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Application Of Copper And Zinc Isotopes To Fingerprint Metal Sources And Identify Attenuation Mechanisms In The Abandoned Waldorf Mine Area, Clear Creek County, Colorado

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APPLICATION OF COPPER AND ZINC ISOTOPES TO FINGERPRINT METAL SOURCES AND IDENTIFY ATTENUATION MECHANISMS IN THE ABANDONED WALDORF MINE AREA, CLEAR CREEK COUNTY, COLORADO.

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To Angel, Gaby, Alberto y Tere.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Acid rock drainage (ARD) is caused by the oxidative weathering of sulfide minerals. Sulfur is oxidized by dissolved oxygen or Fe(III) and sulfate ions, metals, and protons are released into the environment. Hence, the pH of nearby water and soils often decreases in response to ARD while metal concentrations increase. Because a large part of the Rocky Mountains of Colorado are highly mineralized (i.e., the Colorado Mineral Belt), ARD is a serious problem in this region. Moreover, the many abandoned mining areas in the Rocky Mountains that include waste rock piles, tailings impoundments, and surface disturbances add to the problem because they expose enormous quantities of sulfide-rich rocks to the atmosphere. The Colorado mineral belt hosts many streams that have concentrations of metals that are above aquatic life and sometimes even human health water quality standards (EPA) In 2007, the Colorado Division of Reclamation, Mining and Safety (CDRMS) estimated that the Colorado mineral belt contained more than 17,000 hazardous abandoned mines. ARD is a substantial problem even outside Colorado because the Rocky Mountains' snow pack, river basins and aquifers supply water for over sixty million people in the western United States (Bales et. al. 2006).

Infiltration of surface water through mine wastes (tailings, tunnels, waste rock piles, etc.) can be a major source of metal contaminants in a watershed (McDougal and Wirt, 2007). The identification of metal loading pathways is critical for understanding how metals impact terrestrial and aquatic ecosystems and for designing useful remediation strategies (Liu, F., Williams M. W. and Caine, N., 2004). However, in many cases, particularly in mountain watersheds with limited infrastructure and monitoring capacity, metal concentrations alone are

not adequate to identify metal loading sources or transport and attenuation mechanisms. In these cases where hydrology and geochemistry are too complex for a basal approach we suspect that transition metal isotopes may prove to be a useful chemical tool. The stable isotopes of some transition metals can fingerprint sources while others are reflective of the mechanisms during the processes that control their transport, including redox reactions, precipitation, and adsorption.

The Abandoned Waldorf Mine area in Clear Creek County, Colorado, is a good example of a mountain catchment severely impacted by metal contamination where the utility of metal isotopes for unraveling these complexities can be directly evaluated. The site hydrology and metal loading pathways are extremely complex (EPA) and there is limited infrastructure (like monitoring wells) for a thorough hydrogeochemical investigation. Finally, copper (Cu) and zinc (Zn) are present at elevated concentrations over most of the site, and their isotopic compositions can be used to investigate metal cycling. At the Waldorf site contaminated water discharges from the abandoned Wilcox tunnel, as well as from springs at the toe of a waste rock pile. The Wilcox tunnel, established about 1902, is located at the foot of Mount McClellan and leads to approximately 30,000 feet of underground workings. Metal-rich waters from the waste rock pile and tunnel flow through a groundwater-fed wetland that includes ephemeral alpine streams and pools before ultimately discharging to Leavenworth Creek. Leavenworth Creek contributes drinking water for the city of Georgetown, Colorado, and is a tributary of Clear Creek, which supplies water for Golden, Colorado (Malem, 2006).

In this study we measured the Cu and Zn isotopic compositions of water, mineral and ore concentrate samples collected from the abandoned Waldorf mine area in Clear Creek County, Colorado. The objectives of our study were to use the metal isotopic signatures to identify and track metal loading sources and metal transport and attenuation mechanisms in the watershed. To

this end, samples were collected from the Wilcox tunnel, waste-rock pile and wetland areas in and around the abandoned mining area. We additionally measured Zn isotopes in soil pore waters collected from multiple depths at three locations within the wetland. This work will directly benefit remediation efforts in the region and will serve as a case study for the application of these isotopic tools in other systems.

CHAPTER 1

HISTORY AND PREVIOUS INVESTIGATIONS OF THE ABANDONED WALDORF MINE.

The Waldorf site is about 3500 m in elevation and is located 9.6 km SW of the town of Georgetown, Colorado within the Argentine mining district (Figure 1). Mineralization in the district is hosted by the Precambrian Idaho Springs formation, a heavily metamorphosed igneous rock. Near the Wilcox tunnel, there is an outcropping of Precambrian Silver Plume granite (McDougal and Wirt, 2007). Metal production at the Waldorf site began in 1902 (Witte, et al., 2004 and Malem, 2006) and ended around 1920. The Waldorf mine dump, situated at the base of the abandoned Wilcox Tunnel, has an estimated volume of 3800–4600 m^3 of sulfide-rich waste rock material (Colorado Department of Public Health and the Environment, 2000). Silver, lead, and gold along with some zinc and copper were the principal metals produced from the sulfide-rich ores mined at Waldorf. Production data also indicate that ores obtained from other nearby mines were processed at the Waldorf mill (Malem, F. 2006; Witte, K., et. al. 2004).

Previous studies at Waldorf have focused on characterization of metal contaminants and identification of metal loading sources. Witte et al. (2004) compared iron (Fe), copper (Cu), zinc (Zn), cadmium (Cd), manganese (Mn), lead (Pb), strontium (Sr) and sulfate (SO_4) concentrations from top and root layer soils, as well as from tree-rings extracted from trees growing in the area. Metal concentrations in mining-impacted soils were found to be considerably higher compared to control samples of soil collected outside the mining area. The concentrations of Fe, however, remained stable between mining-impacted and control soils. Tree-rings from tailings-impacted

areas contained higher concentrations of Zn, Cu, Fe, and Cd compared to trees from outside the mining area. The concentration of Mn increased over time, even in control trees, while there was no difference in Pb and Sr concentrations between trees in mining-impacted areas and those that were outside the area directly impacted by mining wastes. Tree ring ages demonstrated that contaminant metals were bioavailable in the Waldorf system for uptake into trees for the past 110 years. Malem installed twenty temporary piezometers in the Waldorf mine waste pile to characterize groundwater flow, dissolved oxygen (DO), pH, electrical conductivity, and temperature. The chemistry of these water samples was broken into three distinct groups. The first group was characterized by low-pH (between 2.7 and 4.4) and high Li, Zn, and SO_4 concentrations (up to 0.030 mg/L, up to 180 mg/L, and up to 830 mg/L respectively). The second group was characterized by circumneutral pH and moderate Li, Zn, and SO_4^{-2} concentrations (up to 0.007 mg/L, up to 5.800 mg/L and up to 460 mg/L respectively), while the third group was characterized by circumneutral pH and low concentrations of Li, Zn, and SO_4^{-2} (<0.005 mg/L, up to 3.100 mg/L and up to 340 mg/L respectively). Malem (2006) suggests that these data represent water-rock interaction from multiple flow pathways involving up to three possible groundwater sources that interact with the waste dump; 1) annual snowmelt runoff from the surrounding mountains, 2) discharge from the tunnel, and 3) water from the native soil, fed from underlying fractures in the bedrock under the dump, entering the waste rock pile from below.

McDougal and Wirt (2007) and Fey and Wirt (2007) carried out a series of studies from 2002 through 2004, using geophysical (electromagnetic conductivity and direct current resistivity) and geochemical techniques (NaCl and LiBr tracers, respectively) to understand the water behavior in the abandoned mine area before and after the re-routing of flow from the Wilcox tunnel around the waste rock pile. In 2002 (before the rerouting) McDougal and Wirt

carried out conductivity measurements and groundwater sampling from the waste rock pile after injecting a NaCl tracer solution. The same month, Fey and Wirt conducted a LiBr tracer injection in and around the waste rock pile and sampled various locations in the wetland and the Leavenworth Creek. The study conducted by McDougal and Wirt suggested that two main flow paths occur in the waste rock pile, one traveling through the dump and the other traveling under the dump. Both flow paths impacted the adjacent wetland. They found that increasing precipitation and melting of snowpack caused the discharge from the adit and into the creek to increase by about 7 times from 2002 to 2003, reducing Cu and Zn concentrations in the creek and improving its water quality. However, this was recognized as an ephemeral seasonal affect, and not as evidence of improved water quality attributable to the remediation.

Despite these previous works it is unclear what water flow pathways are the most important in affecting metal concentrations in the Leavenworth Creek. Several important questions remain regarding metal loading and attenuation pathway/mechanisms at the Waldorf mining site. It is also unclear what role the wetland area plays in attenuating metal loads coming from the adit and the waste rock pile. Are metals being diluted from the influx of pristine groundwater or are metals being sorbed onto the soils or taken up into plants? Can multiple sources of water be identified based on water chemistry alone? Is the contaminated water coming from the abandoned mine or perhaps from different groundwater sources? Finally, can zinc (Zn) and copper (Cu) isotopes help to distinguish metal loading sources and pathways? These are some of the key questions we hope to address in this investigation.

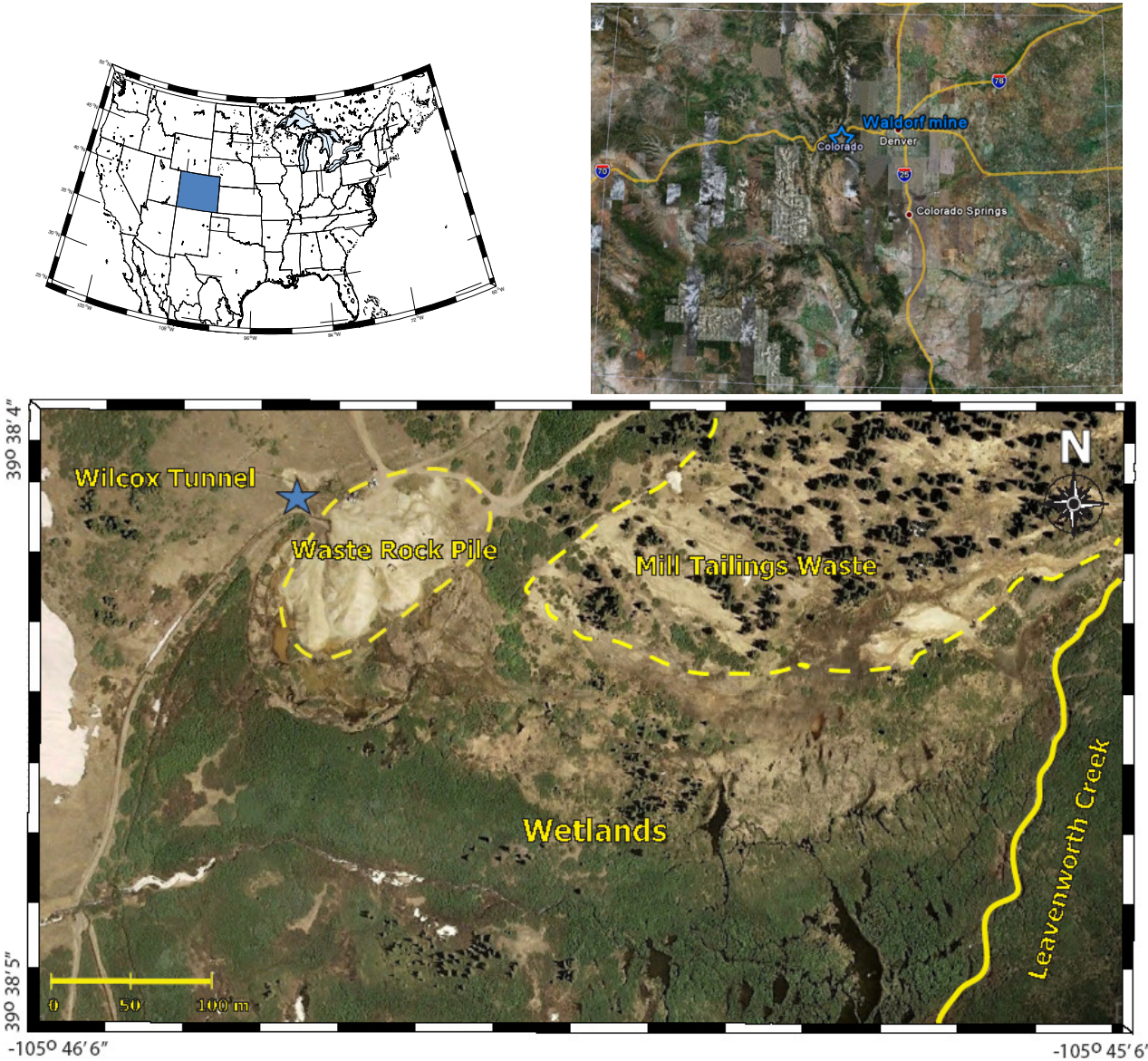

Figure 1. Location of abandoned Waldorf mine: the Tunnel, Waste Rock Pile and Wetland areas are identified. The discolored area of Wetlands (southeast of the Waste Rock Pile) represents metal impacted vegetation.

CHAPTER 2

METHODS

2.1 Sample Locations and Collection.

During the summers of 2008 and 2009, surface water samples were collected from three locations, (1) outflow from the abandoned Wilcox tunnel, (2) seeps around the apron of the waste rock pile, and (3) various locations within the nearby wetland following the direction of the apparent contaminant plume identified by discolored vegetation (Figure 2). In addition to these samples, shallow groundwater (< 1m below ground surface) was collected from two existing piezometers in the wetland and from soil pore waters at multiple depths at three locations within the wetland (Figure 2). Finally, a background sample was collected from an adjacent stream draining snowmelt from the nearby mountains.

Pore water samples were collected at depths ranging from 5 to 60 cm in 5 to 10 cm increments using a vacuum-sealed lysimeter apparatus constructed by the U.S. Geological Survey (e.g., Balistrieri, 2003) (Figure 3). Water quality parameters like pH, specific conductance, dissolved oxygen (DO), and temperature were measured using a multiparameter instrument at each of the surface and pore-water sites. At selected sample sites, DO and Fe(II) concentrations were evaluated in the field using a DO probe and colorimetric kits, respectively. Soil samples were collected using a soil auger from a few locations to compliment the pore water samples. Grab samples of rocks with visible pyrite (FeS_2), sphalerite (ZnS), and/or chalcopyrite ($CuFeS_2$) were collected from the mine dump and a single sample of ore concentrate was

collected from the floor of the nearby abandoned mill building that processed ore from Waldorf and other local mines.

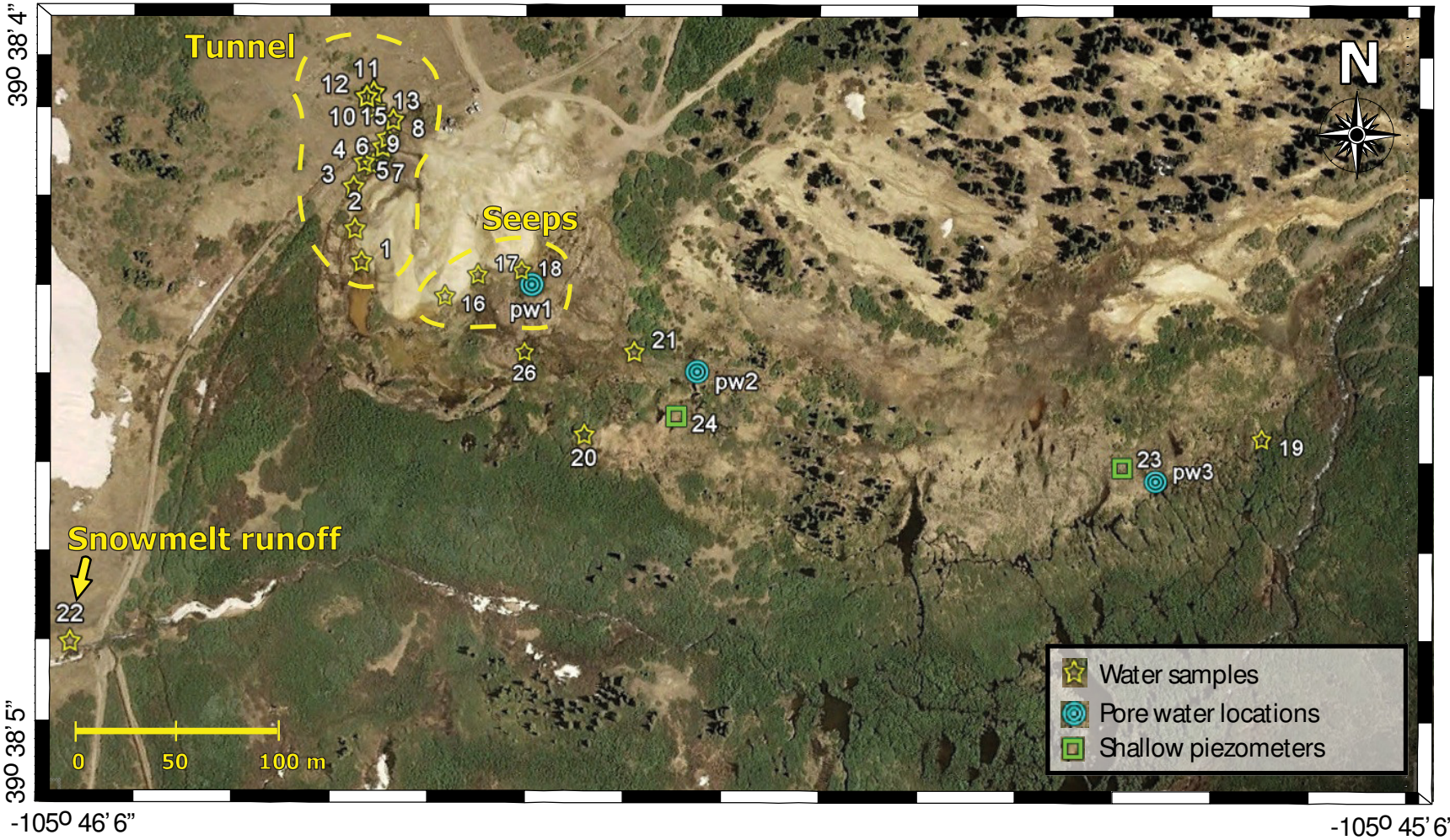

Figure 2. Water samples locations at the Waldorf study site.

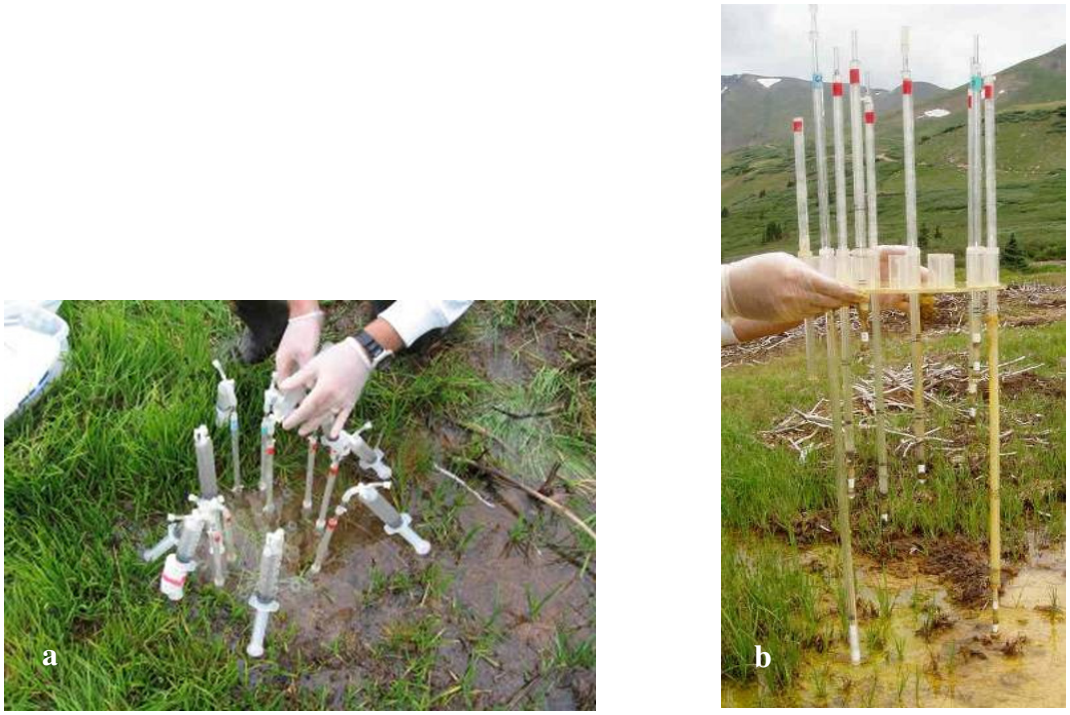

Figure 3. Lysimeter apparatus with syringer in place ready to take water samples (a) and lysimeter pulled out (b).

