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TECHNICAL ARTICLE

Assessment of Metal Attenuation in a Natural Wetland System Impacted by Alkaline Mine Tailings, Cobalt, Ontario, Canada

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Abstract A natural wetland in the Farr Creek drainage basin near Cobalt, Ontario was studied because its floor is covered with alkaline mine tailings that contain elevated levels of metals, including As, Co, Cu, and Zn, due to mining that occurred intermittently from 1904 to the 1980s. Our objectives were to characterize the biogeochemical interactions occurring throughout the wetland and to assess its ability to effectively attenuate the metal contamination. We were not able to conclusively determine if this wetland is a net source or net sink for As, Co, Cu, and Zn; it is not clear whether this wetland has reached its capacity for attenuating these trace elements. Both oxidizing and reducing bacteria were quantified and found to be prevalent throughout the wetland, with similar population densities. It is likely that the presence of localized oxic zones in the root zones of *Typha latifolia* supported the oxidizing bacteria populations observed. The results indicate the importance of understanding the conditions in systems being used to treat mine drainage, as well as the importance of having a detailed understanding of the metals of concern in the mine waste.

Keywords Acid producing bacteria · Alkaline mine drainage · Iron reducing bacteria · Phytoremediation · Sequential extraction · Sulfate reducing bacteria · Trace metals · *Typha latifolia*

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Introduction

Anthropogenic sources of metals, including mine wastes, runoff waste streams, and atmospheric deposition from industrial operations, can contaminate downstream environments and affect the health of aquatic species and humans. It is therefore important to characterize metal distributions and transformations in aquatic environments to better understand the geochemical and biological processes regulating these transformations.

Acid mine drainage (AMD), which results from the oxidation of sulfide bearing material, has received considerable attention and has been the focus of numerous studies (e.g., August et al. 2002; Blowes et al. 1998; Fortin et al. 1996; Machemer et al. 1993). The oxidation of sulfides, which can be catalyzed by oxidizing microbial populations, produces sulfuric acid that can result in extremely low pH waters. The highly acidic conditions enhance metal dissolution. Metals are typically more soluble under low pH conditions due to the increased competition between protons and metal cations; however, organic ligands also allow increased solubility of metals at higher pH values (Schnoor 1996). The dissolved metals have the potential to migrate offsite, resulting in potential negative health impacts to both humans and aquatic organisms. The acidity produced from the oxidation reactions can potentially be neutralized if there is adequate alkalinity in the tailings and receiving waters. This can result in net neutral or alkaline mine drainage (NAMD). NAMD can also be produced from mine wastes containing little or no sulfides. NAMD, although not acidic, can contain elevated dissolved metal concentrations that can potentially impact receiving environments.

Historically, a number of mining companies have used active treatment options for mitigating the impact of mine water on the receiving environment (Berghorn and Hunzeker 2001). These options typically involved the chemical addition of neutralizing agents such as lime, which is expensive (Berghorn and Hunzeker 2001). This sparked a movement towards alternative treatment options such as passive treatment systems, which include the use of constructed or natural wetlands to attenuate metal contamination. These wetland systems are generally classified based on the availability of dissolved oxygen in the system: aerobic vs. anaerobic wetlands.

Aerobic wetlands typically consist of large surface area pond(s) with horizontal surface flows and aquatic vegetation such as cattails (*Typha latifolia*), and water depths of less than 30 cm (Berghorn and Hunzeker 2001). These wetlands are typically effective for NAMD because the predominant metal removal/immobilization pathway is via oxidation reactions (Berghorn and Hunzeker 2001). As such, the operational pH should be maintained above 5.5 (Berghorn and Hunzeker 2001). Under oxic and alkaline conditions, Fe and Mn form amorphous Fe and Mn oxides, hydroxides, and oxyhydroxides, which contain prime adsorption sites for metals. It has also been shown that selected metals, such as As, can co-precipitate with Fe oxides and/or hydroxides (Gambrell 1994).

Anaerobic wetlands make use of subsurface horizontal or vertical flow through an organic substrate layer (Berghorn and Hunzeker 2001). Vegetation may help stabilize the organic layer and provide additional substrate to perpetuate sulfate reduction. The organic substrate stimulates chemical and microbial reduction reactions that generate alkalinity and increase solution pH. Degradation of the organic matter consumes dissolved oxygen, which subsequently allows for iron and sulfate reduction. Anaerobic wetlands are better suited for mine waste streams that have high metal concentrations because the prime method of metal removal is by precipitation as sulfides, which typically have lower solubilities than their oxide/hydroxide counterparts (Berghorn and Hunzeker 2001; Fortin et al. 2002).

