precipitation of ferric hydroxide and manganese oxides. The modeling also predicts that aluminum hydroxides should also precipitate. The precipitation of metal hydroxides can be expected to provide additional removal of other metals (e.g., cadmium and zinc) by adsorption and coprecipitation reactions. Kwong et al (1994, 1997) and MERG (2000) report that high fraction of cadmium and zinc is associated with iron and manganese oxyhydroxides in previous studies of sediment chemistry in nearby wetlands.

    - The 500-level adit discharge, No Cash Creek, and test pit water are oversaturated with CO_2(g) relative to atmospheric conditions. Degassing of CO_2(g) and subsequent increase in pH will promote the precipitation of cadmium, manganese, and zinc carbonates. The maximum concentrations of cadmium, manganese, and zinc in No Cash Creek are in reasonably good agreement with the solubilities of carbonate minerals, including otavite, hydrozincite, and rhodochrosite. Kwong et al. (1994, 1997) have identified hydrozincite in a nearby drainage and determined that most of the zinc is associated with carbonate mineral forms based on sequential extraction tests on sediment samples.

    - The concentrations of cadmium and zinc in test pit water are approximately consistent with the solubilities of metal sulfides under conditions of low dissolved sulfide concentrations. Sediments in the No Cash Creek drainage and surrounding wetlands contain measureable quantities of sulfide-sulfur most likely produced by the sulfate-reducing bacteria in the presence high levels of organic matter in the sediments. MERG (2000) has documented the presence of sulfate-reducing bacteria in nearby wetlands and also in No Cash Creek wetlands. MERG (2000) also determined that most cadmium and approximately half of zinc were associated with sulfide mineral forms based on sequential extraction testing of No Cash Creek wetland sediments.

- The above conclusions made in this study about attenuation processes are consistent with previous studies of metal chemistry in No Cash Creek (Kwong et al. 1994, 1997; MERG, 2000).

- The attenuation mechanisms for metals (cadmium, manganese, and zinc) of mineral precipitation (oxides, hydroxides, carbonates, and sulfides), coprecipitation, and adsorption are natural processes that effectively and sequester metals and reduce concentrations in water. They are the same types of processes that are relied upon for metal polishing in active and semi-passive biological water treatment systems. The attenuated metal forms can be expected to remain as stable sequestration mechanisms as long as chemical conditions are maintained relatively constant. The 500-level adit discharge shows a stable history of pH and metal concentrations since 1982, indicating that the metal loadings to No Cash Creek have been stabilized for the same time period. As a result, the ongoing metal attenuation processes in the No Cash Creek drainage and nearby wetlands are also expected to continue into the future to provide for a chemical stable and reliable removal of metals.

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