Sample bottles were washed overnight in sub-boiling HCl and then rinsed three times with pure water prior to use in the field. Water samples were collected and preserved with concentrated nitric acid for later analysis of dissolved (using 0.45µm and/or 0.1µm nylon syringe filters) and total cations (unfiltered). Samples for the determination of alkalinity and anion concentrations were filtered and refrigerated prior to analysis. Additional samples were collected and filtered into pre-washed amber glass septum vials for the determination of their dissolved organic carbon (DOC) contents. Total metal, dissolved metal and major cation concentrations from water samples and soils (digested using a 4 acid method described by Lamothe et al., 2002) were determined by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) techniques at the United States Geological Survey (USGS) laboratory in Denver, Colorado (Lamothe et al., 2002). Anion

concentrations and alkalinity were also determined by the USGS, (Brinton et al., 1995) while DOC concentrations were measured using a Lach IL 550 TOC/TN analyzer instrument (Method 9060A for Total Organic Carbon) at UTEP.

Sphalerite and chalcopyrite minerals were separated from the rock samples, digested using aqua regia, and analyzed for their metal concentrations using an ICP-OES at UTEP. Ore concentrate samples (3 splits from a 1kg grab sample) were similarly digested and analyzed. The ICP-OES was calibrated using matrix-matched multi-element ICP standards and accuracy was checked by repeatedly analyzing USGS standard reference water sample T-143. Based on replicate analysis of this standard (and other samples, uncertainty was found to be <5% for most elements and <15% for aluminum (Al). Samples were prepared and analyzed for their Cu and Zn isotopic ratios as described below.

CHAPTER 3

ISOTOPIC ANALYSIS

Selected water and digested solid samples were evaporated in Teflon (Savillex®) containers to pre-concentrate Cu and Zn to about 1.5 µg. The evaporated pellet was dissolved in 1 mL of 10M HCl in preparation for anion-exchange column chromatography. Column separations were done in a class 100 clean bench according to the methods outlined in Borrok et al. (2007), which are only briefly reviewed here. Plastic columns were filled with 0.85 mL of pre-cleaned AG MP-1 (Bio-Rad®) anion-exchange resin and cleaned with water and weak nitric acid before being conditioned with 3ml of 10M HCl. The sample (in 10M HCl) was loaded on the column and additional aliquots of 10M HCl were used to separate most matrix elements from the Cu and Zn that remained on the column. Seven mL of 5M HCl were used to separate the Cu while Zn remained on the column. Four ml of 1M HCl were then added to elute Fe (while Zn remained on the column), and finally four mL of pure water were used to collect the Zn fraction. Copper separates were passed through the process twice (using new columns) due to high concentrations of sulfate (up to 354 mg/L) in the water samples (e.g., Pribil et al., 2010). The metal separates were evaporated to dryness twice to remove residual chlorine and then dissolved in 2% HNO_3 for analysis using a Nu Instruments multicollector (MC)-ICP-MS. Samples were introduced to the Argon plasma and run in dry plasma mode (DSN) using 0.1ml/min nebulizer system.Copper samples were analyzed for ^{63}Cu and ^{65}Cu, while Zn samples were analyzed for ^{64}Zn, ^{66}Zn, ^{67}Zn, and ^{68}Zn. The standard-sample-standard bracketing method was used to correct for mass bias (e.g., Cloquet et al., 2007, Borrok et al., 2007, Thapalia et al., 2010). Isotopic data

are reported in standard delta notation with reference to the SRM 976 (NIST) Cu standard solution (see Equation 1) or the Johnson Matthey Zinc standard solution (see Equation 2).

$$\delta^{65}\mathrm{Cu} = \left[\frac{(^{65}\mathrm{Cu}/^{63}\mathrm{Cu})_{sample}}{(^{65}\mathrm{Cu}/^{63}\mathrm{Cu})_{\mathrm{SRM_{ave}}}} - 1\right] \mathrm{x}1000 \quad (1)$$

$$\delta^{65}\mathrm{Zn} = \left[\frac{(^{65}\mathrm{Zn}/^{63}\mathrm{Zn})_{sample}}{(^{65}\mathrm{Zn}/^{63}\mathrm{Zn})_{\mathrm{JRM_{ave}}}} - 1\right] \mathrm{x}1000 \quad (2)$$

The majority of samples were replicated at least 3 times and 2 sigma errors ranged from 0.01 to 0.3 for Cu and Zn. The average 2 sigma (σ) uncertainty of the Zn isotopes samples was 0.096. The uncertainties for column duplicates fell within these ranges. We also performed repeated analysis of an in-house Zn and Cu standard over the multiple analytical sessions covering 7 months. The Cu rod standard 2σ precision was ±0.16‰, (n=11) and the IRMM Zn standard 2σ precision was ±0.12‰ (n=12). Figure 4 is a plot of the ln(68/64) (Fig. 4a) and ln(67/64) (Fig. 4b) Zn ratios versus the ln(66/64) Zn ratio. The best-fit lines for these plots demonstrate that the appropriate mass dependency was achieved and that possible spectral interferences did not impact the data. Similarly Figure 5 is a plot of δ^{66}Zn vs. δ^{67}Zn/1.5 and vs. δ^{68}Zn/2. This convention puts the data on the same mass dependent slope of 1. All the data fall within error of the expected mass dependency line (Slope=1) suggesting that spectral interferences were not a problem.

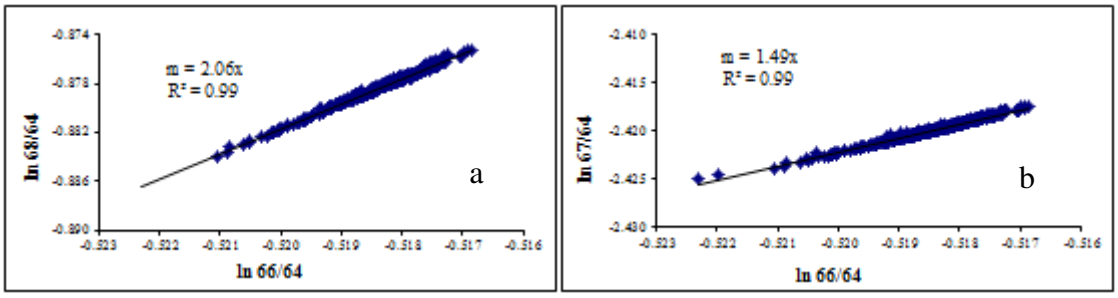

Figure 4. Plot of (a) ln(^{68}Zn/^{64}Zn) and (b) ln(^{67}Zn/^{64}Zn) vs. ln(^{66}Zn/^{64}Zn)

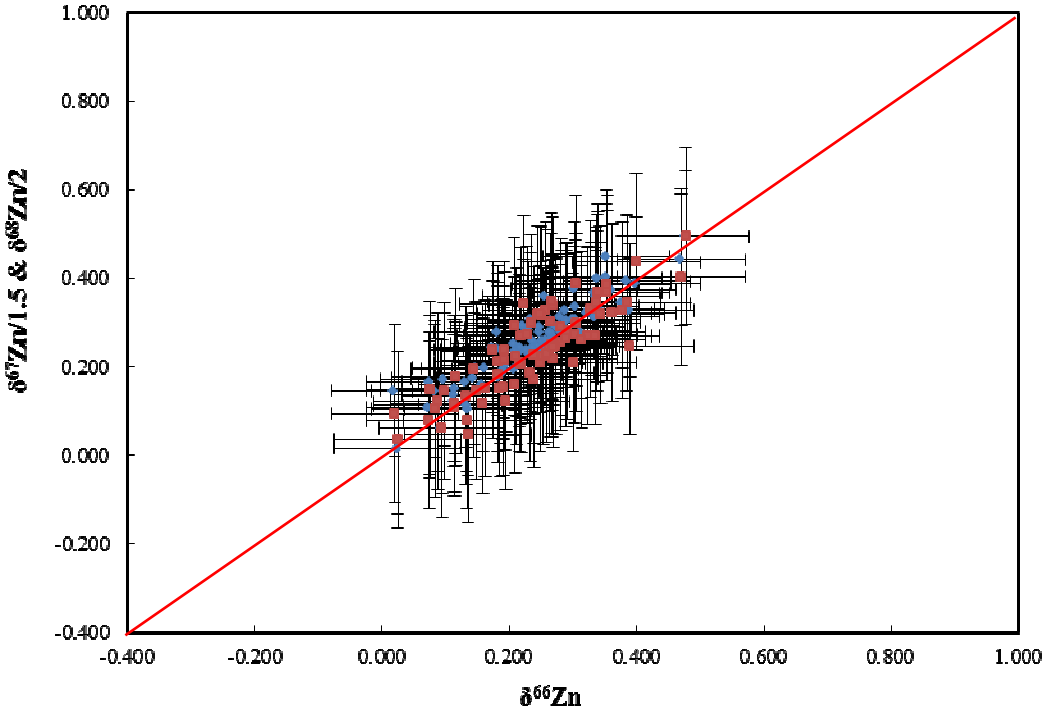

Figure 5. $\delta^{68}Zn/2$ (Red points) and $\delta^{67}Zn/1.5$ (blue points) versus $\delta^{66}Zn$. All the normalized data fit on the expected mass dependency line.

CHAPTER 4

MULTIVARIATE ANALYSIS

Statistical multivariate analysis, specifically principal component factor analysis (PCFA), was employed as a tool to help to evaluate relationships among the different data variables (Takeuchi et al., 1982) and to reduce the number of variables, or factors down to only those that are important in controlling the overall chemistry (Vogt, 2005). PCFA was chosen because it is good for comparing variables with different units (e.g., concentration, temperature, conductivity, etc.) and does not require that the data be normally distributed (Woocay A. 2008). PCFA works by creating factors, which is a set of variables similar to items in a survey (Vogt, 2005) (samplings points, concentrations, pH, temperature, etc.) that can be statistically banded together. Mathematically speaking, factors are eigenvectors of the variance-covariance or correlation matrix of the variables (Davis, 1973). PCFA is conducted using a correlation matrix where independent factors are extracted that group like variables and quantify the amount of variation explained by each factor. The eigenvalue ratio determines the number of relevant factors based on the cumulative variance (e.g., Woocay, 2008). In other words, the eigenvalue ratio quantifies how many of the factors (variable groups) are needed to explain the overall variation in the chemical data. There does not exist a strict mathematical criterion to determine the number of relevant factors (Floyd et al., 1995); the goal is only to explain the bulk of the chemical variability. Once the number of statistically-acceptable factors is decided, it is possible to apply a normalized varimax rotation, which is one of many mathematical methods that can be used to maximize the variance of the factors loadings (Vogt, 2005). This process is used to improve the

degree of correlation between the variables and the factors (Davis 1973). The PCFA was performed on Statistica 8.0 with data from filtered water samples collected from the Tunnel, the Waste Rock Pile and the Wetland. The analysis for the tunnel, waste rock pile and wetlands was analyzed including pH, temperature, DO, conductivity, alkalinity, sulfate, and metal concentrations as variables.

CHAPTER 5

RESULTS

5.1. Spatial distribution of Data.

In order to present and interpret the chemical results as a function of their locations, we have arbitrarily assigned the entrance of the abandoned Wilcox tunnel as the zero or starting point for measuring distances to all the other sample locations (Figure 5).

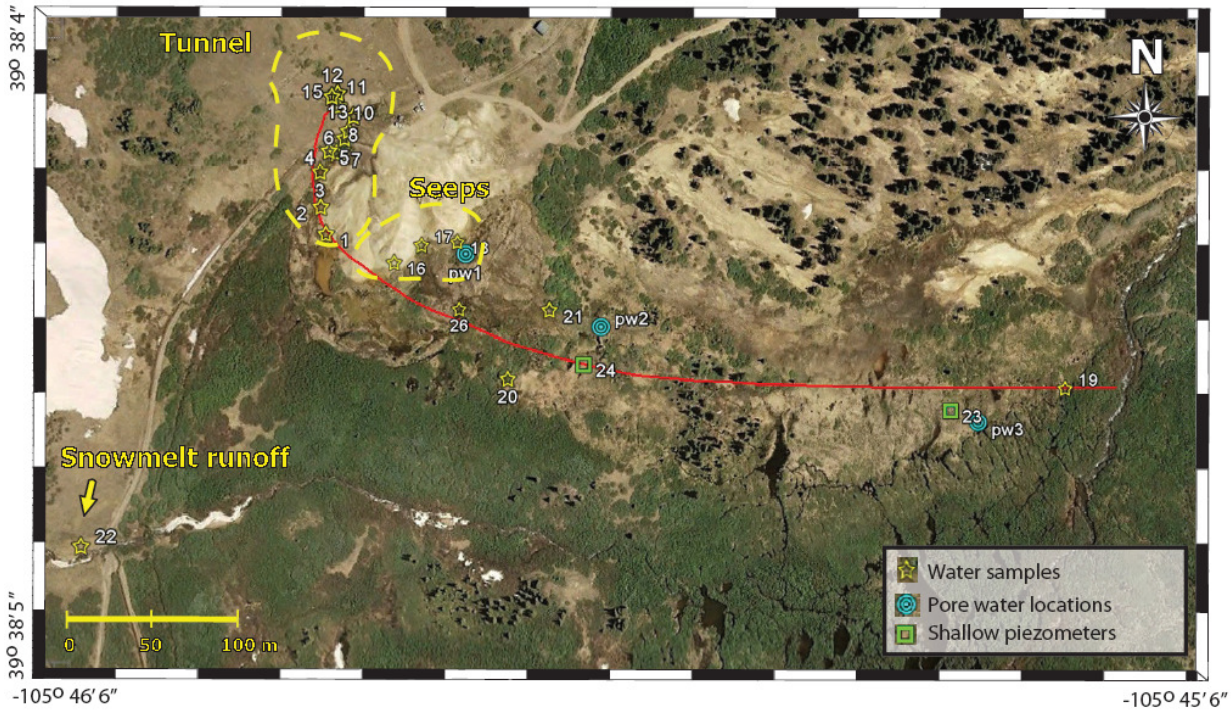

Figure **6.** Sample distances calculated based on the distance from the Tunnel entrance along the red arc. Distances along the arc were determined by the intersection points of perpendicular lines drawn between the sampling points and the arc.

5.2. Tunnel, Mine Waste and Wetland Surface Water Chemistry.

Cation concentrations and field parameters are recorded in Table 1. Samples collected from water flowing from the Wilcox tunnel and the flow from the tunnel that was diverted around the waste rock pile are characterized by their circumneutral pH (6.2-6.8; Figure 7). Samples of water from seeps at the base of the waste rock pile were acidic (3.2–3.9; Figure 7). Sample from the stream fed by snowmelt runoff had the highest pH of 7.5 (Figure 7). The concentrations of Ca, Mg, Mn, SO_4, and alkalinity were generally the greatest for the water emitted from the tunnel area and decreased on average for samples collected from seeps along the waste rock pile and surface waters within the adjacent wetland (Figures 8). Concentrations of dissolved Fe in water collected from the tunnel ranged from 0.08 mg/L to 0.58 mg/L, and colorimetric kits suggest that most of the dissolved Fe was Fe(II) (Table 1). Concentrations of dissolved Fe were slightly greater for the seeps from the waste rock pile, ranging from 0.24 mg/L to 0.84 mg/L (Table 1). DO average concentrations were highest in the wetland, ranging from 8 mg/L to 11.50 mg/L, but were quite low in few samples collected from the tunnel and waste rock areas (Table 1).

Figure 9 presents a comparison of Fe, Cu, and Zn concentrations in unfiltered (raw) versus filtered (0.45µm) samples from the tunnel, waste rock pile and wetland areas. We assume the difference in concentration between unfiltered and filtered samples represents the amount of suspended metal present, and we operationally define the elements passing through the 0.45µm filtering process as dissolved. Figure 9 compares the ratio of the suspended metal concentration to the total metal concentration according to Equation 3:

$$(3) \qquad ([Me]_{unfiltered} - [Me]_{filtered}) / [Me]_{unfiltered}$$

where “Me” is Fe, Cu, or Zn. Concentrations of Fe in the unfiltered samples from the tunnel area were typically an order of magnitude greater than Fe concentrations in the corresponding filtered samples, indicating that suspended Fe minerals were abundant in the tunnel area. The amount of suspended Fe in the waste rock and wetland water samples markedly decreased (Figure 9). The concentrations of Cu in the suspended load were about 0.5 to 1 times greater than dissolved Cu concentrations in the tunnel area, but decreased to very low levels in the waste rock pile and wetland. The concentrations of Zn in the suspended load were quite low in all the water samples, demonstrating that the vast majority of Zn was present in the dissolved form. We additionally evaluated our operationally-defined choice for the dissolved fraction by comparing Fe, Cu, and Zn concentrations of samples filtered with a 0.45µm filter to those from the same location filtered with a 0.1µm filter. For the tunnel samples we found that the 0.1µm filter excluded more Fe and Cu than the 0.45µm filter, but Zn concentrations were the same for both filter sizes (see data in Tables 1 and 2). The presence of measurable Fe and Cu within the 0.45 – 0.1µm particle size range demonstrates that smaller suspended particles, approaching colloidal sizes were present in the tunnel area.

The sample of snow-melt runoff collected from the area adjacent to the Waldorf area (SW, see Fig. 1) had a slightly higher pH (about 7.5) than all of the Waldorf samples and a much lower alkalinity than the samples collected from the Waldorf tunnel area (Fig. 8; Table 1). This sample generally contained lower concentrations of most major and trace ions as compared to the Waldorf samples.

Table 1. (Continued on the next page) Filtered samples (0.45µm), field parameters (altitude, water T, pH, conductivity, DO, Fe(II)), and chemical results for anions, cations, and Cu and Zn isotopes.