The objectives of this research were to characterize the biogeochemical interactions of the predominant metal species (As, Co, Cu, and Zn) throughout a NAMD-impacted natural wetland system and to evaluate the wetland's ability to effectively attenuate these contaminants.

Study Area

The study area is located in the Farr Creek drainage area, near Cobalt, Ontario. The natural wetland is confined to a relatively narrow northeast oriented valley that is bounded to the south by Crosswise Lake and the remnants of a gravel dam, and bounded to the north by a water-level control dam. Alkaline tailings underlie the entire study area as well as up gradient of the study area. Farr Creek flows northeast through the study area from Crosswise Lake. Mill Creek, which transports metal loadings from several upstream tailings deposits and organic loadings from the municipal wastewater lagoon**,** flows into Farr Creek (Fig. 1). The northern portion of the site is maintained under water cover (average 60 cm water cover) for much of the open water season, whereas the southern portion of the site is relatively dry throughout the summer and fall. This is further evidenced by the establishment of grasses and sedges in the drier areas, while waterlogged areas are primarily populated with cattails.

Mining in the Cobalt silver camp began in 1904 and continued nonstop into the 1930s, with only periodic activity from then until the last mine closed in the 1980s. The entire study site is floored by a 0.5 to 1.5 m thick layer of tailings lying over a sequence of glacial lake varved clays and is covered by up to 1.0 m of organic-rich sediments in the wetland. The tailings are an extension of those deposited directly into Crosswise Lake by at least five mills operating during the first half of the 20th century.

Methodology

Field Methods

Five sediment cores, 5 cm in diameter and from 0.9 to 1.4 m in length, were collected from the study area in

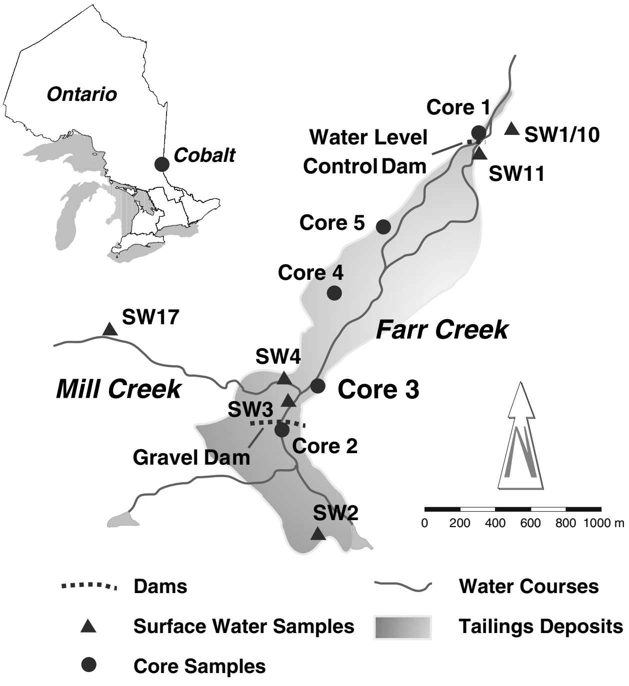


Fig. 1 Map of field site

September 2004. Surface water samples were collected throughout the study area from both Farr Creek and Mill Creek. The locations of the cores and surface water samples are presented in Fig. 1. Surface water samples were analyzed for alkalinity, using Hach test kits. Surface water samples were also analyzed for pH, dissolved oxygen, and electrical conductivity. The pH was determined using an Oakton pH meter, and dissolved oxygen and electrical conductivity were measured using a YSI model 85 multiprobe. Average stream velocities were measured for Farr Creek and Mill Creek at various locations. Measurements of stream width and depth were also made to determine approximate stream flows. Cattail (*T. latifolia*) leaf samples were collected near each of the core locations. Several leaf samples were cut and placed in labeled Ziplock plastic bags. All cores, cattail leaf samples, and surface water samples were kept in the refrigerator and transported in coolers with icepacks to ensure that the samples remained below 4°C. They were kept refrigerated in the Environmental Earth Sciences Laboratory at Carleton University (Ottawa, ON, Canada) until they were prepared for analysis.

Laboratory Methods

Sediment samples were removed from the cores at approximately 25 cm intervals and analyzed for acid-producing bacteria (APB), iron-reducing bacteria (IRB), sulfate-reducing bacteria (SRB), and sequentially extracted metals. Pore water was extracted from the remaining sediment samples by ultracentrifugation. Porewater samples were analyzed for alkalinity, Fe(II), sulfate, and sulfide using Hach test kits. Porewater and surface water samples were analyzed for pH, dissolved oxygen, electrical conductivity, and dissolved trace elements. The pH was determined using an Oakton pH meter, and dissolved oxygen and electrical conductivity were measured using a YSI model 85 multiprobe. Dissolved metals were measured by inductively coupled plasma mass spectrometery (ICPMS).

Sixteen sediment samples were analyzed for APB, IRB, and SRB. The growth medium used for the APB consisted of 5 g/L dextrose, 1 g/L beef extract, 10 g/L protease peptone, 10 g/L NaCl, and 0.1 g/L bromothymol blue, buffered to pH 7.2. The growth medium containing the reducing agent used for the IRB consisted of 2.5 g/L $NaHCO_3$, 1.5 g/L NH_4Cl, 0.6 g/L NaH_2PO_4, 0.1 g/L $CaCL_2{\cdot}4H_2O$, 0.1 g/L KCl, 0.1 g/L $MgCl_2\ 6H_2O$, 0.005 g/L $MnCl_2{\cdot}4H_2O$, 0.001 g/L Na_2MoO_4, 1.84 g/L ferric EDTA, and 1.5 g/L peptone, buffered to pH 7. The Postgate growth medium was used for the SRB samples. This medium and reducing reagents consisted of 0.5 g/L KH_2PO_4, 1 g/L NH_4Cl, 4.5 g/L Na_2SO_4, 0.04 g/L $CaCL_2{\cdot}6H_2O$, 0.06 g/L $MgSO_4{\cdot}7H_2O$, 2.94 g/L Na lactate, 1.28 g/L Na acetate, 1 g/L yeast extract, 0.004 g/L $FeSO_4{\cdot}7H_2O$, 0.3 g/L Na citrate dihydrate, and 0.4% resazurin, buffered to pH 7.5. Ten different dilutions at 1 mL in 10 mL were completed with five replicates of each dilution. The most probable number (MPN) technique was used to estimate the number of APB, IRB, and SRB in each sample. Most probable number values were calculated for each set of samples from statistical tables (Cochran 1950) and the results were expressed as colony forming units per gram of sediment dry weight (CFU/gdw). This method provides a rough estimate of the order of magnitude of bacterial populations, not the absolute population densities.

Sixteen duplicate sediment samples, taken at depths corresponding to the microbiology samples, were analyzed for sequential metal extractions (SMEs) using a method outlined by Tessier et al. (1979). This method separates metals into five fractions: exchangeable, bound to carbonates, bound to iron and manganese oxides (oxides), bound to organic matter (OM), and bound to residuals. Blank samples, containing deionized water, were assessed in duplicate for 10% of the samples and the samples were stored below 4°C immediately after digestion until further analysis.

Microprobe analysis was conducted on the coarse sand fraction of tailings sediment from the five core samples. The sand fraction of the tailings was separated by washing. Metallic grains were hand picked under a microscope, mounted and analyzed by microprobe at Carleton University to determine mineralogy and metal content.

Seven cattail (*T. latifolia*) leaf samples were washed with deionized water, dried, manually broken into small pieces, and crushed using a mortar and pestle. Thirty milliliter of 4:1 HNO_3:HCl mixture was added to 200 mg of crushed cattail leafs and the mixture was digested at 100–130°C until the solution became clear. The samples were then stored at a temperature below 4°C until the total metal analysis was conducted. Blank samples containing deionized water were run in duplicate on 10% of the samples. All of the samples were analyzed for metals by ICPMS at Health Canada laboratory facilities (Ottawa, ON, Canada).

Results

Sediment Stratigraphy

The general stratigraphy observed across the site, as observed from the five cores collected, is summarized below, starting at the ground surface:

- Grey to brown silty tailings, 60–100 cm thick;
- Layered silty clay, 10–40 cm thick; possibly tailings slimes:
- An organic layer underlies the layered silty clay unit. The cores collected from the southern portions of the

wetland (cores 2 and 3) indicated that the organic layer was 2–10 cm thick. A thicker organic layer was observed in the northern portion of the wetland (cores 1 and 5) where the layer extended from 20 cm to greater than 60 cm in thickness; and

- Massive brown varved clay was observed to underlie the layered clay and organics.

All analyses are for samples collected above the buried organic layer.

Porewater Chemistry

Table 1 presents the porewater concentration data for As, Cu, Co, Zn, Ca, sulfate, sulfide, Fe(II), dissolved oxygen, and pH. Arsenic porewater concentrations ranged from 0.295 mg/L (Core 2, 25 cm depth) to 8.4 mg/L (Core 1, 25 cm depth). Cobalt porewater concentrations ranged from 0.025 mg/L (Core 1, 75 cm depth) to 0.821 mg/L (Core 4, 50 cm depth). Copper porewater concentrations ranged from 0.015 mg/L (Core 1, 75 cm depth) to 0.325 mg/L (Core 1, 50 cm depth). Zinc porewater concentrations ranged from 0.029 mg/L (Core 1, 75 cm depth) to 0.566 mg/L (Core 1, 50 cm depth). All As, Cu, and Zn concentrations in the porewater were greater than the Canadian Council of Ministers of the Environment (CCME) freshwater aquatic life (FAL) Guidelines of 0.005, 0.002, and 0.03 mg/L, respectively. There currently are no CCME FAL Guidelines for Co. Calcium concentrations ranged from 33.5 mg/L (Core 5, 75 cm depth) to 341 mg/L (Core 1, 50 cm depth).