	Distances m.	$\delta^{65}Cu$ ‰	2s	n	Rep	$\delta^{66}Zn$ ‰	2s	n	Altitude m.	Water T °C	pH	Cond µs/cm	DO mg/L	Fe(II) mg/L	$CaCO_3$ mg/L	SO_4 mg/L	Al mg/L	As mg/L	Ba mg/L	Ca mg/L
Tunnel																				
1	90	1.26	0.1	6	3	0.20	0.01	2	3560.06	6.3	6.68	670	9.60	0.13	64.60	215	0.077	<0.001	0.013	87.80
2	72.7	1.11	0	2		0.27	0.00	2	3553.66	6.1	6.74	670	10.40	0.08	65.21	222	0.078	<0.001	0.013	86.80
3	51	1.12	0	2		0.16	0.08	2	3553.36	5.9	6.76	710	11.70	0.09	63.23	210	0.078	<0.001	0.012	89.30
4	36	1.78	0.2	2		0.22	0.08	2	3553.05	5.9	6.73	720	7.70	0.09	64.17	223	0.088	<0.001	0.013	89.10
5	25.7	1.05	0.1	3	1	0.27	0.09	2	3553.66	4.8	6.65	720	6.50	0.1	64.24	228	0.090	<0.001	0.013	88.40
6	19.6	0.87		1		0.19	0.09	2	3550.31	5.5	6.67	710	6.20	0.08	65.34	225	0.091	<0.001	0.013	89.70
7	37	1.59	0.2	2		0.20	0.19	2	3546.35	4.8	6.72	720	7.10	0.09	66.75	223	0.091	<0.001	0.013	88.30
8	11	0.95	0.1	2		0.27		1	nm	4	6.58	700	nm	0.11	66.54	225	0.094	<0.001	0.013	90.90
9	11	1.12	0.3	2		0.22	0.09	2	nm	3.9	6.67	730	nm	0.16	65.82	226	0.096	<0.001	0.013	91.30
10	4.44	1.21		1		0.28	0.13	3	3551.22	4	6.58	720	1.20	0.11	65.73	232	0.098	<0.001	0.013	90.60
11	3.63	1.03	0.1	2		0.23	0.03	2	3543.30	4.5	6.53	720	3.00	0.2	66.03	229	0.095	<0.001	0.013	88.70
12	3.63	1.20	0.2	3	1	0.22	0.04	3	3543.30	4.4	6.54	nm	nm	0.2	65.65	219	0.094	<0.001	0.014	86.00
13	0.69	1.25	0.1	5	1	0.30	0.12	3	3554.27	4	6.47	730	1.80	0.13	65.15	228	0.099	<0.001	0.014	87.10
14	0.69	1.34	0.1	2		0.36	0.04	3	3554.27	4.1	6.71	720	1.60	0.58	64.62	237	0.103	<0.001	0.014	89.60
15	0.69	1.19	0.1	2		0.36	0.08	2	3554.27	4.9	6.23	700	1.00	0.58	65.30	232	0.101	<0.001	0.013	85.50
WR pile																				
16	137	1.13	0.1	3	1	0.30		1	3540.56	7.5	3.27	570	6.20	0.02	nm	204	1.280	<0.001	0.014	51.70
17	146	1.15	0.3	2		0.29	0.09	5	3545.74	6.1	3.19	610	6.00	0.03	nm	177	1.800	<0.001	0.014	38.00
18	171	2.11	0.3	2		0.30	0.06	3	nm	8.7	3.34	670	nm	0.11	nm	216	4.040	<0.001	0.017	43.70
26	186	1.38	0.1	4		0.12	0.09	2	3544.82	11	3.90	640	nm	nm	nm	243	1.720	<0.001	0.021	53.60
PW1-0	177	1.82	0.2	2		0.25	0.06	4	nm	6.5	3.88	630	nm	5.5	nm	214	3.490	<0.001	0.018	44.600
Wetland																				
19	598	nm	nm	nm		0.38	0.07	2	3478.68	9.2	5.84	140	11.50	0.10	8.67	39	0.024	<0.001	0.014	15.60
20	232	nm	nm	nm		0.25	0.12	2	3512.82	11.2	6.01	510	nm	nm	14.84	186	0.049	<0.001	0.009	64.50
21	244	nm	nm	nm		0.25	0.07	2	3538.42	13.9	6.58	550	8.00	0.10	19.73	214	0.038	<0.001	0.008	72.90
22	nm	nm	nm	nm		0.28	0.02	2	3571.04	5	7.52	60	nm	nm	9.63	12	0.004	<0.001	0.010	6.07
23	538	nm	nm	nm		nm	nm	nm	3497.28	13	5.87	nm	nm	nm	0	126	0.016	<0.001	0.034	35.50
24	273	nm	nm	nm		nm	nm	nm	3532.94	8.6	6.49	nm	nm	nm	nm	139	0.083	<0.001	0.022	43.70
25	nm	nm	nm	nm		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	2	0.002	<0.001	<0.001	<0.0001
PW2-0	281	nm	nm	nm		0.22	0.02	2	nm	9.3	6.67	550	nm	nm	12.92	192	0.055	<0.001	0.008	72.000
PW3-0	515	nm	nm	nm		0.23	0	2	nm	10.5	7.08	10.5	nm	nm	11.97	134	0.045	<0.001	0.016	48.000

nm = not measured; nd = non detected, 2σ = 2 sigma deviation calculated from "n" replicates; "Rep" = column chemistry replicates (included in the total number of analysis "n").

Table 1. (Continued on the next page) Filtered samples (0.45µm), field parameters (altitude, water T, pH, conductivity, DO, Fe(II)), and chemical results for anions, cations, and Cu and Zn isotopes.

	Cd mg/L	Co mg/L	Cr mg/L	Cu mg/L	Fe mg/L	K mg/L	Li mg/L	Mg mg/L	Mn mg/L	Na mg/L	Ni mg/L	P mg/L	Pb mg/L	SiO_2 mg/L	Sr mg/L	U mg/L	Zn mg/L
Tunnel																	
1	0.017	0.008	<0.001	0.099	0.130	1.100	0.005	14.800	11.900	4.620	0.028	<0.00001	<0.00005	11.200	1.030	0.003	7.110
2	0.018	0.008	<0.001	0.102	0.080	1.220	0.005	14.300	11.900	4.600	0.029	<0.00001	<0.00005	11.100	1.070	0.003	7.390
3	0.017	0.008	<0.001	0.097	0.090	1.230	0.005	13.400	12.000	4.400	0.028	<0.00001	<0.00005	10.600	1.020	0.003	6.870
4	0.018	0.008	<0.001	0.107	0.090	1.190	0.005	14.200	12.100	4.510	0.029	<0.00001	<0.00005	11.400	1.080	0.003	7.380
5	0.018	0.008	<0.001	0.108	0.100	1.240	0.005	27.900	12.000	4.520	0.030	<0.00001	<0.00005	11.500	1.090	0.003	7.700
6	0.018	0.008	<0.001	0.109	0.080	1.190	0.006	31.600	12.200	4.590	0.029	<0.00001	<0.00005	11.500	1.070	0.003	7.640
7	0.018	0.008	<0.001	0.105	0.090	1.160	0.005	22.100	11.900	4.480	0.029	<0.00001	0.0001	11.400	1.070	0.003	7.470
8	0.018	0.009	<0.001	0.115	0.110	1.240	0.006	31.800	12.500	4.520	0.029	<0.00001	0.0001	11.600	1.090	0.003	7.620
9	0.018	0.009	<0.001	0.114	0.160	1.180	0.006	30.600	12.500	4.530	0.030	<0.00001	<0.00005	11.600	1.090	0.003	7.670
10	0.019	0.009	<0.001	0.114	0.110	1.200	0.006	14.100	12.400	4.570	0.030	<0.00001	<0.00005	12.000	1.110	0.004	7.780
11	0.018	0.008	<0.001	0.101	0.200	1.210	0.005	13.900	11.900	4.490	0.029	<0.00001	0.0001	11.600	1.090	0.003	7.700
12	0.018	0.008	<0.001	0.113	0.200	1.210	0.005	14.100	12.100	4.690	0.028	<0.00001	<0.00005	11.400	1.040	0.003	7.420
13	0.018	0.009	<0.001	0.119	0.130	1.300	0.006	13.800	12.100	4.900	0.029	<0.00001	0.0002	11.800	1.090	0.003	7.680
14	0.019	0.009	<0.001	0.112	0.580	1.210	0.006	13.900	12.300	4.750	0.031	<0.00001	0.0002	12.200	1.130	0.004	7.900
15	0.019	0.009	<0.001	0.106	0.580	1.190	0.006	14.000	12.000	4.670	0.031	<0.00001	0.0001	12.200	1.110	0.004	7.790
WR pile																	
16	0.030	0.002	<0.001	1.020	0.241	0.989	0.004	14.100	5.790	3.440	0.032	<0.00001	0.085	11.200	0.649	0.005	8.070
17	0.033	0.010	<0.001	0.980	0.847	0.845	0.003	13.500	7.510	2.680	0.031	<0.00001	0.106	10.800	0.436	0.008	7.940
18	0.047	0.015	<0.001	1.910	0.522	0.906	0.004	13.600	11.000	2.730	0.047	<0.00001	0.564	14.400	0.468	0.020	12.400
26	0.032	0.009	<0.001	0.970	1.840	0.989	0.004	8.390	7.950	3.210	0.038	<0.00001	0.191	13.600	0.620	0.007	8.940
PW1-0	0.035	0.014	<0.001	1.150	0.003	0.082	0.000	10.000	0.002	0.000	0.010	<0.00001	0.020	0.012	0.000	0.001	11.3000
Wetland																	
19	0.000	<0.00002	<0.001	0.002	0.038	0.267	0.001	12.900	0.018	1.660	0.001	<0.00001	0.0001	5.300	0.190	<0.0001	0.233
20	0.003	<0.00002	<0.001	0.004	<0.0002	1.070	0.004	13.100	0.001	4.010	0.004	<0.00001	<0.00005	11.500	0.814	0.000	1.620
21	0.005	0.000	<0.001	0.023	<0.0002	1.150	0.004	8.730	0.822	4.280	0.010	<0.00001	0.0007	12.400	0.873	0.001	2.560
22	0.000	<0.00002	<0.001	<0.0005	<0.0002	0.372	0.001	8.330	0.000	1.090	<0.0004	<0.00001	<0.00005	4.000	0.049	<0.0001	0.048
23	0.000	0.001	<0.001	0.001	3.150	1.340	0.000	8.360	1.290	5.610	0.003	<0.00001	0.0004	8.000	0.420	<0.0001	0.055
24	0.005	0.001	<0.001	0.007	0.052	13.000	0.001	8.370	4.570	3.500	0.012	<0.00001	0.0011	8.700	0.611	0.000	1.760
25	<0.00002	0.000	<0.001	<0.0005	<0.0002	<0.00003	0.001	8.460	<0.0001	0.100	<0.0004	<0.00001	<0.00005	<0.2	<0.0005	<0.0001	0.001
PW2-0	0.003	0.000	<0.001	0.029	0.000	0.002	0.000	0.013	0.002	0.000	0.010	<0.00001	0.0003	0.000	0.000	0.001	1.610
PW3-0	0.002	0.000	<0.001	0.005	0.000	0.000	0.000	0.001	0.002	0.000	0.010	<0.00001	0.0000	0.000	0.000	<0.0001	0.946

nm = not measured; nd = non detected, 2σ = 2 sigma deviation calculated from "n" replicates; "Rep" = column chemistry replicates (included in the total number of analysis "n").

Table 1. (Continued on the next page) Filtered samples (0.45µm), field parameters (altitude, water T, pH, conductivity, DO, Fe(II)), and chemical results for anions, cations.

	Depth m.	pH	DO mg/L	Fe(II) mg/L	SO_4 mg/L	Al mg/L	As mg/L	Ba mg/L	Ca mg/L	Cd mg/L	Co mg/L	Cr mg/L	Cu mg/L
Pore Waters													
PW1-5	0.05	3.98	nm	>10	200	4.790	<0.001	0.023	44.700	0.045	0.014	<0.001	1.770
PW1-10	0.1	5.59	nm	>10	244	1.590	0.002	0.025	40.700	0.016	0.017	<0.001	0.051
PW1-15	0.15	4.7	nm	>10	190	4.630	0.003	0.024	44.200	0.012	0.014	<0.001	0.024
PW1-20	0.2	6.75	nm	>10	306	0.134	0.004	0.015	79.900	0.000	0.040	<0.001	0.002
PW1-25	0.25	6.91	nm	>10	317	0.018	<0.001	0.015	86.000	<0.00002	0.011	<0.001	0.001
PW1-30	0.3	6.62	nm	>10	263	0.365	0.003	0.020	65.900	<0.00002	0.014	<0.001	0.001
PW1-40	0.4	7.09	nm	>10	326	0.118	<0.001	0.018	74.200	<0.00002	0.000	<0.001	0.001
PW1-50	0.5	6.48	nm	>10	345	0.146	<0.001	0.019	94.200	<0.00002	0.000	<0.001	0.001
PW2-5	0.05	6.48	3.9	nd	212	0.070	<0.001	0.009	69.000	0.003	<0.00002	<0.001	0.031
PW2-10	0.1	6.42	5.3	nd	218	0.086	<0.001	0.010	71.700	0.004	<0.00002	<0.001	0.027
PW2-15	0.15	6.16	1.2	nd	223	0.097	<0.001	0.013	69.700	0.004	0.000	<0.001	0.030
PW2-20a	0.2	6.09	1.8	nd	222	0.075	<0.001	0.009	71.000	0.003	0.000	<0.001	0.017
PW2-20b	0.2	6.19	1.8	nd	219	0.065	<0.001	0.004	72.600	0.002	0.000	<0.001	0.014
PW2-25	0.25	6.18	1.2	nd	226	0.057	<0.001	0.004	68.300	0.003	0.000	<0.001	0.017
PW2-30	0.3	6.2	1	nd	225	0.104	<0.001	0.009	66.600	0.001	0.004	<0.001	0.040
PW2-40	0.4	6.16	0.9	nd	220	0.128	<0.001	0.006	65.600	0.002	0.001	<0.001	0.017
PW2-50	0.5	6.09	1.1	nd	219	0.295	<0.001	0.013	67.100	0.003	0.000	<0.001	0.012
PW2-60	0.6	6.04	0.9	nd	212	0.312	<0.001	0.015	69.900	0.004	0.000	<0.001	0.014
PW3-5	0.05	6.05	3.2	nd	126	0.075	<0.001	0.017	43.500	0.003	<0.00002	<0.001	0.004
PW3-10	0.1	6.01	2.6	nd	135	0.086	<0.001	0.018	42.100	0.002	<0.00002	<0.001	0.007
PW3-15	0.15	6.03	2.8	nd	139	0.062	<0.001	0.018	45.900	0.002	<0.00002	<0.001	0.005
PW3-25	0.25	6.15	2.7	1	136	0.036	<0.001	0.023	45.700	0.002	0.003	<0.001	0.007
PW3-30	0.3	6.29	1.55	7.5	113	0.036	<0.001	0.021	40.900	0.000	0.000	<0.001	0.003
PW3-40	0.4	6.17	1.1	1.5	78	0.098	<0.001	0.024	36.900	0.000	0.000	<0.001	0.001
PW3-50	0.5	6.16	1.2	0.6	46	0.111	<0.001	0.017	30.800	0.000	0.000	<0.001	0.001

nm = not measured; nd = non detected, 2σ = 2 sigma deviation calculated from "n" replicates; "Rep" = column chemistry replicates (included in the total number of analysis "n")

Table 1. (Continued) Filtered samples (0.45µm), field parameters (altitude, water T, pH, conductivity, DO, Fe(II)), and chemical results for anions, cations.

	Fe mg/L	K mg/L	Li mg/L	Mg mg/L	Mn mg/L	Na mg/L	Ni mg/L	P mg/L	Pb mg/L	SiO_2 mg/L	Sr mg/L	U mg/L	Zn mg/L
Pore Waters													
PW1-5	10.000	1.110	0.005	6.310	10.400	2.760	0.045	<0.01	2.400	14.900	0.506	0.012	11.200
PW1-10	60.600	5.420	0.005	0.013	10.000	2.830	0.061	<0.01	0.590	18.000	0.510	0.002	11.300
PW1-15	10.500	1.460	0.004	0.014	10.300	2.720	0.052	<0.01	0.786	15.300	0.487	0.002	12.100
PW1-20	47.800	2.550	0.010	0.028	25.700	3.020	0.069	<0.01	0.005	18.200	0.884	0.003	8.090
PW1-25	55.100	2.560	0.007	0.032	26.200	3.200	0.002	<0.01	0.000	17.800	0.903	0.003	0.248
PW1-30	33.700	2.040	0.008	0.022	20.500	2.990	0.028	<0.01	0.001	19.400	0.714	0.001	4.630
PW1-40	59.000	1.980	0.005	0.032	25.900	6.420	0.000	0.010	0.000	18.400	0.787	0.001	0.015
PW1-50	52.700	2.300	0.002	0.031	8.830	4.130	0.000	<0.01	0.000	13.200	1.070	<0.0001	0.018
PW2-5	<0.02	1.010	0.002	0.014	0.027	3.730	0.005	<0.01	0.000	12.000	0.788	0.001	1.720
PW2-10	<0.02	1.690	0.002	0.014	0.028	3.820	0.007	<0.01	0.001	12.200	0.791	0.000	1.800
PW2-15	<0.02	0.847	0.002	0.014	0.255	4.100	0.006	<0.01	0.001	13.200	0.786	0.000	2.460
PW2-20a	<0.02	1.180	0.002	0.014	0.351	4.120	0.005	<0.01	0.001	13.300	0.841	0.000	2.360
PW2-20b	<0.02	0.994	0.002	0.014	0.188	4.090	0.003	<0.01	0.000	13.800	0.867	0.000	1.400
PW2-25	<0.02	1.030	0.002	0.014	0.651	4.080	0.004	0.010	0.000	14.500	0.877	0.000	1.750
PW2-30	<0.02	1.320	0.003	0.014	4.770	4.060	0.005	0.010	0.002	15.500	0.805	0.001	0.834
PW2-40	<0.02	0.959	0.002	0.014	4.230	4.100	0.004	0.020	0.001	17.000	0.798	0.001	0.351
PW2-50	<0.02	0.937	0.001	0.013	3.210	3.790	0.007	0.020	0.000	16.900	0.789	0.000	0.429
PW2-60	<0.02	0.996	0.003	0.013	2.310	3.900	0.006	<0.01	<0.00005	12.200	0.798	0.000	0.464
PW3-5	<0.02	0.765	0.001	0.008	0.004	3.220	0.004	0.010	0.001	9.000	0.497	0.000	0.900
PW3-10	<0.02	0.631	0.001	0.008	0.004	3.110	0.004	0.010	0.003	9.800	0.532	<0.0001	0.902
PW3-15	0.051	0.658	0.001	0.008	0.016	3.160	0.004	0.010	0.002	10.100	0.553	<0.0001	0.869
PW3-25	0.880	0.930	0.001	0.008	1.250	3.230	0.005	<0.01	0.007	10.300	0.543	<0.0001	0.619
PW3-30	5.830	0.916	0.001	0.008	0.264	3.130	0.002	0.010	0.018	11.000	0.516	0.000	0.060
PW3-40	1.150	0.855	0.000	0.008	0.268	3.140	0.001	0.020	0.002	11.900	0.437	0.000	0.006
PW3-50	0.454	0.829	0.000	0.006	0.264	2.990	0.001	0.020	0.001	11.600	0.367	0.000	0.007

nm = not measured; nd = non detected, 2σ = 2 sigma deviation calculated from "n" replicates; "Rep" = column chemistry replicates (included in the total number of analysis "n").

Table 2. Ion concentrations for raw unfiltered and filtered (0.1µm) samples.

	Cu mg/L	Fe mg/L	Zn mg/L
Raw samples			
1	0.139	0.838	7.580
2	0.146	0.881	7.110
3	0.153	1.090	7.250
4	0.156	0.872	7.350
5	0.161	0.936	7.360
6	0.162	0.885	7.380
7	0.161	0.886	7.300
8	0.225	1.720	7.410
9	0.162	0.952	7.530
10	0.165	1.100	7.690
11	0.185	1.560	7.620
12	0.662	12.700	7.840
13	0.204	1.920	7.730
14	0.189	3.470	7.680
15	0.157	0.953	7.700
16	1.030	1.850	7.890
17	1.050	4.460	7.900
18	1.990	1.390	12.100
19	0.002	0.079	0.242
20	0.004	<0.005	1.700
21	0.033	0.173	2.660
22	0.001	<0.005	0.047
23	0.003	2.390	0.070
24	nm	nm	nm
25	<0.0005	<0.005	0.001
26	1.000	2.430	8.730
PW1-0	1210.000	2.480	11.500
PW2-0	33.600	<0.005	1.670
PW3-0	6.500	<0.005	0.988

nm = non measure

	Cu mg/L	Fe mg/L	Zn mg/L
0.1µm filtered samples			
1	0.0927	0.0255	7.030
2	0.0448	0.0324	7.350
3	0.0639	0.0433	7.400
4	0.0712	0.0493	7.310
5	0.117	0.0557	7.560
6	0.0846	0.0561	7.600
7	0.0833	0.062	7.590
8	0.125	0.0631	7.760
9	0.0923	0.0776	7.230
10	0.091	0.0611	7.460
11	0.0841	0.0453	7.330
12	nm	nm	nm
13	0.092	0.0679	7.780
14	nm	nm	7.900
15	0.123	0.0576	nm
16	1.060	0.225	8.580
17	1.060	0.822	8.260
18	2.080	0.488	12.700
19	0.003	0.0339	0.244
20	0.004	<0.05	1.660
21	0.025	<0.05	2.620
22	<0.005	<0.05	0.045
23	nm	nm	nm
24	nm	nm	nm
25	<0.005	<0.05	<0.005
26	1.040	1.84	8.990
PW1_0	1.260	1.47	11.500
PW2_0	0.029	<0.05	1.690
PW3_0	0.005	<0.05	1.040

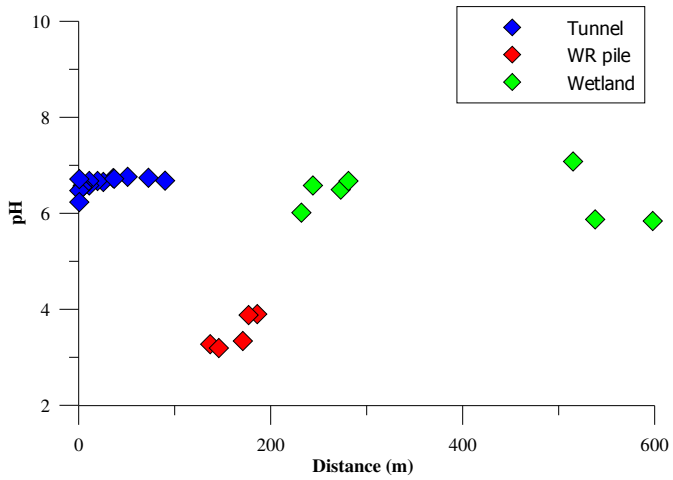

Figure 7. Changes in pH of water collected from Tunnel, Waste Rock Pile and Wetland as a function of distance. Figure 5 shows how the distance was calculated.