Reductions in porewater sulfate concentrations with depth were noted in all of the cores. Only cores 3, 4, and 5 showed increased or even measurable concentrations of Fe(II) and sulfide with depth, which would indicate the development of reducing conditions with depth. The pH values were relatively consistent throughout the entire porewater profile, averaging 7.0 (std. deviation = 0.87).

Surface Water Chemistry

Table 2 presents the surface water concentrations for As, Cu, Co, Zn, Ca, Fe, Mn, electrical conductivity, and pH. Arsenic concentrations ranged from 0.064 mg/L (SW2) to 0.556 mg/L (SW17). Cobalt concentrations ranged from 0.001 mg/L (SW2, SW3) to 0.034 mg/L (SW4). Copper concentrations ranged from 0.003 in all of the samples collected from Farr Creek (SW2, SW3, SW11, SW1, SW10) to 0.004 in all the samples collected from Mill Creek (SW17, SW4). Zinc concentrations ranged from <0.005 at several sample locations to 0.008 (SW4). All As and Cu concentrations in the surface water were greater than the CCME FAL Guidelines of 0.005 and 0.002 mg/L, respectively. There currently are no CCME FAL Guidelines for Co.

Table 1 Pore water concentrations for various parameters

Parameter	Depth (cm)	Concentration (mg/L)				
		Core 1	Core 2	Core 3	Core 4	Core 5
Sulfate	25	125	312.5	325	525	425
	45	375	237.5	312.5	437.5	350
	75	250	212.5	437.5	588.2	166
	105	NA	200	214.3	162.5	100
Sulfide	25	0.1	<0.1	0.2	0.6	<0.1
	45	<0.1	<0.1	0.2	0.15	0.1
	75	<0.1	0.1	0.1	0.1	0.5
	105	NA	<0.1	0.7	0.1	0.7
Ferrous iron	25	0.1	<0.1	<0.1	0.1	<0.1
	45	<0.1	<0.1	0.1	0.2	<0.1
	75	<0.1	<0.1	0.5	0.1	<0.1
	105	NA	<0.1	<0.1	0.2	<0.1
Dissolved oxygen	25	1.87	1.95	2	2	2
	45	2.1	2	1.49	1.68	1.6
	75	1.9	2	0.69	1.49	0.9
	105	NA	2.5	2.15	1.5	0.68
pH	25	7.15	6.18	7.7	7.6	5.36
	45	7.1	7.32	7.9	7.64	5.42
	75	6.8	7.21	7.97	7.78	5.92
	105	NA	7.2	6.96	7.78	6.24
Calcium	25	49.2	38.8	84.2	84.3	119
	50	341	NA	75.3	104	48.3
	75	45.2	51.1	56	NA	33.5
	130	49.9	50.8	NA	48.3	NA
Arsenic	25	8.4	0.295	0.38	1.61	1.11
	50	5.3	NA	3.85	3.31	2.7
	75	5.2	2.05	2.01	NA	1.69
	130	2.94	2.08	NA	2.2	NA
Cobalt	25	0.375	0.117	0.206	0.324	0.499
	50	0.364	NA	0.327	0.821	0.431
	75	0.025	0.377	0.029	NA	0.192
	130	0.313	0.295	NA	0.081	NA
Copper	25	0.161	0.074	0.051	0.09	0.054
	50	0.325	NA	0.187	0.103	0.145
	75	0.015	0.149	0.024	NA	0.108
	130	0.226	0.102	NA	0.017	NA
Zinc	25	0.165	0.068	0.051	0.17	0.129
	50	0.566	NA	0.197	0.201	0.246
	75	0.029	0.354	0.338	NA	0.137
	130	0.288	0.35	NA	0.099	NA

NA Not analyzed

The electrical conductivity measured throughout the wetland ranged from 69 to 309 μS/cm, which is typical of

Table 2 Surface water concentrations (mg/L) for various parameters; electrical conductivity (EC) in µS/cm

Location		Date	pH	EC	Calcium	Arsenic	Cobalt	Copper	Zinc
Mill Creek	SW17	2004	8.84	338	44.5	0.556	0.023	0.004	<0.005
	SW4	2004	8.43	275	44.8	0.573	0.034	0.004	0.008
Farr Creek	SW2	2004	8.37	148	21.4	0.064	0.001	0.003	0.007
	SW3	2004	8.06	103	21.8	0.074	0.001	0.003	<0.005
	SW16	2004	7.72	147	25.0	0.283	0.006	0.004	<0.005
	SW13	2004	7.42	172	29.1	0.347	0.007	0.003	<0.005
	SW15	2004	8.22	148	27.0	0.347	0.009	0.004	<0.005
	SW14	2004	7.47	175	29.4	0.374	0.007	0.003	<0.005
	SW11	2004	7.37	69.4	30.7	0.378	0.015	0.003	<0.005
		2004	7.82	247	33.6	0.500	0.015	0.004	<0.005
	SW10	2004	7.53	168	30.5	0.411	0.014	0.003	<0.005

most fresh waters. The pH values were relatively consistent throughout the wetland, ranging from 7.37 to 8.84.

It should be noted that during surface water sample collection, a portion of the south gravel dam was damaged, resulting in higher flows of water being transported through Farr Creek. This may have affected the wetlands ability to attenuate dissolved trace elements being transported by this higher flow of water.

Microprobe Analysis

The separated mineral grains represented less than 2% of the total tailings sediment; the remainder was composed of carbonate and silicate minerals. The mineralogy of the selected grains included native silver, sulfides (pyrite, chalcopyrite, pyrrhotite, galena, and sphalerite), and sulfarsenides (cobaltite, gersdorffite, and arsenopyrite), which together provide a primary source of Fe, Cu, Co, Ni, Pb, Zn, Ag, As, and S. The sulfarsenide mineralogy is typical of the silver-bearing veins mined in the area, while the sulfides are typical of massive sulfide lenses containing Ag veins within the local Pre-Cambrian volcanics. No secondary alteration minerals were visible during sample processing.

Sequential Extractions

Figures 2a through 2e present the results of the sequential metal extractions for As, Co, Cu, Zn, and Fe, respectively from the five cores collected in September, 2004. Arsenic (Fig. 2a) was predominantly associated with the residual fraction, ranging from 35 to 75%. Arsenic associated with the oxides fraction ranged from less than 5 to 31% and generally decreased with depth. Arsenic associated with the OM fraction of the sediment ranged from 10 to 35%.

Cobalt (Fig. 2b) was strongly associated with the OM fraction of the sediment, ranging from 22 to 80%. Cobalt was also associated with the residual fraction, ranging from 5 to 40%, while Co associated with the oxides fraction ranged from less than 5 to 32% and generally decreased with depth.

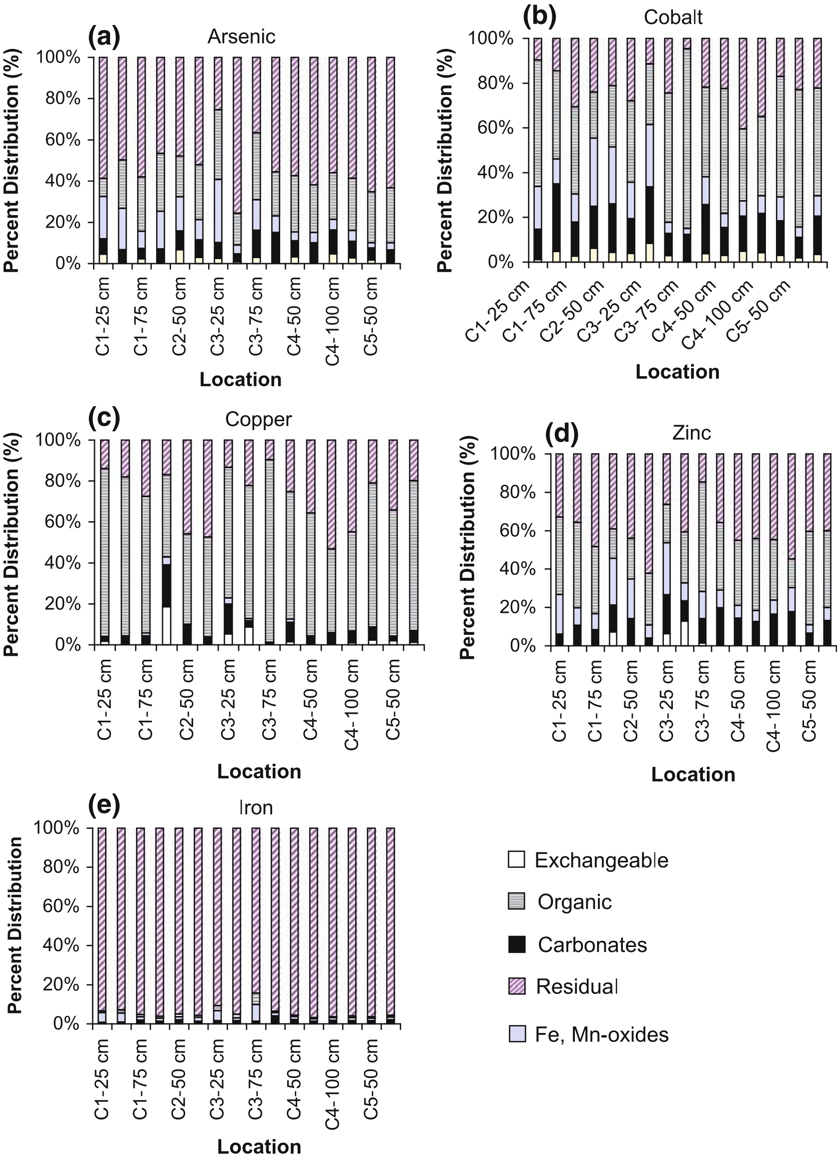
Copper (Fig. 2c) was predominantly associated with the OM fraction of the sediment, ranging from 40 to 85% and the residual fraction of the sediment, ranging from 10 to 50%. Zinc (Fig. 2d) was predominantly associated with the residual fraction, ranging from 15 to 65%, while the OM fraction of the sediment ranged from 35 to 45%.