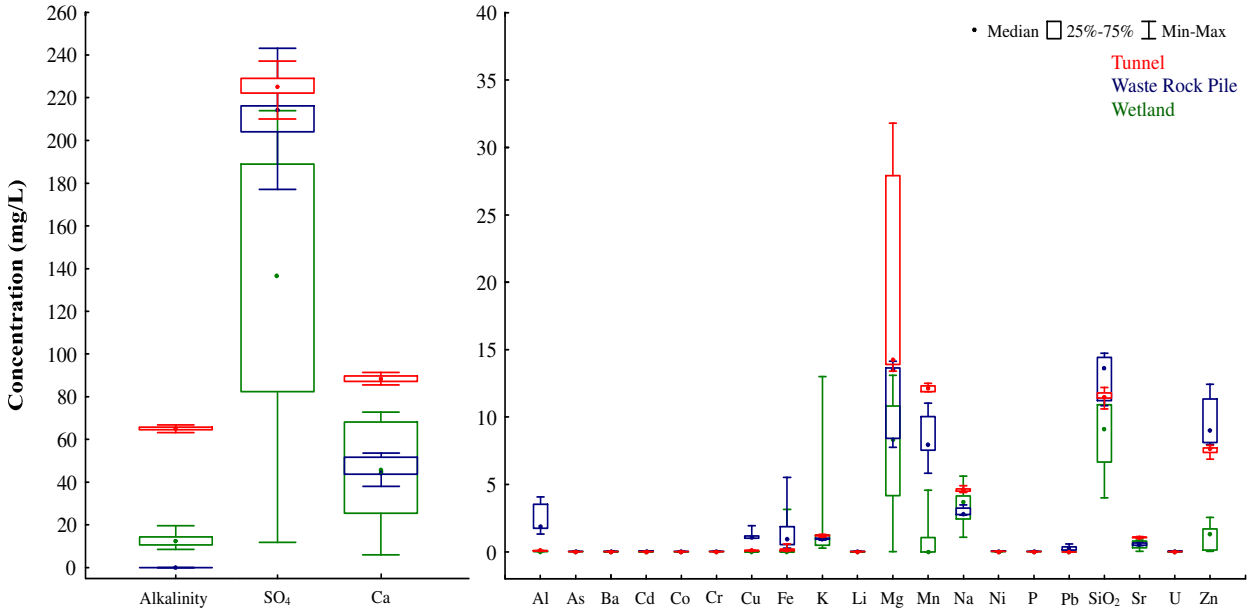

Figure 8. Ion concentration for waters from the Tunnel, Waste Rock Pile and Wetland in the vicinity of the Waldorf Mine.

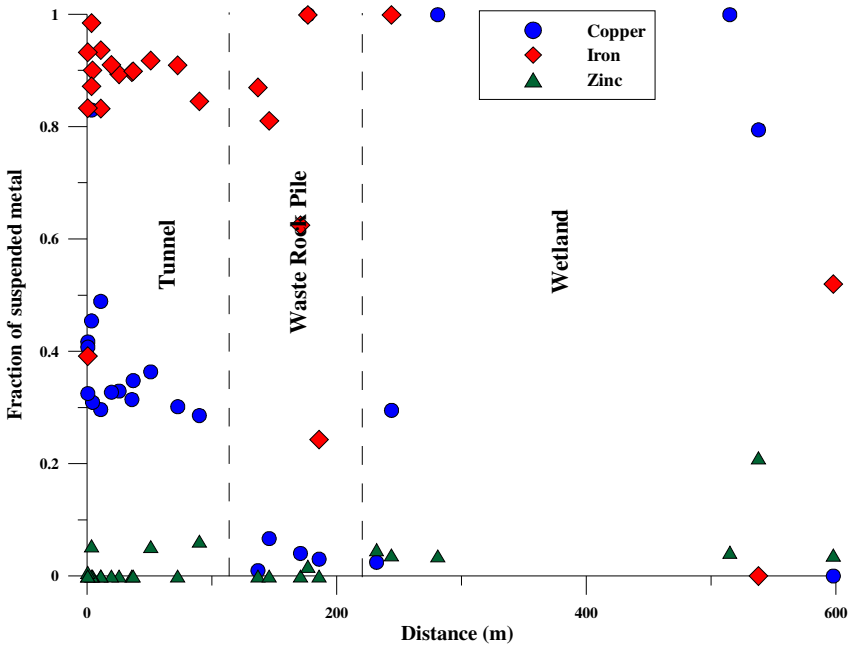

Figure 9. Raw and dissolved sample concentration in the mining area.

5.2.1 Copper and Zinc Concentrations

The concentrations of dissolved Cu and Zn in the water from the tunnel are presented in Figure 9 and ranged from 0.097 mg/L to 0.119 mg/L (Fig. 10a) and 6.870 mg/L to 7.900 mg/L (Fig. 10b), respectively. Cu showed only a small variation in concentration with distance from the tunnel entrance (Fig. 10a), but Zn concentrations decreased measurably with increasing distance from the tunnel (Fig. 10b). Cu and Zn concentrations were greatest in the samples collected from seeps at the edge of the waste rock apron, ranging from 0.970 mg/L to 1.910 mg/L (Fig. 10a) and 7.940 mg/L to 12.40 mg/L (Fig. 11b), respectively. The elevated concentrations of Cu in seeps along the waste apron abruptly ended in the nearby wetlands where

Cu was not detected (<2µg/L) in most samples (Fig. 11a). Conversely, concentrations of Zn in the wetland area remained elevated, gradually decreasing with distance (Fig. 11b).

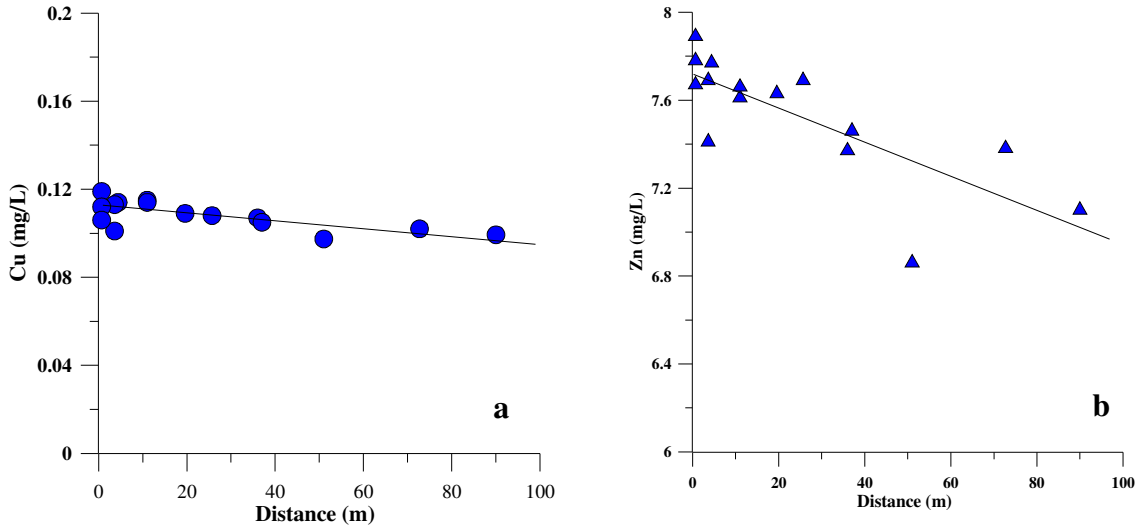

Figure 10. Copper (a) and zinc (b) concentrations as a function of distance from the Tunnel entrance. Best-fit trend lines are also despicted from illustration purposes.

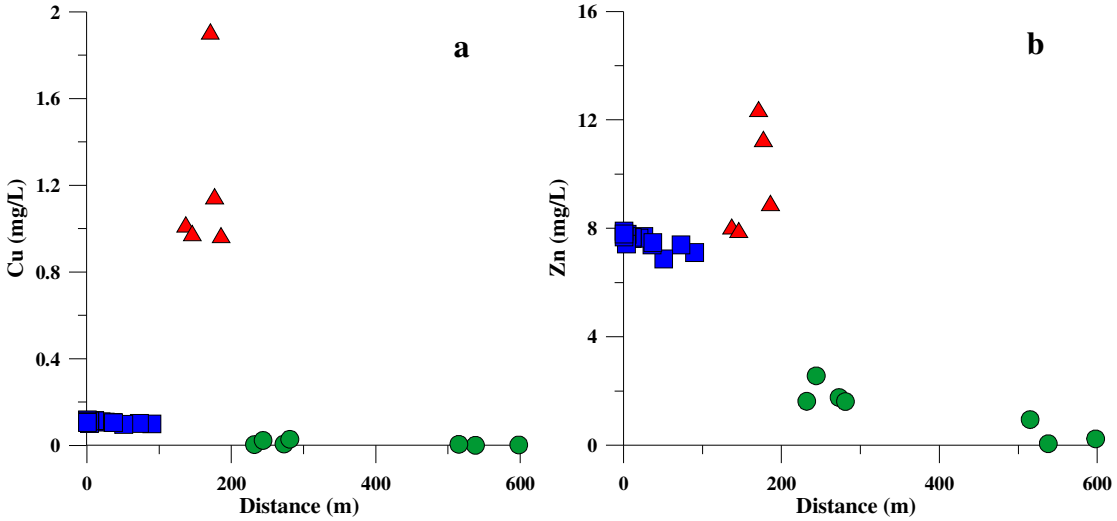

Figure 11. Copper (a) and zinc (b) concentrations of samples from the Tunnel (blue squares), Waste Rock Pile (red triangles) and wetland (Green circles).

5.3. Pore Water Chemistry.

The distributions of dissolved major and trace element concentrations for the pore water samples (see location map in Figure 2) are presented in Figure 12, and a complete summary of these data are provided in Table 1. Similar to the waters associated with the tunnel, pore waters in the wetland contained elevated concentrations of Ca, Mn, and SO_4. However, the concentrations of Mg the pore waters were small relative to those from the tunnel. The pore water samples collected closest to the waste rock pile (location 1, Figure 2) contained much higher concentrations of metals, including Al, Fe, Mn, Si, and Zn, than the pore waters collected further from the waste pile (Fig. 12).

The pH and concentrations of DO, Cu, Zn, Fe(II), and SO_4 in pore waters are plotted as a function of depth in Figure 13. The pH of the pore waters from location 1 increased from pH 3.9 to about 7 as a function of depth. However, the pH of the pore waters from locations 2 and 3 were relatively invariant as a function of depth, starting at a pH 7 near the ground surface and shifting to pH ≈ 6 with depth. The concentrations of Zn and Cu in pore waters from location 1 decreased as a function of depth. The concentration of Cu was below detection (<0.03 mg/L) in samples collected below 0.15 m depth, while Zn was below detection (<0.02 mg/L) in samples collected below 0.4 m. The concentrations of Cu in pore waters from locations 2 and 3 were small and relatively invariant as a function of depth (Fig. 13). The concentrations of Zn were higher (ranging up to 2 mg/L near the surface) before decreasing substantially with increasing depth (Figure 13).

The sulfate concentrations of the pore waters from location 1 increased from about 200 mg/L to 345 mg/L as a function of depth. However, the sulfate concentrations of the pore waters

from location 2 were relatively invariant as a function of depth, ranging from 212 to 226 mg/L. Sulfate in the pore waters from location 3 decreased from about 139 mg/L at 0.15 m depth to 46 mg/L at 0.5 m depth. The concentrations of Fe in pore waters from location 1 varied as a function of depth from 5.5 mg/L to 60.6 mg/L. Iron concentrations in location 2 were quite low (< than the 20 µg/L detection limit). Iron concentrations in location 3 were below the detection limit (<20 µg/L) until a rapid increase to 7.5 mg/L around 0.3 m depth followed by a sharp decrease back to low concentrations by 0.5 m depth. Dissolved oxygen was not measured for location 1. The concentration of DO in location 2 decreased from about 5 mg/L near the surface to 1.2 mg/L at 0.15 m depth and below (Figure 13). Dissolved oxygen in location 3 started at ~3.2 mg/L near the surface and decreased to ~2.7 mg/L below a depth of 0.25 m. Moreover, in samples collected at and below 0.4 m depth in location 3, the reduction of SO_4 to H_2S gas was suggested by the "rotten egg" odor of gas in the head space of these samples.

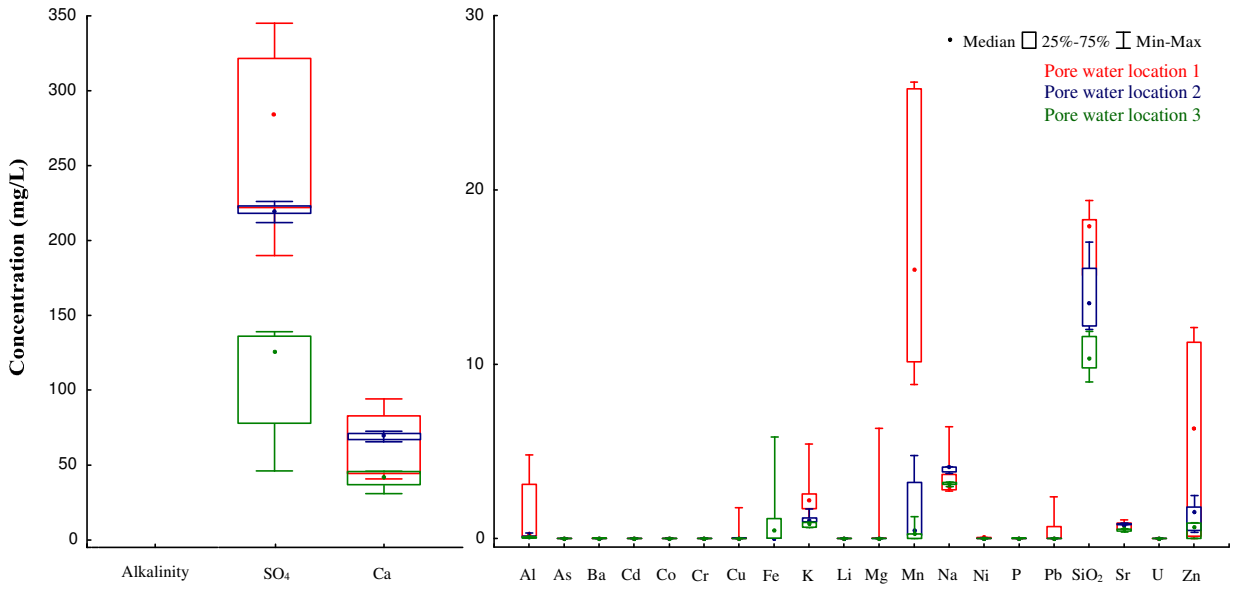

Figure 12. Ion concentration for Pore waters at location 1, 2 and 3 at the Waldorf mine. Alkalinity was not measured for Pore water samples.

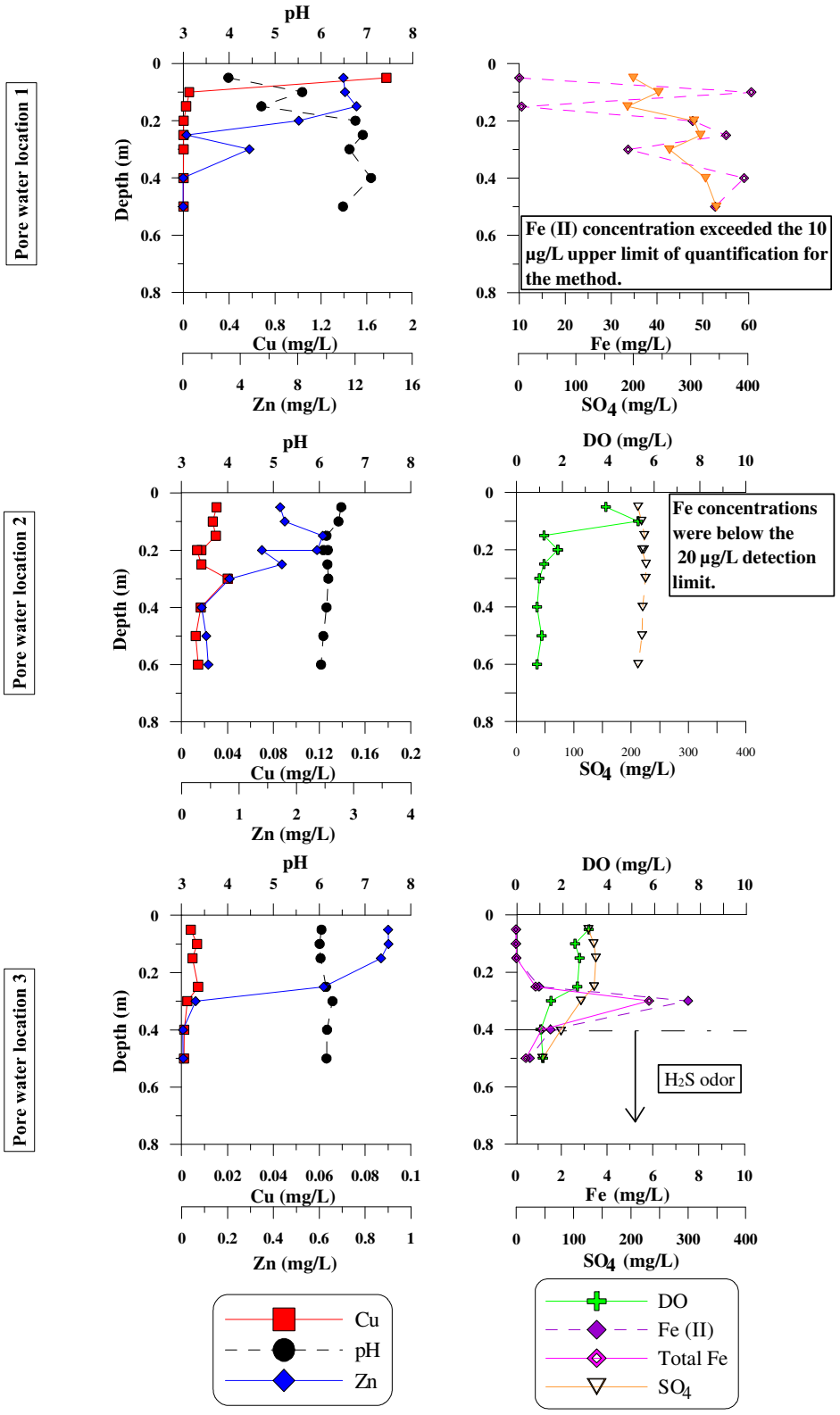

Figure 13. pH and concentrations of Cu, Zn, DO, Fe(II), and SO_4 as a function of depth in pore water samples collected from three locations at the Waldorf site.

5.4. Major Elements in the Water.

Water collected from the Tunnel, Waste Rock Pile and the Pore waters are plotted as a function of their major element chemistries in the Piper diagram illustrated in Figure 13. For comparison, we have also included in the gray shaded regions, the chemistry of water samples collected in the Tunnel and piezometers within the Waste Rock Pile by Malem (2006). All the water samples are characterized by their high sulfate and calcium concentrations, which generally overlap and span a narrow range. Sample 22, collected outside the immediate Waldorf area from a stream draining snowmelt (Figure 2), has a higher alkalinity, magnesium concentration, and a lower sulfate content than all of the samples from the Waldorf site.

5.5. Chemistry of Wetland Soils.

The distributions of major and trace element concentrations for the wetland soil samples collected from 0-40 cm depth from the 3 pore water locations are presented in Figure 14. A complete summary of these data are provided in Table 3. The soil samples contained concentrations of metals like Al, Cu, Fe, Mn, Pb, and Zn that were in great excess of the concentrations of these same elements in the pore water fluids (Figures 12 and 13). For example, the median concentrations of Cu in the soils from locations 1, 2, and 3 were 904.5 mg/kg, 3590 mg/kg, and 6980 mg/kg. Similarly the median concentrations of Zn in the soils from locations 1, 2, and 3 were 3740 mg/kg, 6790 mg/kg, and 3000 mg/kg. The soils also contained tremendous amounts of Fe with median values of 12% and 13% of the total soil sample mass for locations 2 and 3, respectively. Furthermore, the distributions of Cu, Zn, and Fe in the soil samples typically

decreased as a function of sample depth (Figure 16). In location 3, metal concentrations dropped off significantly below 40 cm depth. Samples were not collected substantially below this depth in locations 1 and 2.

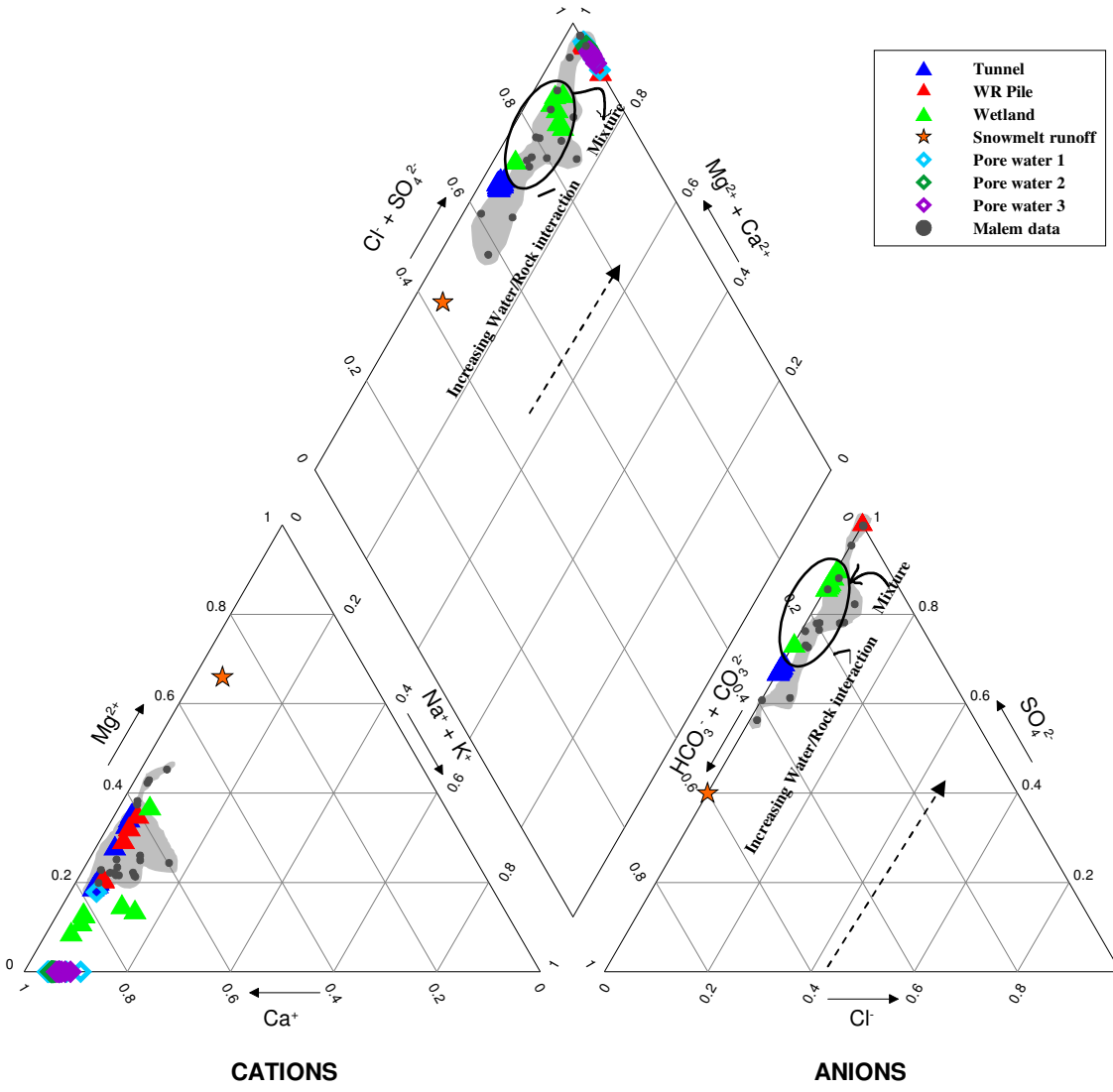

Figure 14. Piper diagram illustrating the distributions of major ions in water samples collected from the Tunnel, Waste Rock Pile and Wetland. The gray region shows the distribution of data from

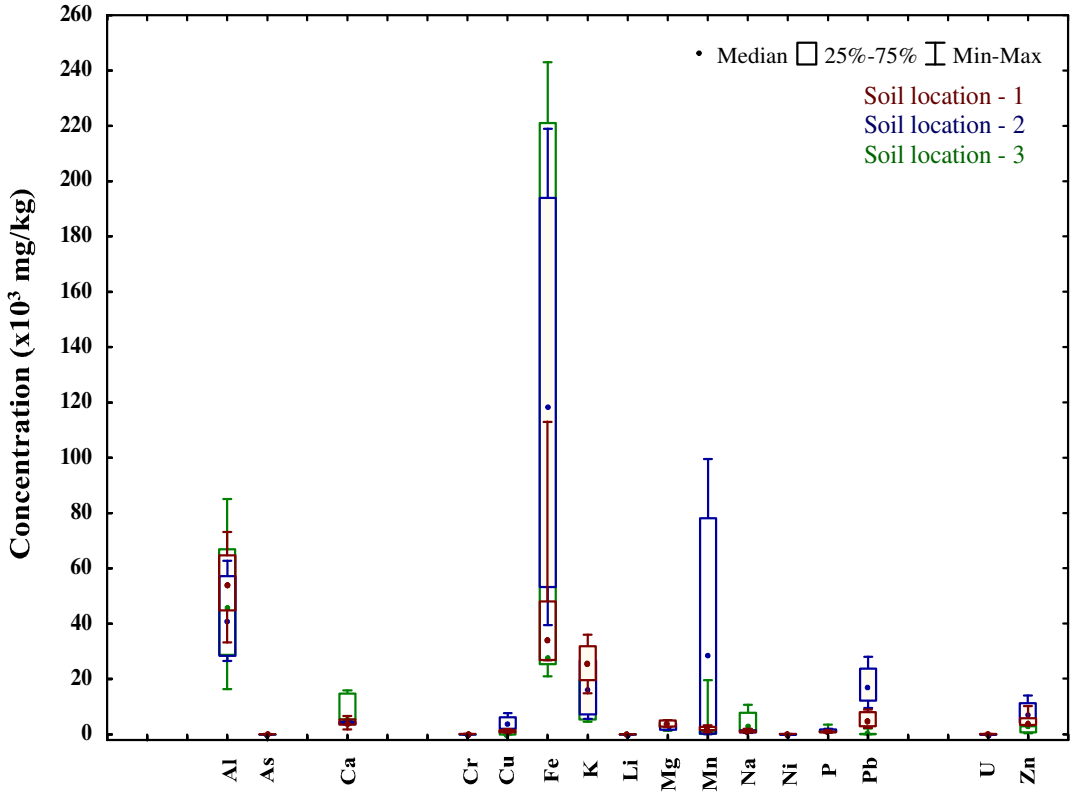

Figure 15. Ion concentrations in soil samples collected from locations 1, 2 and 3.

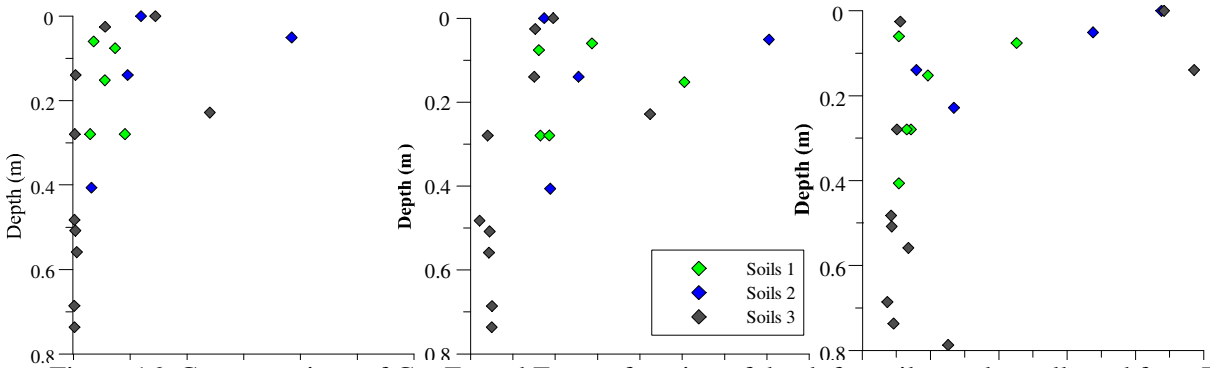

Figure 16. Concentrations of Cu, Zn and Fe as a function of depth for soil samples collected from Pore water sampling locations 1, 2 and 3.

Table 3. Ion concentrations for the soil samples at the locations 1, 2 and 3.

	Depth	Al	As	Ca	Cd	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	U	Zn
	m.	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Soils																		
PW1-a	0.060	33200	12.500	6520	14.200	40.200	709.0	26700	14700	7.400	2470	1470	1280	56.4	766	2290	42.500	5740
PW1-b	0.080	47100	18.100	1670	13.000	55.200	1460.0	113000	22600	11.200	2710	655	782	35.5	920	2850	30.600	3230
PW1-f	0.152	44700	17.600	5270	18.600	53.600	1100.0	48000	19500	9.000	3050	1410	1940	48.8	1330	3240	48.200	10100
PW1-c	0.279	73100	34.100	3470	15.400	79.000	1810.0	35600	36000	15.500	4960	2540	616	31.1	730	8850	16.200	3300
PW1-d	0.279	64600	22.000	4000	21.300	62.400	581.0	32500	31800	14.000	4880	3190	682	38.8	586	6680	11.800	3720
PW1-e	0.406	60100	22.000	4370	23.100	61.400	628.0	26800	28400	12.700	4350	2660	887	54.9	643	7970	8.630	3760
PW2	0.000	30200	22.800	4000	13.000	17.100	2380.0	219000	5740	5.400	1820	600	1070	21.2	876	19600	15.900	3480
PW2-a	0.051	26600	71.500	4720	97.300	56.000	7690.0	169000	8960	3.900	1610	nr	608	112.0	2090	28100	89.600	14100
PW2-b	0.140	62800	22.000	3700	38.900	62.400	1910.0	39600	29600	13.200	4430	56800	1510	41.6	964	9630	72.300	5100
PW2-c	0.229	51600	46.300	4220	61.900	55.200	4800.0	67100	23700	11.200	3540	99600	1650	158.0	1510	14900	79.600	8480
PW3	0.000	45800	19.900	5860	28.000	19.600	2880.0	221000	5400	8.900	1360	19700	733	52.1	987	2170	19.400	3900
PW3-i	0.025	16400	6.800	15900	2.500	18.800	1110.0	27800	4660	6.900	2640	1050	1380	29.5	1480	178	27.600	3050
PW3-g	0.140	28700	7.900	14800	19.200	32.900	69.8	243000	8640	8.900	3270	1210	2950	28.8	3550	179	5.940	3000
PW3-h	0.279	85100	4.000	5220	5.300	87.600	37.2	25400	19600	38.100	5240	216	7840	12.9	950	188	9.400	804
PW3-f	0.483	67000	2.600	5440	4.200	57.100	27.0	21100	24200	20.400	4180	202	10800	16.4	1260	154	9.860	425
PW3-a	0.508	70900	1.900	4910	29.400	62.000	59.3	21500	31200	21.400	6430	496	13500	26.1	933	108	6.250	898
PW3-e	0.559	78100	5.500	4920	1.300	102.000	114.0	33700	29000	28.300	6210	410	9660	31.6	1050	378	47.600	874
PW3-d	0.686	68800	1.700	4410	15.900	52.600	23.2	18400	32800	17.300	5310	292	12100	28.5	809	172	6.300	1010
PW3-c	0.737	69900	1.800	4970	1.600	60.500	27.0	22800	31900	19.600	6000	359	11400	45.2	891	196	10.700	1000
PW3-b	0.787	50900	5.800	5280	16.100	74.600	42.2	62900	28500	11.600	3000	368	8670	42.8	884	140	18.800	2730
MT	0.000	45900	40.600	1220	5.400	40.100	165.0	28900	23600	12.200	2420	322	374	3.4	682	3020	1.210	1040
MT-redox zone	0.152	54400	44.300	1880	3.900	52.900	282.0	42800	26100	13.300	3230	1080	1470	5.6	986	4700	2.230	906

PW = Pore water; MT = Mill Tailings.

5.6. Copper and Zinc Isotopes.

Cu and Zn isotopic data are summarized in Table 1 and are plotted as a function of distance from the Tunnel entrance in Figure 16. The gray bars on these figures represent the range in Cu or Zn isotopic compositions measured for minerals (sphalerite and chalcopyrite collected from the waste rock pile) and mill tailings (i.e., processed minerals) and are summarized in Table 4. Note that the mill tailings contained 224 mg/kg Cu and 973 mg/kg Zn. The δ^{65}Cu of the water samples collected from the tunnel area ranged from +0.87‰ to +1.78‰ (Figure 17a) with the heaviest 2 values (δ^{65}Cu = +1.78‰ and 1.59‰) occurring at a distance of about 17 m from the tunnel entrance. The δ^{66}Zn of the tunnel samples ranged from +0.16‰ to +0.36‰ (Figure 17b) with the heaviest values occurring closest to the tunnel entrance and (on average) slightly decreasing away from the tunnel. The δ^{65}Cu of the mill tailings and chalcopyrite separates ranged from +0.49‰ to +0.55‰ (Figure 17a), which was substantially lighter than the δ^{65}Cu of the water samples. The δ^{66}Zn of the digested sphalerite, and mill tailings samples ranged from +0.31‰ to +0.41‰ (Figures 17b), which overlapped with the δ^{66}Zn of the water samples. The δ^{65}Cu of the water samples collected from the waste rock pile overlapped with those of the tunnel, ranging from +1.13‰to +2.11‰ (Figure 18a). Cu concentrations in most samples from the wetland area were too low for evaluation of Cu isotopes. The δ^{66}Zn of the samples collected from the waste pile and wetland ranged from +0.12‰ to +0.38‰, overlapping with the δ^{66}Zn of samples from the tunnel and Zn ores (Figure 18b). There were no apparent trends relating δ^{65}Cu to Cu concentration (Figure 19). However the concentration of Zn in the water samples from the tunnel appeared to be linearly related to the δ^{66}Zn (Figure 20a); but no

such trend was identified for the waste rock and wetland samples (Figure 20b). Currently, we do not have isotopic data for the pore water samples. This will be presented in a future contribution.

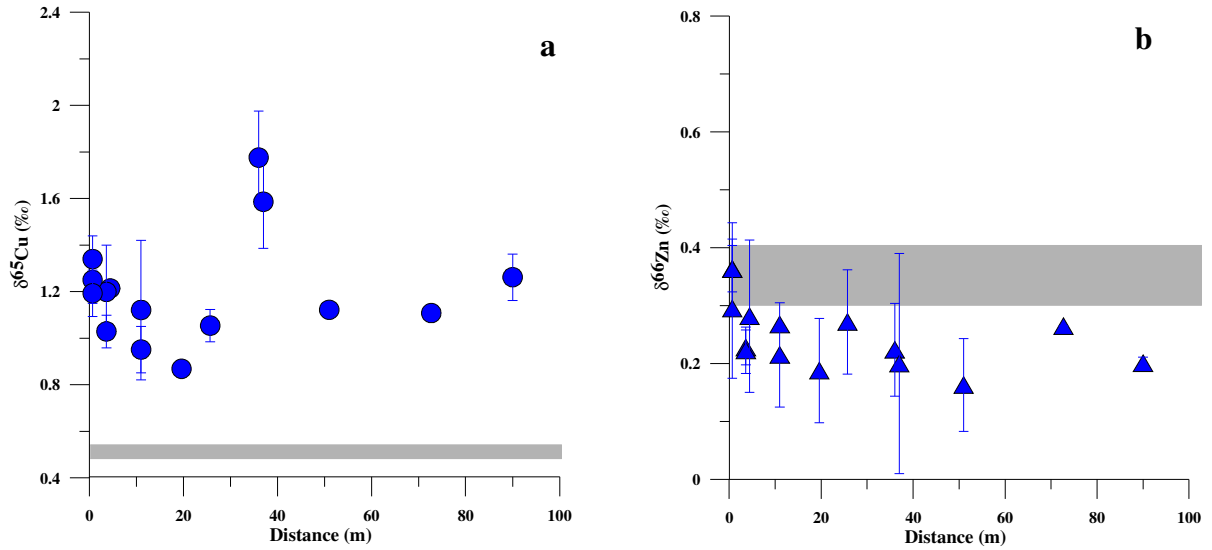

Figure 17. δ^{65}Cu (a) and δ^{66}Zn (b) as a function of distance from the Tunnel entrance. Gray bars represent the measured range of δ^{65}Cu (a) and δ^{66}Zn (b) for ore minerals and mill tailings samples.

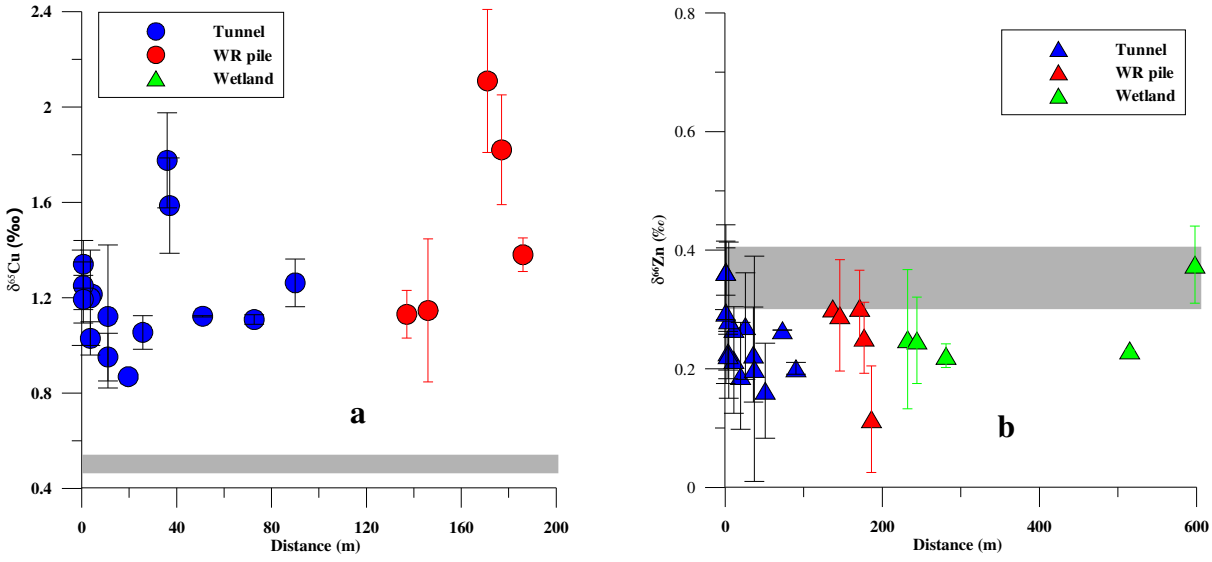

Figure 18. δ^{65}Cu (a) and δ^{66}Zn (b) as a function of distance from the tunnel entrance. Gray bars represent the measured range in δ^{65}Cu (a) and δ^{66}Zn (b) for ore minerals and mill tailings samples.