Zinc associated with the oxides fraction ranged from less than 10 to 25%, and generally decreased with depth. Iron (Fig. 2e) was predominantly associated with the residual fraction of the sediment, ranged from 88 to over 99%; the oxides fraction of the sediment ranged from 0 to 6%.

Vegetation

Table 3 shows that significant concentrations of As, Co, Cr, Cu, Fe, Mn, and Zn accumulated in the cattail (*T. latifolia*) leaves. Generally, much higher metal concentrations were extracted from the leaf samples collected near the wetland inlet (Core 2, 3), as expected due to higher metal loadings anticipated at these locations. This observation is supported by other studies (Miller et al. 1983; O'Sullivan et al. 2004). Background conditions were not known for the *T. latifolia* in the area; however, the vegetation was flourishing in the study area and so it did not appear that the presence of metals at these concentrations was having a negative effect on *T. latifolia*. In general, the concentrations of most metals in *T. latifolia* decreased through the wetland. Arsenic appeared to be the only exception. There was also considerable variability between sample locations, most likely due to variations in metal loadings at each location.

Fig. 2 Sequential extraction results



Microbiology

The results from the bacterial enumerations are outlined in Table 4. The bacterial populations were found to be relatively consistent throughout the wetland, both spatially and with depth. There also appeared to be an even distribution of acid producing (oxidizing) bacteria and reducing bacteria, with populations ranging from 10^2 to 10^6 CFU/gdw. The presence of all three types of microorganisms throughout the entire wetland, with a relatively consistent range of population densities with depth at each core location, may indicate that both oxic and anoxic conditions exist throughout the wetland.

Table 3 Metal accumulations (mg/kg) in *T. latifolia* leaf samples

Samples	Arsenic	Cobalt	Copper	Iron	Manganese	Zinc
Core 1	NA	NA	2,070	21,175	50,400	7,830
Core 1	NA	NA	1,545	27,000	24,350	9,990
Core 2	27,300	25,650	2,955	453,000	99,450	14,715
Core 3	21,900	1,500	1,695	50,250	101,700	10,125
Core 3	19,830	2,500	2,025	57,000	32,700	9,525
Core 4	NA	3,465	2,160	157,500	65,700	9,795
Core 5	27,600	NA	1,125	31,800	56,250	7,545

NA not analyzed

Mass Balance Calculations

A simplified mass balance for As, Co, and Cu through the wetland is summarized in Table 5. The porewater mass loading for each trace element was calculated using the

Table 4 Microbial population enumeration results (CFU/gdw)

Samples	Microbial Population	Depth (cm)			
		25	50	75	100
Core 1	APB	1.10E+05	7.00E+06	3.30E+04	NA
	IRB	1.70E+04	2.20E+04	1.10E+03	NA
	SRB	2.20E+02	7.90E+05	1.30E+05	NA
Core 2	APB	4.90E+04	4.90E+02	4.90E+03	NA
	IRB	1.40E+04	1.70E+03	1.40E+02	NA
	SRB	2.20E+02	4.90E+03	7.90E+02	NA
Core 3	APB	3.30E+04	1.30E+04	1.30E+05	NA
	IRB	2.30E+04	4.60E+02	1.10E+04	NA
	SRB	2.20E+05	3.30E+04	4.90E+04	NA
Core 4	APB	7.90E+03	2.30E+04	4.90E+04	7.90E+04
	IRB	7.90E+02	7.90E+02	1.30E+02	3.30E+02
	SRB	2.20E+02	1.10E+02	2.80E+04	2.30E+04
Core 5	APB	1.30E+05	2.30E+03	7.90E+02	NA
	IRB	1.80E+03	3.30E+02	1.30E+02	NA
	SRB	3.50E+03	2.20E+03	2.20E+03	NA