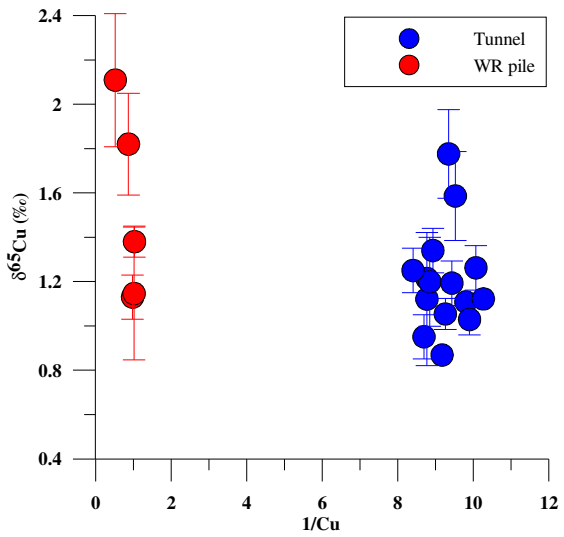

Figure 19 . δ^{65}Cu plotted as a function of Cu concentration. Wetland samples were not measured

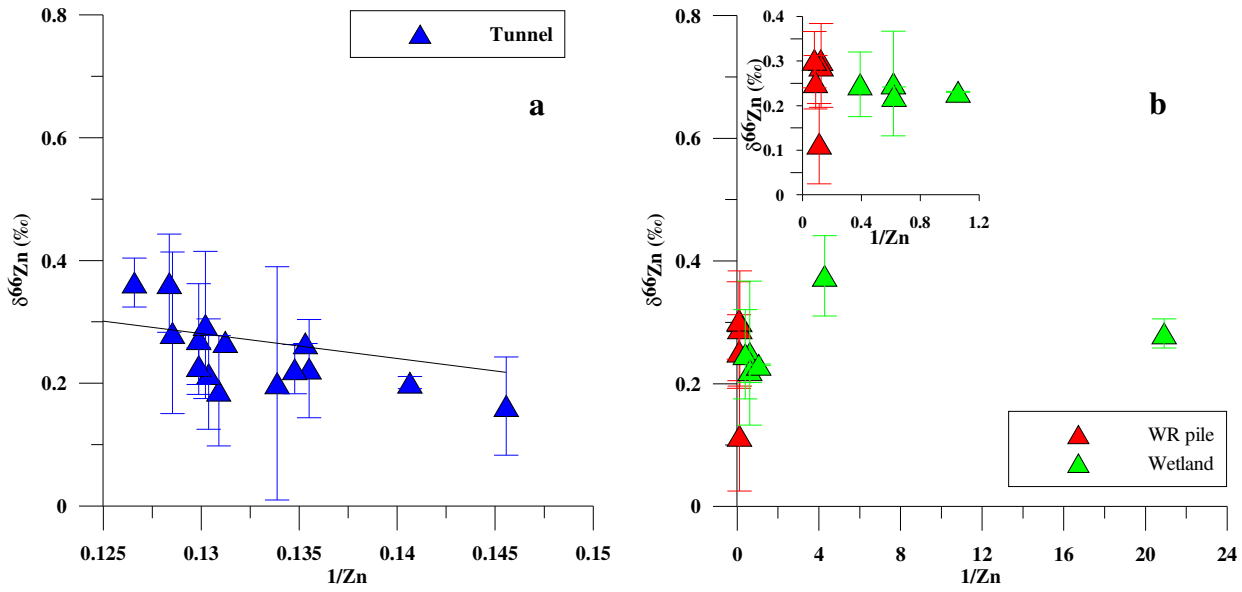

Figure 20. δ^{66}Zn plotted as a function of Zn concentration for the Tunnel (a) and Waste Rock + Wetland (b) samples. The solid line in panel a is the calculated fractionation line assuming an initial δ^{66}Zn = 0.3‰ , a loss of 12% Zn, and the $\Delta^{66}Zn_{solid\text{-}solution}$ separation factor developed by Balistrieri et al. (2008) for Zn adsorption onto Fe(III)-oxides.

Table 4. Ion concentration for dissolved rocks from the Waste Rock Pile and the Mill Tailings.

	$\delta^{65}Cu$	2σ	n	Rep	$\delta^{66}Zn$	2σ	n	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Sr	Zn
	‰				‰			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Rocks																									
MTR	0.493	0	5	3	0.405	0.04	5	398.547	5.357	33.633	379.746	21.395	9.895	<0.008	5812.863	48510.915	378.468	0.192	<0.008	29.572	95.362	16.692	8057.082	4.009	3893.842
$CuFeS_2$	0.555	0.1	4	2	0.497	0.02	2	109.996	181.683	572.628	4159.304	12.985	71.601	<0.008	26314.232	370692.739	33.001	0.440	1109.466	948.744	1.262	14.908	1469.928	11.185	470.130
ZnS	nm	nm	nm	nm	0.309	0.01	4	38.248	<0.008	8.195	13.468	3418.173	1.475	0.376	644.253	16709.315	16.835	0.846	2.535	332.342	<0.008	6.034	20.056	<0.008	492214.451
FeS_2	nm	nm	nm	nm	0.472	nm	1	35.722	<0.008	22.320	367.042	3.893	37.106	3.424	40.646	436161.361	130.386	1.104	<0.008	6.957	12.157	19.662	1438.517	11.570	611.086

MTR = Mill Tailing Rocks.; 2σ = 2 sigma deviation calculated from "n" replicates; "Rep" = column chemistry replicates (included in the total number of analysis "n").

5.7. Factor Analysis.

5.7.1. Surface Waters

Eigenvalues from the statistical analysis of the data matrixes are presented in Table 5. The first five extracted factors account for ~90% of the chemical variation. However, in this case, the first two factors (that account for ~67% of the total chemical variation) are the most relevant factors and the factors most likely to reflect the major processes impacting water chemistry in the abandoned mining area. Hence, we focus on presenting the results of the first 2 factors here, but also evaluate the remaining factors to see if they have any relevance (see discussion section below).

Table 5. Eigenvalues associated with factors and their contribution to the total surface water variance.

Factor #	Eigenvalue	% total Variance	Cumulative Eigenvalue	Cumulative %
1	10.400	39.998	10.400	39.998
2	6.954	26.747	17.354	66.746
3	3.052	11.738	20.406	78.484
4	1.695	6.520	22.101	85.004
5	1.205	4.633	23.306	89.637

A normalized varimax rotation was applied to the factor loadings. This process best-quantifies the positive and negative correlations among the variables and their factors (Table 6). A perfect positive correlatioon is 1 and a perfect negative correlation is -1. Hence, factor loading values (correlations) closest to -1 and +1 are chosen for further interpretation while the others are eliminated from consideration. For the interpretation, any level of correlation can be chosen, from -0.4 to -1 and +0.4 to +1 for exploratory purposes (Floyd et al., 1995). However, cutoff

values are most often chosen within the ranges of -0.5 to -1 and +0.5 to +1 (Woocay, 2006) and sometimes -0.6 to -1 or +0.6 to +1 (Szynkiewicz, in press). In this study we chose the more stringent cutoff of -0.6 to -1 and +0.6 and +1. These values are highlighted in red within Table 6.

Table 6. (Varimax) Rotated factor loadings for water samples from the Tunnel, the Waste Rock Pile and the Wetland. The factor loadings (numbers) represent the correlation between each variable (first column), and each factor. The red colored factor loadings indicate a high positive or high negative association of the variable within the group of variables that comprise the factor.

	Factor 1	Factor 2
pH	0.224	-0.850
Cond	0.887	0.224
DO	-0.658	-0.061
Fe(II)	-0.102	0.136
$CaCO_3$	0.813	-0.482
SO_4	0.809	0.186
Al	-0.128	0.897
Ba	-0.225	0.127
Ca	0.815	-0.373
Cd	0.433	0.848
Co	0.688	0.506
Cu	-0.057	0.969
Fe	-0.117	0.137
K	-0.057	-0.111
Li	0.933	0.016
Mg	0.680	-0.060
Mn	0.926	0.084
Na	0.746	-0.261
Ni	0.757	0.542
P	-0.121	0.163
Pb	-0.045	0.925
Rb	0.755	0.274
SiO_2	0.739	0.236
Sr	0.906	-0.260
U	0.275	0.894
Zn	0.700	0.606

CHAPTER 6

DISCUSSIONS

6.1. Evolution of water Chemistry at the Waldorf Site.

The bulk chemistry of fluids collected from all the sampling sites at Waldorf appears to span a limited concentration range, making it difficult to distinguish individual sources. Major elements like SO_4, Ca, and Mg that are found in elevated concentrations in the Tunnel are also elevated in concentration in samples collected from the waste rock pile and wetland. The similarities in major element chemistry are best illustrated in the piper diagram (Fig. 14). It is clear in this diagram that the chemistries of samples from the tunnel, waste rock pile, and wetland span a limited range with the samples collected from the Tunnel and Waste Rock Pile representing end member compositions in plots associated with Cl, SO_4, and alkalinity (the Mg vs. Ca vs. Na+K ternary plot does not effectively separate the chemistries). Moreover, the chemical data for water collected by Malem (2006) from the tunnel and piezometers within the waste rock pile plot in the same field as our samples. This suggests that the bulk water chemistry throughout the Waldorf site is not only similar, but hasn't changed at all over the 10 year gap between sampling events (Malem's samples were collected in 1999 and ours in 2008 and 2009). The spatial and temporal sameness of the fluid compositions at Waldorf are probably best explained conceptually by the impact of differing degrees of weathering (i.e., water/rock interaction) of rocks/minerals that are broadly similar in composition and the mixing of fluids

from different weathering/flow pathways. In this scenario the chemistry of the water is mainly controlled by the contact time (e.g., flow pathways) and weathering regimes (e.g., anaerobic, vs. aerobic conditions). Here the sample of water from the rapidly flowing snow-melt runoff would represent water chemistry impacted by only a small degree of chemical weathering (Figure 14), while the samples from the Tunnel represent a higher degree of weathering and samples from the Waste Rock Pile reflect the strongest degree of weathering. Samples collected in the Wetland likely represent mixing between the Tunnel and Waste Rock Pile end member compositions (Figure 14). The chemistries of the pore water samples tend to cluster with those from the Waste Rock Pile, indicating high SO_4 and low alkalinity conditions. Unlike the major element chemistry, trace metal concentrations of the fluids within the Waldorf system are highly variable. This variability is best explained by secondary precipitation and adsorption reactions controlled by the pH and DO contents of the fluids.

6.2. Tunnel.

Water collected from the tunnel entrance and the associated water diverted around the waste rock pile is characterized by its circumneutral pH and high alkalinity. We speculate that the water rock reaction pathway that controls this fluid composition likely involves a combination of sulfide weathering and buffering of the sulfide weathering products to higher pH with carbonate minerals. The degree of initial sulfide weathering is likely controlled by the available DO concentrations in the fluid. Oxygen is necessary either as the direct electron acceptor (Eq. 4), where pyrite is oxidized to form sulfuric acid, or as the indirect electron acceptor for the transformation of Fe(II) to Fe(III) (Eq. 5). Fe(III) can also act as an electron acceptor for sulfide weathering (Eq. 6).

Eq. 4 $FeS_{2(s)} + 3.5O_2 + H_2O$ ---- $Fe^{2+} + 2SO_4^{2-} + 2H^+$

Eq. 5 $Fe^{2+} + 0.25O_2 + H^+$ ---------- $Fe^{+3} + 0.5H_2O$

Eq. 6 $FeS_{2(s)} + 14Fe^{3+} + 8H_2O$ --------- $15Fe^{2+} + 2SO_4^{2-} + 16H^+$

Available DO in the tunnel is likely limited so the reaction (either Eq. 4 or 5) cannot go to completion. The presence of carbonate minerals within the tunnel is supported by the high alkalinity of the fluids (even higher than the higher-pH background sample collected from snow-melt runoff adjacent to the site), and the abundance of Ca, Mg, and Mn. Lovering (1935) lists rhodochrosite ($MnCO_3$) and calcite ($CaCO_3$) among the important gangue minerals mapped within the Waldorf Mine. Factor 1 of the statistical analysis (Tables 6) fits this interpretation. In factor 1 the alkalinity is correlated with low DO and high Ca, Co, Mg, Rb, Sr, and Mn. The Ca and Mg are major weathering products of carbonate minerals, while Sr, Rb, Co and Mn are hosted in important accessory phases in carbonates and in some cases can be present as their own mineral phases (i.e., rhodochrosite). The correlation with other elements like Li, Na, and SiO_2 is likely attributable to primary silicate weathering reactions. Finally, the additions of Zn and SO_4 are an indication that sulfide weathering did occur, but was buffered by the carbonate phases. The validity of the factor analysis interpretation is supported by direct comparison to the element phases that are most abundant in the tunnel water. Here, alkalinity, SO_4, Ca, Mg, Mn, Na, and Li are more abundant in the tunnel samples than in the waste rock pile or wetland (Figure 8).

Dissolved Fe in the tunnel waters was present as Fe(II), demonstrating that the waters were anoxic as they exited the tunnel. Once the Fe(II) was exposed to oxygen outside the tunnel, Fe(III)-hydroxides were rapidly formed. In addition to the visible Fe(III)-precipitates lining the

stream channel, evidence of Fe precipitation includes the vast difference in concentrations of unfiltered and filtered Fe (Figure 8). The concentration of Fe in the unfiltered samples was orders of magnitude higher than the dissolved concentration because the unfiltered samples included freshly-precipitated Fe(III)-mineral phases. It is clear that significant amounts of Cu were adsorbed to these particles (Fig. 10a), and only small concentrations of dissolved Cu remained (less than 120 µg/L). Moreover, Cu, like Pb and Al, is relatively insoluble at pH values around 6.5. Hence, the precipitation of Cu-oxyhydroxide phases may have additionally limited Cu concentrations in the tunnel waters. Conversely, Zn concentrations in the tunnel waters were high (largely between 7 and 8 mg/L). Zn remains soluble at pH 6.5 and our samples indicate that it was only weakly impacted by adsorption to the Fe(III)-precipitates (Fig. 11a).

6.3. Waste Rock Pile.

Water collected from the waste rock pile is characterized by its low pH and high metal concentrations. The water rock reaction pathway that controls this fluid composition likely involves sulfide weathering in the presence of abundant DO. The availability of DO and the apparent lack of carbonate minerals in the waste dump to neutralize acid, allows for the sulfide weathering reaction to progress, producing acid and solubilizing metals (e.g., Eq. 4 and 6). The apparent lack of carbonate minerals in the waste dump may actually be the result of long-term acid production simply out-weighing the long-term buffering capacity of the rock, resulting in complete dissolution of all carbonate minerals. Factor 2 of the statistical analysis (Table 6) fits this interpretation. We interpret factor 2 as an ARD signature. In factor 2 low pH's are correlated with high Al, Cd, Cu, U, and Zn concentrations. The low pH is produced from

aggressive sulfide weathering and the elements that were insoluble at neural pH like Al, Pb, and Cu become solubilized under these acidic conditions. The aggressive weathering also solubilizes more Zn and some U. The lack of a significant correlation with Fe and SO_4 in Factor 2 is likely caused by the precipitation of secondary Fe(III)-sulfate minerals like jarosite ($KFe_3(OH)_6(SO_4)_2$), which was identified by Malem (2006) as precipitating within the Waste Rock Pile. The raw vs. filtered samples (Figure 9) shows that only modest adsorption of Zn or Cu is occurring under the low pH conditions, but Fe(III)-minerals are still precipitating to a large extent.

The flow pathways for springs and seeps exiting at the toe of the waste rock pile were discussed previously by Malem (2006). A shallow nest of piezometers screened at the base of the waste dump and in the soil just below the pile, indicated that ground water was entering the lower section of the waste pile from the soils below. This water spans a large concentration range, overlapping with the Tunnel, Waste Rock Pile, and Wetland chemistries (Figure 14). This likely suggests that the degree of water-rock interaction at the base of the Waste-Rock pile is controlled by heterogeneous flow pathways with variable amounts of DO to drive sulfide oxidization reactions (Malem, 2006).

6.4. Wetland and Pore Water Samples.

Surface water samples collected from the Wetland area are generally intermediate in composition when compared to the Tunnel or Waste Rock Pile samples (Figure 14). Because water from the Tunnel and Waste Rock Pile flows directly into the Wetland, it is likely that this "intermediate" chemical composition reflects a mixing of the end-member Tunnel and Waste Rock Pile sources. Furthermore, surface water in the Wetland is characterized by its

circumneutral pH. Under these conditions metals like Cu, Fe, Al, and Pb are relatively insoluble (Fig.8; Fig. 13). Although Zn remains soluble, its concentration in the Wetland is attenuated as a function of distance from the Tunnel (Figure 11).

The concentrations of metals in the pore water fluids vary substantially as a function of depth and as a function of distance from the Waste Rock Pile. Concentrations of Zn, Mn, Pb, and Al are greater in location 1 (close to the Waste Rock Pile) than they are in locations 2 or 3. Concentrations of Cu and Zn decrease as a function of depth and become consistently low below about 30 cm (Figure 13). The attenuation of metal concentrations with distance in the wetland and depth is likely attributable to adsorption of metals on soil and soil organic matter. The concentrations of metals in the soils are extremely high and decrease with depth (Figure 16; similar to the pore water concentrations). For example, the concentrations of Cu are ~4000 times higher in the upper soil layers (Figure 16) than they are in the corresponding pore water samples. The concentrations of Zn are ~800 times higher than corresponding pore water samples (Figure 16; Figure 13). Fe concentrations are > 4000 times higher in the soils than in corresponding pore water samples. Similar results can be seen for Pb, Cd, Al, and other metals (Figures 12 & 15).

The concentration gradients described above suggest that metals in the Wetland area are originating solely from the Tunnel and Waste Rock Pile area. Because metal concentrations decrease with depth in the pore waters and soil samples, it does not appear that deeper groundwater flow pathways that probably intersect the Wetland carry significant concentrations of Zn or Cu.

6.5 Copper and Zinc Isotopes.

As with the bulk chemistry of water samples collected from the Waldorf site, the $\delta^{66}Zn$ and $\delta^{65}Cu$ of the water samples were relatively consistent among the tunnel (Fig. 17), waste rock pile and wetland (Fig. 18) areas. This may suggest that Cu and Zn were derived from the same source rocks in all cases. Additional investigation of Cu and Zn isotopes in pore water and soil samples would be necessary to further evaluate flow pathways and attenuation mechanisms.

The $\delta^{65}Cu$ of all the water samples ranged from +0.87 to +2.11‰ heavier than the $\delta^{65}Cu$ of the parent rock material (Figures 17a and 18a). This positive shift in isotopic values from Cu in sulfide minerals to Cu in water has been seen in previous investigations of ARD-impacted sites. For example, in the Kimball et al. (2009) investigation, the $\delta^{65}Cu$ of dissolved Cu in stream water was ~ +1.37‰ heavier than chalcopyrite ($CuFeS_2$) samples from the same region. Similarly, Mathur et al. (2005) measured a $\delta^{65}Cu$ of 0.58‰ for chalcopyrite and a $\delta^{65}Cu$ of 1.90‰ for fluid leached from the same mineral. Fernandez and Borrok (2009) performed leaching experiments with chalcopyrite-rich rocks and found up to 2.0‰ shifts from the rock to the low-pH solutions. They suggested that this behavior was a reflection of the oxidation of Cu(I) in chalcopyrite to Cu(II) in the leachate fluids. Borrok et al. (2008) and updates in Pribil et al. (2010) document similar shifts. Vance et al. (2010) measured the $\delta^{65}Cu$ of dissolved and suspended Cu in major river systems. They found similar results in that dissolved Cu was isotopically heavier than the $\delta^{65}Cu$ of average continental crust. However, to explain these values they suggested that Cu was isotopically fractionated between dissolved (heavy) and suspended (light) fractions. A comparison of the ranges of $\delta^{65}Cu$ measured for dissolved Cu in

river, stream, or experimental waters and Cu in sulfide minerals linked to these systems is presented in Figure 21. As suggested by Kimball et al. (2009) some of the variation in the δ^{65}Cu of dissolved Cu in stream waters may be attributable to adsorption reactions. Cu adsorbed to Fe(III)-oxide minerals becomes enriched in ^{65}Cu relative to the fluid phase (e.g., Balistrieri et al., 2008). Hence, adsorption of Cu would cause the pool of dissolved Cu to evolve to a lower δ^{65}Cu (see trend arrow in Figure 21). Fernandez and Borrok (2009) also demonstrate that changes in the rate and extent of chemical weathering can cause variations in the δ^{65}Cu of stream waters. In this case the δ^{65}Cu of the stream water evolves to lighter values as a function of the extent of leaching (see trend arrow in Figure 21). Because adsorption and weathering rates play such an important role in controlling δ^{65}Cu, it is surprising that the Tunnel and Waste Rock Pile samples have such similar Cu isotopic signatures. Plots of δ^{65}Cu versus pH and δ^{65}Cu versus the fraction of suspended Cu also do not reveal any important correlations with weathering rate or adsorption (Figures included in Appendix A). It is possible that a difference in δ^{65}Cu of the Tunnel samples (as compared to the Waste Rock Pile samples) attributable to weathering is off-set by the impact of higher amounts of Cu adsorption in the Tunnel area.

The δ^{66}Zn of all the water samples ranged from +0.11 to +0.37‰. This was largely within the range of the parent rock material (Figures 17a and 18a), suggesting that the weathering process had little impact on the Zn isotopic signature of dissolved Zn. This observation is consistent with the study of Fernandez and Borrok (2009) that showed little Zn isotopic change during the leaching of sphalerite. The authors attributed the lack of isotopic change to the fact that Zn (unlike Cu) did not change oxidation state during the reaction. Few studies have examined the δ^{66}Zn of dissolved Zn in rivers and streams in mining-impacted areas. Borrok et al. (2008) found that the δ^{66}Zn of 11 streams impacted by ARD ranged from +0.02‰

to +0.46‰. Borrok et al. (2009) additionally described a variation in δ^{66}Zn of +0.2 to +0.4 for a single mountain watershed impacted by multiple sources of ARD. A comparison of the ranges of δ^{66}Zn measured for dissolved Zn in these studies and in ours is presented in Figure 22. The proposed world-wide average δ^{66}Zn for sphalerite ore (Sonke et al., 2008) is also presented for comparison (Figure 22). The results show that there is little variation in Zn isotopes from the isotopic compositions of their geologic source rock. This fact suggests Zn might be useful for tracing sources with even small differences in δ^{66}Zn. However, some variation in δ^{66}Zn may also be attributed to adsorption reactions. As described above for Cu, Zn adsorbed to Fe(III)-oxide minerals is enriched in ^{66}Zn relative to the fluid. Hence, adsorption would cause the pool of dissolved Zn to evolve to lower δ^{66}Zn (see trend arrow in Figure 22). The trend of decreasing Zn concentration with distance from the Tunnel entrance suggests that modest amounts of Zn (about 12% of the total dissolved Zn) are being adsorbed onto freshly-precipitated Fe(III)-oxide phases (Figure 9). The δ^{66}Zn of the dissolved Zn seems to evolve towards a lighter composition as a function of Zn concentration (and distance from the Tunnel entrance), suggesting that adsorption is impacting the dissolved δ^{66}Zn (Figures 17, 20). The expected trend for the δ^{66}Zn based on the experimental fractionation factor derived by Balistrieri et al. (2008) is presented as a solid line (The line assumes and initial δ^{66}Zn = 0.3‰ and a loss of 12% Zn to adsorption). The predicted trend-line provides a reasonable fit to the data, suggesting that the δ^{66}Zn is indeed impacted by adsorption. However, this impact is modest and does not seem to impact direct comparisons to the δ^{66}Zn signatures of the Waste Rock Pile and Wetland samples. Because of the limited variation in δ^{66}Zn among all the sample locations, it is reasonable to assume that all the Zn was derived from a single isotopically homogeneous source.

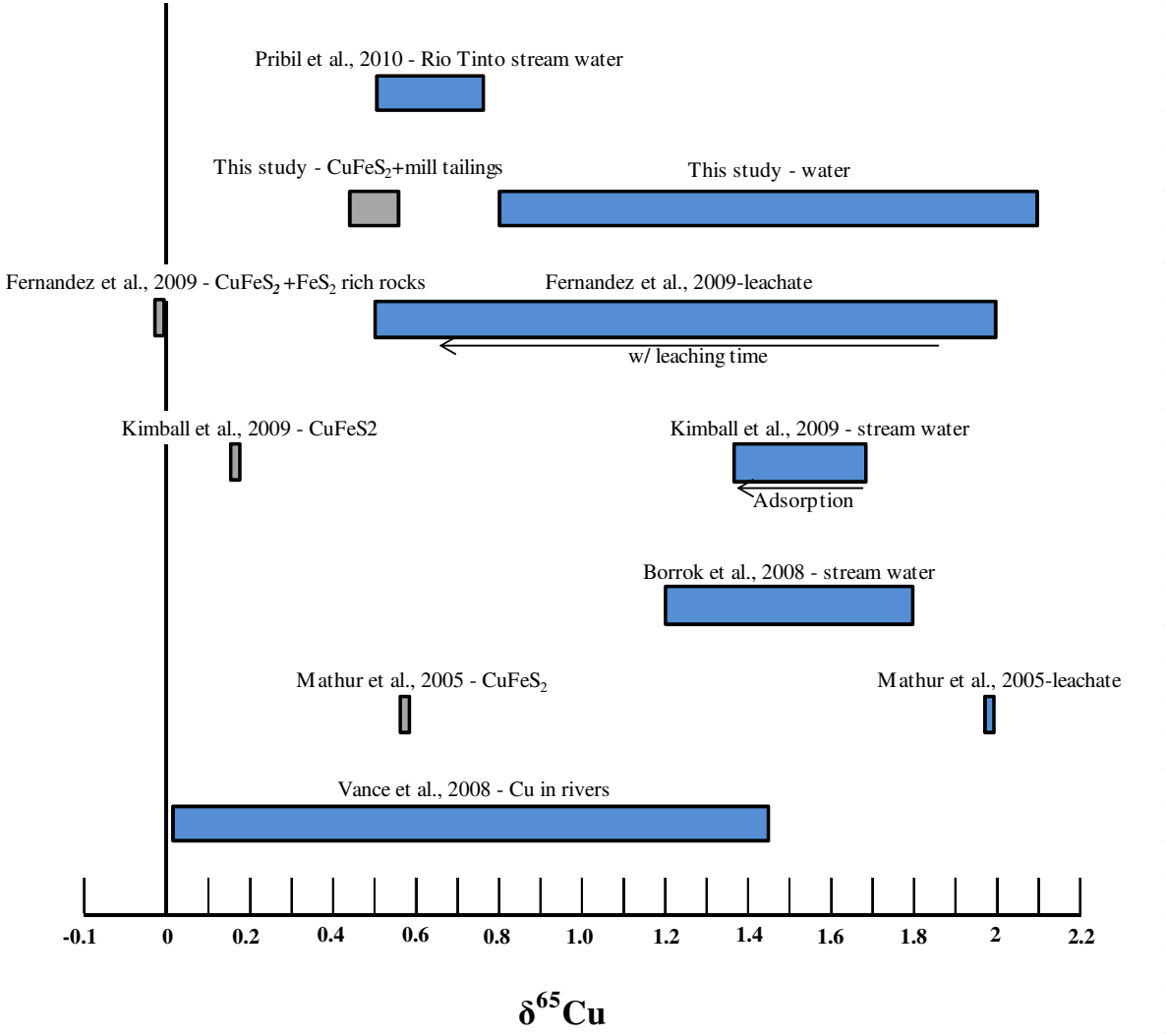

Figure 21. Reported $\delta^{65}Cu$ for dissolved Cu in streams and rivers and for associated Cu minerals.

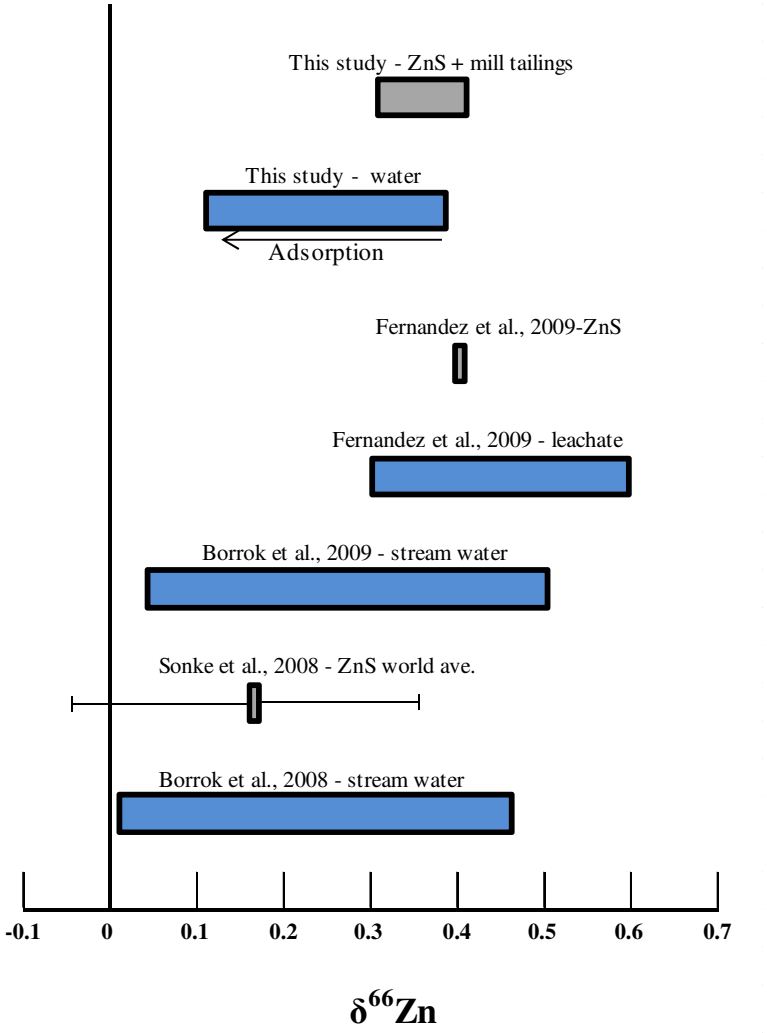

Figure 22. Reported Zn for dissolved Zn in streams and rivers and associated sphalerite.

CHAPTER 7

CONCLUSIONS

The results of our investigation demonstrate that the extent of water/rock interaction (i.e., chemical weathering) likely controls the bulk chemistry of the fluids associated with the Tunnel and Waste Rock Pile. The bulk chemistry of the fluids in the Wetland is a mixture of these end-member compositions. The concentrations of metals like Cu and Zn at the Waldorf site are largely controlled by secondary processes, including adsorption and precipitation reactions, and not by differing sources of these metals. The consistency of Cu and Zn isotopic signatures throughout the site also support the idea of a single metal source. Although additional information regarding metal concentrations in plants and the isotopic compositions of the pore waters and soils is necessary to complete the picture, our initial investigation is sufficient to address the following key questions regarding the Waldorf site:

1) Are metals being diluted from the influx of pristine groundwater or are metals being sorbed onto the soils or taken up into plants? The enormous concentrations of metals sequestered in the Wetland soils (3 to 4 orders of magnitude larger than metal concentrations in pore waters) is strong evidence for attenuation via adsorption. Although some dilution with pristine water may occur at depth, the near-surface soils are clearly acting like a sponge and adsorbing metals coming from the Tunnel and Waste Rock Pile.

2) Can multiple sources of water be identified based on water chemistry alone? We were able to distinguish water from the Tunnel from water associated with the Waste Rock Pile based on the different degrees of chemical weathering involved. Although there is a single "source" of water, the differing flow pathways and weathering regimes (e.g., DO and pH) control its chemistry and the primary chemistry in turn controls the distribution of metals.

3) Is the contaminated water coming from the abandoned mine or perhaps from different groundwater sources? It appears that metal-rich water is exiting the Tunnel and coming up beneath the Waste Rock Pile. We found no evidence for the presence of additional metal-rich groundwater flow pathways that intersect the Wetland. Concentration gradients suggest that metal contaminants are being transported mainly in surface waters in the Wetland, as metal concentration in soils and pore waters decrease with sampling depth.

4) Can Zn and Cu isotopes help to distinguish metal loading sources and pathways? The $\delta^{66}Zn$ of the Tunnel, Waste Rock Pile, and Wetlands varied over a narrow range, suggesting that Zn was coming from a single, isotopically homogeneous source. Surprisingly the $\delta^{65}Cu$ also varied over a narrow range. Because the isotopes of Cu are more impacted by weathering rates and adsorption reactions than Zn, we expected to see more variation. The lack of variation could be attributed to a relatively homogeneous source area, but more work needs to be done to investigate the $\delta^{65}Cu$ in pore waters and soils.

Overall, our results suggest that the Wetland is acting as a natural remediation buffer for metals coming from the Tunnel and Waste Rock Pile. Because groundwater is flowing into the

base of the Waste Rock Pile, Re-routing of the Tunnel Water around the Waste Rock Pile has had (and will continue to have) little impact on metal loads entering the Wetland. Removal of the Waste Rock Pile and re-vegetation of the underlying soil may significantly improve the water quality, but would not completely eliminate the problem.

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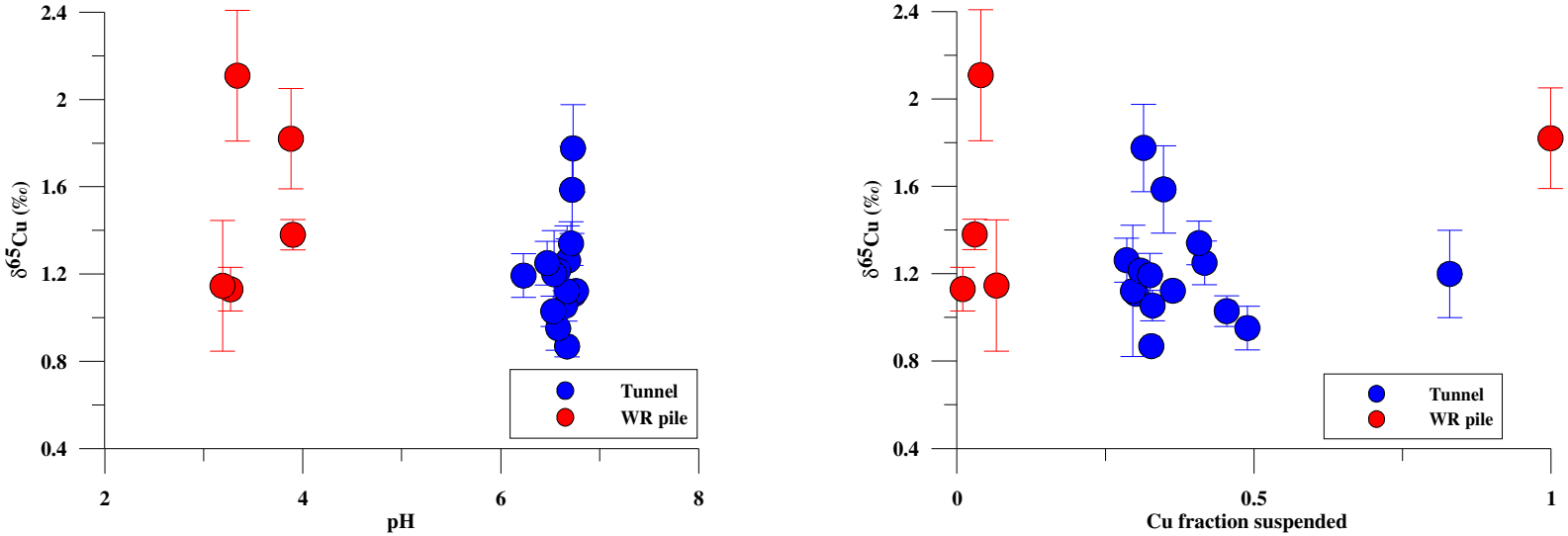
APPENDIX



Appendix A. Plots of δ^{65}Cu versus pH and δ^{65}Cu versus the fraction of suspended Cu.

Appendix B. (continued on the next page) Bulk chemistry preferred master values from ICP-AES and ICP-MS for filtered (0.45µm) samples from the Tunnel, Waste Rock Pile and Wetland