APB acid producing bacteria, *IRB* iron reducing bacteria, *SRB* sulfate reducing bacteria, *NA* not analyzed

Table 5 Mass balance summary (mg/day)

	Arsenic		Cobalt		Copper	
	1994	2004	1994	2004	1994	2004
Farr Creek, up-gradient of Mill Creek						
Pore water mass loading	ND	88	ND	242	ND	96.8
Surface water mass loading	4.91E+06	1.01E+06	5.46E+04	1.37E+04	4.10E+04	4.10E+04
Mill Creek, up-gradient of Farr Creek						
Pore water mass loading	ND	88	ND	209	ND	95.7
Surface water mass loading	2.20E+07	7.43E+06	1.43E+06	4.41E+05	7.78E+04	5.18E+04
Farr Creek at North Dam						
Pore water mass loading	ND	231	ND	319	ND	198
Surface water mass loading	7.86E+06	1.51E+07	4.23E+05	4.54E+05	6.05E+05	1.21E+05
Mass balance	1.91E+07	−6.68E+06	1.06E+06	8.23E+02	−4.86E+05	−2.82E-04

ND Not determined

average porewater concentration multiplied by the calculated average groundwater flow rate of 1.1 m^3/day. The groundwater flow rate was calculated assuming a hydraulic conductivity of 1×10^{-5} m/s and an effective porosity of 0.3 (Freeze and Cherry 1979). A hydraulic gradient of 0.009 m/m was calculated based on water elevation measurements collected throughout the wetland (Kelly 2006). The surface water mass loading for each trace element was calculated using the measured surface water concentration multiplied by the average surface water flow rate measured in 2004 in Farr Creek upstream of Mill Creek (158 L/s), in Mill Creek upstream of Farr Creek (150 L/s), and Farr Creek downstream of Mill Creek near the north dam (350 L/s). Historical surface water data collected by Percival et al. (2004) was also included in the analysis for comparison purposes. Historical pore water concentration data were not available for the locations tested in 2004.

The mass balance calculations indicate that the wetland was a net sink for As in 1994 and a net source in 2004. A possible explanation for this is that over the past 10 years, the wetland has reached its limit in attenuating As within the system. It is also possible that the elevated concentrations of As measured in the surface water in Farr Creek near the north dam in 2004 is mainly attributed to the destruction of the gravel dam along the south boundary of the study site during the surface water sampling activities. Had the south dam not been damaged at the time of sampling, lower concentrations may have been measured.

The mass balance calculations indicated that for both 1994 and 2004, the wetland was a net sink of Co and a net source of Cu leaving the system. It should be noted, however, that the Cu concentration measured near the north dam was unusually high (0.02 mg/L) and could be attributed to laboratory error as opposed to the actual Cu concentration at that location.

It should be noted that this mass balance is simplified and that a detailed hydrogeological assessment of the system would be required to confirm these findings.

Discussion

Sequential extractions were completed for five separate fractions of the sediment: exchangeable, carbonates, oxides, OM, and residuals. Metals associated with the exchangeable fraction have been found to be typically highly mobile and are often correlated with the cation exchange capacity (CEC) of the sediment (Grambrell et al. 1991).

The surfaces of oxides, OM, and carbonates are also prime adsorption sites for metals. The residual fraction accounts for silicate minerals and sulfides, as noted from the microprobe analysis. This is important since one of the sinks for most metals is the formation of metal sulfide precipitates under reducing conditions, which consequently immobilizes the metals.

Previous studies (Fuller 1993; Langmuir et al. 1999) have shown that As (Fig. 2a) has a high affinity for Fe oxides and oxyhydroxides. The results from the SMEs indicated that much of the Fe was associated with the residual fraction of the sediment and not in the form of iron oxides (Fig. 2e). As a result, much of the As was associated with both the residual and OM fractions of the sediment (Fig. 2a).

Copper (Fig. 2c) and zinc (Fig. 2d) were predominantly associated with the OM and residual fractions of the sediments (Fig. 2c, d). Cobalt was also predominantly associated with the OM and residual fraction (Fig. 2b); however, it was also largely associated with carbonates. Cobalt has known affinities for carbonates (Brookins 1988) and therefore competition for sorption sites between carbonates and other fractions of the sediment (such as OM and oxides) may be enhanced.

The changes in porewater sulfate and sulfide concentrations with depth (Table 1) indicated that sulfate reduction was occurring throughout the wetland, especially at greater depth. The microbiology results (Table 3) identified the presence of APB populations in consistent numbers with the SRB and IRB populations. This may indicate that all of these bacterial populations are active and the acid produced by these populations is immediately neutralized by the dissolution of carbonate minerals within the tailings. Above pH 6.3, which was the case throughout much of the study area, the dissolution of one mole of calcite consumes one mole of H^+ as shown in the following equation:

$$CaCO_3 + H^+ \rightarrow Ca^{2+}_{(aq)} + HCO^-_{3(aq)}$$

This would also account for the elevated dissolved concentrations of Ca^{2+} in the pore water (Table 1). It is also possible that APB populations are supported in the vicinity of vegetation root zones throughout the wetland. Oxygen is transported by wetland plants to the root zones generating localized zones of oxidation (Champagne 2007). This could allow for sustained populations of APBs throughout the wetland. In regions located away from the root zones, conditions are likely anoxic, which are favorable for biogenic iron and sulfate reduction (Jacob and Otte 2004).

From the microbiology results, it appears that there is considerable competition between bacteria species for organic substrates. This was supported by changes in population trends at different locations within the study area, where there were only small changes in sulfate and reduced Fe concentrations. Previous studies have shown the competitiveness between SRB and IRB, which appear to be dependent on electron donor availability and porewater chemistry (Fortin et al. 2002). It should also be noted that Fe reduction can occur both biotically and abiotically, whereas sulfate reduction can only proceed with the aid of SRB (Fortin et al. 1996).

Results with respect to the extraction of metals from *T. latifolia* leaf samples indicate that considerable metal uptake has occurred throughout this wetland. Studies have shown that metal uptake by plant materials can be over 90% of the total mass distribution (Jackson et al. 1993; Mays and Edwards 2001). There was a large fluctuation (non-detect to 20%) in metals being taken up by *T. latifolia* at different core locations. This could be attributed to differential metal loadings at different locations in the wetlands.

Previous studies have reported metal uptake in both the leaves and root zones of *T. latifolia* and found much higher percentages of metals associated with the roots than the leaves (Jackson et al. 1993). This would suggest that phytoremediation could be a powerful mechanism for metal immobilization in this wetland. This could be an interesting topic for future study in this wetland system. There has been conflicting research findings regarding the ability of wetland plants to immobilize metals in the long term. This is in part due to the fact that plants transport oxygen to their roots, generating a zone of radial oxygen loss. This can result in the generation of localized oxic conditions in the immediate vicinity of the roots, which can cause reduced sulfur and iron species to oxidize. Under these conditions, metals such as As and Co may adsorb or co-precipitate with Fe oxides; however, metals such as Zn would likely remain dissolved (Jacob and Otte 2004).

The water-saturated portion of the wetland was covered with *T. latifolia* and there did not appear to be any limitation on the growth of this plant species. It is possible, however, that the growth of other wetland plants was inhibited due to the elevated metal loadings into the wetland system. In addition, background metal concentrations in *T. latifolia* and other vegetation species in the area are not known. Such a study would aid in determining the degree of metal uptake by *T. latifolia* as a direct result of the mine tailings deposits.

The preliminary mass balance calculations are inconclusive in determining if this wetland is a net source or net sink for As, Co, and Cu. Based on these results, it is not clear as to whether this wetland has reached its capacity for attenuating As, Co, and Cu. A more extensive hydrogeological assessment of the system would allow for a more detailed mass balance, which could confirm the finding found in the current study.

Conclusions

The data collected suggest that this is a relatively stable system. However, should the current state of the system change, such as the input of a waste stream elevated in organic substrate, it is likely that a considerable amount of the metals adsorbed to Fe and Mn oxides within this system would become mobilized in the short term. Over time, the geochemical processes regulating metal mobilizations throughout the system would change, such as increased activity of SRBs and increased adsorption of metals to the additional organic substrate, resulting in different biogeochemical controls of the metals throughout the system.

Alkaline drainage systems can immobilize metals under oxic conditions, through adsorption onto OM or oxide precipitates, and uptake by wetland vegetation, as well as under anoxic conditions via microbial transformations, such as biogenic sulfate reduction generating sulfides that can then form metal sulfide precipitates. Acidic drainage systems typically require the formation of strongly reducing conditions in order to immobilize metals. These results indicate the importance of considering the geochemical conditions of the wetland or system being used to treat the mine water, as well as having a detailed understanding of the metals of concern within the mine waste. Different metals will exhibit different geochemical interactions based on the redox conditions, presence of sulfides, Fe and Mn oxides, and organic matter.

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