Site no.	SO_4-icp-ms mg/L	Alkalinity	Ag ug/L	Al ug/L	As ug/L	Ba ug/L	Be ug/L	Bi ug/L	Ca mg/L	Cd ug/L	Ce ug/L	Co ug/L	Cr ug/L	Cs ug/L	Cu ug/L	Dy ug/L	Er ug/L	Eu ug/L	Fe ug/L	Ga ug/L	Gd ug/L
08CO-01	215	64.6	<1	77.3	<1	12.9	0.6	<0.2	87.8	16.9	0.13	7.88	<1	0.18	99.3	0.01	0.008	<0.005	43.3	0.1	0.01
08CO-02	222	65.21	<1	77.5	<1	13.1	0.6	<0.2	86.8	17.5	0.13	8.09	<1	0.18	102	0.02	0.01	<0.005	45.8	0.1	0.01
08CO-03	210	63.23	<1	78.4	<1	12.3	0.7	<0.2	89.3	16.5	0.13	7.82	<1	0.18	97.4	0.01	0.01	<0.005	48.5	0.1	0.009
08CO-04	223	64.17	<1	87.5	<1	12.8	0.7	<0.2	89.1	17.8	0.15	8.3	<1	0.19	107	0.01	0.01	<0.005	57.3	0.1	0.01
08CO-05	228	64.24	<1	90.1	<1	13.1	0.7	<0.2	88.4	18.2	0.16	8.3	<1	0.19	108	0.01	0.01	<0.005	60.2	0.1	0.02
08CO-06	225	65.34	<1	91.4	<1	12.9	0.7	<0.2	89.7	17.8	0.15	8.31	<1	0.19	109	0.02	0.01	<0.005	69.1	0.1	0.01
08CO-07	223	66.75	<1	90.7	<1	12.7	0.7	<0.2	88.3	17.8	0.16	8.2	<1	0.19	105	0.02	0.01	<0.005	59.4	0.1	0.01
08CO-08	225	66.54	<1	93.7	<1	12.9	0.8	<0.2	90.9	18.3	0.17	8.62	<1	0.19	115	0.02	0.01	<0.005	71.8	0.1	0.02
08CO-09	226	65.82	<1	95.6	<1	12.8	0.8	<0.2	91.3	18.2	0.15	8.56	<1	0.2	114	0.01	0.009	<0.005	56.6	0.1	0.01
08CO-10	232	65.73	<1	97.8	<1	12.9	0.7	<0.2	90.6	18.5	0.18	8.81	<1	0.2	114	0.02	0.01	<0.005	68.6	0.1	0.01
08CO-11	229	66.03	<1	94.9	<1	12.7	0.8	<0.2	88.7	18.1	0.16	8.34	<1	0.19	101	0.01	0.01	<0.005	50.1	0.09	0.02
08CO-12	219	65.65	<1	94	<1	13.5	0.7	<0.2	86	17.5	0.16	8.25	<1	0.18	113	0.01	0.01	<0.005	54.1	0.1	0.01
08CO-13	228	65.15	<1	98.6	<1	13.9	0.8	<0.2	87.1	18.2	0.17	8.64	<1	0.19	119	0.02	0.01	<0.005	75.2	0.1	0.02
08CO-14	237	64.62	<1	103	<1	14	0.7	<0.2	89.6	18.8	0.2	8.86	<1	0.18	112	0.02	0.008	<0.005	58.3	0.1	0.02
08CO-15	232	65.3	<1	101	<1	13.4	0.7	<0.2	85.5	18.7	0.19	9.11	<1	0.2	106	0.02	0.01	<0.005	53.7	0.1	0.01
08CO-16	204		<1	1280	<1	14.3	0.9	<0.2	51.7	30.2	29.2	1.75	<1	0.14	1020	1.55	0.66	0.49	241	0.54	2.45
08CO-17	177		<1	1800	<1	13.9	1	<0.2	38	32.5	80.8	10.3	<1	0.17	980	3.21	1.34	1.1	847	1.3	5.23
08CO-18	216		<1	4040	<1	17.3	2.7	<0.2	43.7	46.8	174	14.5	<1	0.08	1910	6.39	2.7	2.24	522	2.7	10.6
08CO-19	39	8.666	<1	23.8	<1	14.1	<0.05	<0.2	15.6	0.48	0.04	<0.02	<1	<0.02	2.4	<0.005	<0.005	<0.005	38	<0.05	0.005
08CO-20	186	14.84	<1	49.3	<1	8.95	0.1	<0.2	64.5	3.09	<0.01	<0.02	<1	0.04	4	0.02	0.008	0.005	<20	<0.05	0.03
08CO-21	214	19.73	<1	38.1	<1	7.88	0.2	<0.2	72.9	5.26	1.15	0.33	<1	0.08	23.2	0.04	0.02	0.02	<20	<0.05	0.083
08CO-22	12	9.63	<1	3.6	<1	10.4	<0.05	<0.2	6.07	0.2	<0.01	<0.02	<1	0.04	<0.5	<0.005	<0.005	<0.005	<20	<0.05	0.009
08CO-23	126		<1	15.6	<1	33.9	0.05	<0.2	35.5	0.04	0.06	0.53	<1	<0.02	0.7	0.008	0.005	<0.005	3150	<0.05	0.01
08CO-24	139		<1	82.8	<1	21.5	<0.05	<0.2	43.7	4.9	0.54	0.69	<1	0.1	6.8	0.04	0.02	0.01	52.4	0.06	0.063
08CO-25	<2		<1	2.1	<1	<1	<0.05	<0.2	<0.1	<0.02	<0.01	<0.02	<1	<0.02	<0.5	<0.005	<0.005	<0.005	<20	<0.05	<0.005
08CO-26	243	0	<1	1720	<1	21.3	1.2	<0.2	53.6	32.1	54.2	9	<1	0.08	970	2.53	1.09	0.8	1840	0.93	3.94
08CO-pw1-0	214		<1	3490	<1	18.1	2.2	<0.2	44.6	34.9	172	13.9	<1	0.09	1150	6.17	2.61	2.08	1410	2.7	10.3
08CO-pw1-5	200		<1	4790	<1	22.8	3.2	<0.2	44.7	44.8	238	13.6	<1	0.11	1770	9.68	4.13	3.06	4400	3.7	15.4
08CO-pw1-10	244		<1	1590	2	24.9	1	<0.2	40.7	15.8	74.5	16.6	<1	0.24	50.8	2.36	1	0.83	60600	1.1	4.15
08CO-pw1-15	190		<1	4630	3	23.8	3.3	<0.2	44.2	12.4	328	13.5	<1	0.07	23.6	11.4	4.86	3.27	10500	4.9	19.2
08CO-pw1-20	306		<1	134	4	15	0.2	<0.2	79.9	0.07	1.39	40	<1	0.08	1.7	0.06	0.02	0.02	47800	0.22	0.094
08CO-pw1-25	317		<1	18	<1	14.5	0.08	<0.2	86	<0.02	0.13	10.5	<1	0.09	1.2	0.01	0.008	<0.005	55100	0.2	0.02
08CO-pw1-30	263		<1	365	3	19.8	0.4	<0.2	65.9	<0.02	0.46	13.9	<1	0.12	1.3	0.03	0.01	0.008	33700	0.2	0.04
08CO-pw1-40	326		<1	118	<1	18.4	0.2	<0.2	74.2	<0.02	0.21	0.06	<1	0.07	1	0.02	0.009	0.006	59000	0.21	0.03
08CO-pw1-50	345		<1	146	<1	18.6	<0.05	<0.2	94.2	<0.02	0.15	0.06	<1	0.03	1	0.006	<0.005	<0.005	52700	0.07	0.01
08CO-pw2-0	192	12.92	<1	55.3	<1	8.05	0.2	<0.2	72	2.62	0.67	<0.02	<1	0.04	28.6	0.059	0.03	0.02	<20	<0.05	0.14
08CO-pw2-5	212		<1	70.2	<1	8.74	0.2	<0.2	69	2.92	1.1	<0.02	<1	0.04	30.5	0.056	0.02	0.02	<20	<0.05	0.12
08CO-pw2-10	218		<1	86.4	<1	9.89	0.2	<0.2	71.7	3.89	1.28	<0.02	<1	0.05	27.2	0.04	0.02	0.02	<20	<0.05	0.091
08CO-pw2-15	223		<1	96.6	<1	13.2	0.1	<0.2	69.7	3.79	1.29	0.21	<1	0.04	29.8	0.04	0.02	0.01	<20	<0.05	0.078
08CO-pw2-20a	222		<1	75	<1	9.21	0.1	<0.2	71	2.82	0.43	0.36	<1	0.04	17.4	0.02	0.01	0.007	<20	<0.05	0.03
08CO-pw2-20b	219		<1	64.8	<1	4.44	0.1	<0.2	72.6	1.99	0.41	0.06	<1	0.04	13.6	0.02	0.01	0.007	<20	<0.05	0.04
08CO-pw2-25	226		<1	56.7	<1	3.88	0.09	<0.2	68.3	2.88	0.48	0.27	<1	0.05	17.2	0.03	0.02	0.01	<20	<0.05	0.063
08CO-pw2-30	225		<1	104	<1	9.43	0.05	<0.2	66.6	1.17	1.08	3.5	<1	0.03	40.2	0.055	0.02	0.02	<20	0.07	0.1
08CO-pw2-40	220		<1	128	<1	5.95	0.1	<0.2	65.6	1.83	0.69	0.61	<1	<0.02	16.7	0.03	0.01	0.01	<20	0.06	0.059
08CO-pw2-50	219		<1	295	<1	13	0.1	<0.2	67.1	2.66	0.67	0.14	<1	<0.02	12.3	0.05	0.02	0.01	<20	<0.05	0.074
08CO-pw2-60	212		<1	312	<1	15	0.1	<0.2	69.9	4.1	0.84	0.06	<1	<0.02	14.4	0.056	0.02	0.02	<20	<0.05	0.096
08CO-pw3-0	134	11.97	<1	45.2	<1	15.9	0.08	<0.2	48	2.2	0.01	<0.02	<1	0.02	5.4	<0.005	<0.005	<0.005	<20	<0.05	<0.005
08CO-pw3-5	126		<1	74.9	<1	17.3	0.07	<0.2	43.5	2.59	0.02	<0.02	<1	<0.02	4	<0.005	<0.005	<0.005	<20	<0.05	<0.005
08CO-pw3-10	135		<1	85.5	<1	17.7	0.1	<0.2	42.1	2.14	0.04	<0.02	<1	<0.02	6.8	0.005	<0.005	<0.005	<20	<0.05	0.006
08CO-pw3-15	139		<1	618	<1	18	0.07	<0.2	45.9	2.07	0.06	<0.02	<1	<0.02	4.8	<0.005	<0.005	<0.005	50.9	<0.05	0.01
08CO-pw3-25	136		<1	36.3	<1	23.1	0.05	<0.2	45.7	2.25	0.11	2.89	<1	0.03	7.2	0.008	<0.005	<0.005	880	<0.05	0.008
08CO-pw3-30	113		<1	35.5	<1	21.4	<0.05	<0.2	40.9	0.07	0.26	0.34	<1	0.04	2.5	0.02	0.01	0.007	5830	<0.05	0.03
08CO-pw3-40	78		<1	97.7	<1	23.6	0.1	<0.2	36.9	<0.02	0.28	0.08	<1	<0.02	1.1	0.03	0.02	0.009	1150	<0.05	0.03
08CO-pw3-50	46		<1	111	<1	16.9	0.1	<0.2	30.8	<0.02	0.5	0.08	<1	<0.02	1	0.04	0.02	0.01	454	<0.05	0.063

Appendix B. (continued on the next page) Bulk chemistry preferred values from ICP-AES and ICP-MS for filtered (0.45µm) samples from the Tunnel, Waste Rock Pile and Wetland.

site no.	Ge ug/L	Ho ug/L	K mg/L	La ug/L	Li ug/L	Lu ug/L	Mg mg/L	Mn ug/L	Mo ug/L	Na mg/L	Nb ug/L	Nd ug/L	Ni ug/L	P mg/L	Pb ug/L	Pr ug/L	Rb ug/L	Sb ug/L	Sc ug/L	Se ug/L	SiO_2 mg/L	Sm ug/L	Sr ug/L
08CO-01	<0.05	<0.005	1.1	0.17	5.1	<0.1	16.4	11900	<2	4.62	0.33	0.03	28	<0.01	<0.05	0.01	2.43	1.22	1	<1	11.2	<0.01	1030
08CO-02	<0.05	<0.005	1.22	0.18	5.1	<0.1	16.3	11900	<2	4.6	0.26	0.04	29	<0.01	<0.05	0.01	2.48	0.73	1.1	<1	11.1	<0.01	1070
08CO-03	<0.05	<0.005	1.23	0.18	4.8	<0.1	16.3	12000	<2	4.4	0.2	0.04	27.6	<0.01	<0.05	0.01	2.39	0.52	1	<1	10.6	<0.01	1020
08CO-04	<0.05	<0.005	1.19	0.21	5.4	<0.1	16.7	12100	<2	4.51	<0.2	0.04	29.2	<0.01	<0.05	0.01	2.51	0.39	1.1	<1	11.4	<0.01	1080
08CO-05	<0.05	<0.005	1.24	0.21	5.2	<0.1	16.7	12000	<2	4.52	<0.2	0.04	30	<0.01	<0.05	0.01	2.54	<0.3	1.1	<1	11.5	<0.01	1090
08CO-06	<0.05	<0.005	1.19	0.21	5.5	<0.1	16.7	12200	<2	4.59	<0.2	0.04	29	<0.01	<0.05	0.01	2.54	<0.3	1	<1	11.5	<0.01	1070
08CO-07	<0.05	<0.005	1.16	0.2	5.3	<0.1	16.4	11900	<2	4.48	<0.2	0.05	29	<0.01	0.08	0.01	2.49	<0.3	1	<1	11.4	<0.01	1070
08CO-08	<0.05	<0.005	1.24	0.21	5.5	<0.1	16.9	12500	<2	4.52	<0.2	0.05	29.4	<0.01	0.08	0.01	2.52	<0.3	1.1	<1	11.6	<0.01	1090
08CO-09	<0.05	<0.005	1.18	0.21	5.6	<0.1	16.8	12500	<2	4.53	<0.2	0.04	29.5	<0.01	<0.05	0.01	2.55	<0.3	1.1	<1	11.6	<0.01	1090
08CO-10	<0.05	<0.005	1.2	0.24	5.6	<0.1	16.5	12400	<2	4.57	<0.2	0.06	30.3	<0.01	<0.05	0.02	2.58	<0.3	1.1	<1	12	<0.01	1110
08CO-11	<0.05	<0.005	1.21	0.2	5.2	<0.1	16.2	11900	<2	4.49	<0.2	0.05	29.2	<0.01	0.06	0.01	2.51	<0.3	1	<1	11.6	<0.01	1090
08CO-12	<0.05	<0.005	1.21	0.2	5.2	<0.1	15.8	12100	<2	4.69	<0.2	0.05	28.4	<0.01	<0.05	0.02	2.42	<0.3	1	<1	11.4	<0.01	1040
08CO-13	<0.05	<0.005	1.3	0.22	5.6	<0.1	16.5	12100	<2	4.9	<0.2	0.05	29.4	<0.01	0.2	0.01	2.55	<0.3	1.1	<1	11.8	<0.01	1090
08CO-14	<0.05	<0.005	1.21	0.28	5.9	<0.1	16.4	12300	<2	4.75	<0.2	0.08	30.8	<0.01	0.2	0.02	2.58	<0.3	1.1	<1	12.2	<0.01	1130
08CO-15	<0.05	<0.005	1.19	0.23	5.7	<0.1	16.1	12000	<2	4.67	<0.2	0.05	30.6	<0.01	0.05	0.02	2.59	<0.3	1.1	<1	12.2	<0.01	1110
08CO-16	0.09	0.24	0.989	16.1	3.7	<0.1	14.4	5790	<2	3.44	<0.2	16	31.6	<0.01	84.6	4.1	2.46	<0.3	1.4	<1	11.2	2.78	649
08CO-17	0.2	0.51	0.845	36.2	2.9	0.1	12.9	7510	<2	2.68	<0.2	37.8	30.8	<0.01	106	9.75	2.1	<0.3	1.4	<1	10.8	6.21	436
08CO-18	0.36	0.99	0.906	74.1	4.2	0.2	15.1	11000	<2	2.73	<0.2	80.2	46.7	<0.01	564	20.4	3.41	<0.3	1.7	1	14.4	13.1	468
08CO-19	<0.05	<0.005	0.267	0.04	0.6	<0.1	3.01	18.1	<2	1.66	<0.2	0.04	1	<0.01	0.1	<0.01	0.52	<0.3	<0.6	<1	5.3	<0.01	190
08CO-20	<0.05	<0.005	1.07	0.45	3.6	<0.1	12.4	0.6	<2	4.01	<0.2	0.19	4	<0.01	<0.05	0.05	2.37	<0.3	0.8	<1	11.5	0.02	814
08CO-21	<0.05	0.009	1.15	1.38	4.4	<0.1	14	822	<2	4.28	<0.2	0.71	9.5	<0.01	0.69	0.19	2.49	<0.3	1	<1	12.4	0.09	873
08CO-22	<0.05	<0.005	0.372	0.03	0.5	<0.1	1.01	0.3	<2	1.09	<0.2	0.04	<0.4	<0.01	<0.05	<0.01	0.67	<0.3	<0.6	<1	4	<0.01	49
08CO-23	<0.05	<0.005	1.34	0.06	0.3	<0.1	7.88	1290	<2	5.61	<0.2	0.06	3.3	<0.01	0.4	0.01	1.17	<0.3	0.7	<1	8	<0.01	420
08CO-24	<0.05	0.006	13	0.3	0.8	<0.1	8.84	4570	<2	3.5	<0.2	0.32	11.5	0.01	1.1	0.07	2.72	<0.3	0.7	<1	8.7	0.06	611
08CO-25	<0.05	<0.005	<0.03	<0.01	1.1	<0.1	<0.1	<0.2	<2	<0.1	<0.2	<0.01	<0.4	<0.01	<0.05	<0.01	<0.01	<0.3	<0.6	<1	<0.2	<0.01	<0.5
08CO-26	0.2	0.41	0.989	28.6	4.3	0.1	14.4	7950	<2	3.21	<0.2	26	37.6	<0.01	191	6.86	2.57	<0.3	1.2	<1	13.6	4.23	620
08CO-pw1-0	0.34	1	0.898	82.3	4.2	0.2	14.8	10000	<2	2.78	0.28	76.4	45	<0.01	332	20.1	2.8	<0.3	1.7	1.3	14.7	12.2	539
08CO-pw1-5	0.46	1.56	1.11	104	4.6	0.4	14.3	10400	<2	2.76	<0.2	108	44.6	<0.01	2400	28.1	3.97	<0.3	1.3	1.2	14.9	16.9	506
08CO-pw1-10	0.2	0.38	5.42	35.6	5.2	<0.1	13.4	10000	<2	2.83	<0.2	31.6	61.1	<0.01	590	8.5	17.8	<0.3	1.5	<1	18	4.7	510
08CO-pw1-15	0.57	1.89	1.46	152	4.2	0.4	14.2	10300	<2	2.72	<0.2	131	52.3	<0.01	786	37.8	4.74	<0.3	1.3	1.6	15.3	17.1	487
08CO-pw1-20	<0.05	0.01	2.55	0.96	10.4	<0.1	27.9	25700	<2	3.02	<0.2	0.58	69	<0.01	5.2	0.16	10.1	<0.3	1.5	<1	18.2	0.08	884
08CO-pw1-25	<0.05	<0.005	2.56	0.09	7.4	<0.1	31.6	26200	<2	3.2	<0.2	0.08	2.3	<0.01	0.4	0.02	8.67	<0.3	1.5	<1	17.8	0.01	903
08CO-pw1-30	<0.05	<0.005	2.04	0.42	7.6	<0.1	22.1	20500	<2	2.99	<0.2	0.17	27.5	<0.01	0.92	0.05	4.85	<0.3	1.8	<1	19.4	0.03	714
08CO-pw1-40	<0.05	<0.005	1.98	0.13	4.6	<0.1	31.8	25900	<2	6.42	<0.2	0.12	<0.4	0.01	0.4	0.03	3.02	<0.3	1.5	<1	18.4	0.03	787
08CO-pw1-50	<0.05	<0.005	2.3	0.14	2.1	<0.1	30.6	8830	<2	4.13	<0.2	0.07	0.4	<0.01	0.1	0.02	3.28	<0.3	1	<1	13.2	0.01	1070
08CO-pw2-0	<0.05	0.01	0.99	2.42	2.3	<0.1	14.1	13.2	<2	3.77	<0.2	0.97	5.1	<0.01	0.2	0.29	1.9	<0.3	0.8	<1	10.3	0.11	798
08CO-pw2-5	<0.05	0.009	1.01	2.12	1.8	<0.1	13.9	27	<2	3.73	<0.2	0.88	5.4	<0.01	0.3	0.26	1.99	<0.3	0.8	<1	12	0.11	788
08CO-pw2-10	<0.05	0.008	1.69	1.55	2.2	<0.1	14.1	28.3	<2	3.82	<0.2	0.67	6.5	<0.01	0.64	0.19	3.2	<0.3	0.8	<1	12.2	0.07	791
08CO-pw2-15	<0.05	0.006	0.847	1.36	2.2	<0.1	13.8	255	<2	4.1	<0.2	0.56	5.8	<0.01	0.91	0.17	1.81	<0.3	0.9	<1	13.2	0.06	786
08CO-pw2-20a	<0.05	<0.005	1.18	0.67	2.4	<0.1	13.9	351	<2	4.12	<0.2	0.26	5.3	<0.01	0.63	0.07	2.19	<0.3	0.9	<1	13.3	0.04	841
08CO-pw2-20b	<0.05	0.005	0.994	0.65	2.4	<0.1	14	188	<2	4.09	<0.2	0.27	3.2	<0.01	0.4	0.08	2.01	<0.3	0.9	<1	13.8	0.04	867
08CO-pw2-25	<0.05	0.005	1.03	0.66	2.2	<0.1	14.1	651	<2	4.08	<0.2	0.42	3.9	0.01	0.4	0.1	2.05	<0.3	1	<1	14.5	0.07	877
08CO-pw2-30	<0.05	0.009	1.32	0.75	2.5	<0.1	13.5	4770	<2	4.06	<0.2	0.67	4.5	0.01	1.9	0.17	1.96	<0.3	1.1	<1	15.5	0.12	805
08CO-pw2-40	<0.05	0.006	0.959	0.47	1.5	<0.1	13.6	4230	<2	4.1	<0.2	0.42	4.4	0.02	0.54	0.1	1.83	<0.3	1.2	<1	17	0.08	798
08CO-pw2-50	<0.05	0.008	0.937	0.7	1.2	<0.1	12.9	3210	<2	3.79	<0.2	0.46	6.6	0.02	0.1	0.12	2.1	<0.3	1.2	<1	16.9	0.05	789
08CO-pw2-60	<0.05	0.009	0.996	1.07	2.8	<0.1	13.1	2310	<2	3.9	0.52	0.6	5.9	<0.01	<0.05	0.17	2.42	1.11	1.1	<1	12.2	0.07	798
08CO-pw3-0	<0.05	<0.005	0.607	0.04	1.3	<0.1	8.73	0.6	<2	3.22	0.29	0.02	3.2	<0.01	0.1	<0.01	1.23	0.6	0.8	<1	9.4	<0.01	545
08CO-pw3-5	<0.05	<0.005	0.765	0.05	1	<0.1	8.33	3.6	<2	3.22	0.2	0.02	3.6	0.01	0.52	<0.01	1.44	0.36	0.8	<1	9	<0.01	497
08CO-pw3-10	<0.05	<0.005	0.631	0.08	0.9	<0.1	8.36	3.5	<2	3.11	<0.2	0.03	3.7	0.01	2.9	<0.01	1.36	0.33	0.8	<1	9.8	<0.01	532
08CO-pw3-15	<0.05	<0.005	0.658	0.07	1.2	<0.1	8.37	15.9	<2	3.16	<0.2	0.05	3.6	0.01	2	0.01	1.37	<0.3	0.8	<1	10.1	<0.01	553
08CO-pw3-25	<0.05	<0.005	0.93	0.08	1.4	<0.1	8.46	1250	<2	3.23	<0.2	0.06	5.2	<0.01	6.6	0.02	1.6	<0.3	0.9	<1	10.3	<0.01	543
08CO-pw3-30	<0.05	0.005	0.916	0.13	0.6	<0.1	8.39	264	<2	3.13	<0.2	0.18	2.2	0.01	18.4	0.04	1.14	0.31	1	<1	11	0.03	516
08CO-pw3-40	<0.05	0.005	0.855	0.16	<0.1	<0.1	7.71	268	<2	3.14	<0.2	0.2	1.4	0.02	2.3	0.04	0.84	<0.3	1	<1	11.9	0.04	437
08CO-pw3-50	<0.05	0.007	0.829	0.31	<0.1	<0.1	6.31	264	<2	2.99	<0.2	0.39	0.6	0.02	1.2	0.09	1.49	<0.3	1	<1	11.6	0.06	367

Appendix B. (continued) Bulk chemistry preferred values from ICP-AES and ICP-MS for filtered (0.45µm) samples from the Tunnel, Waste Rock Pile and Wetland.

site no.	Tb ug/L	Th ug/L	Ti ug/L	Tl ug/L	Tm ug/L	U ug/L	V ug/L	W ug/L	Y ug/L	Yb ug/L	Zn ug/L	Zr ug/L
08CO-01	<0.005	<0.2	2	<0.1	<0.005	3.26	<0.5	0.61	0.34	0.007	7110	<0.2
08CO-02	<0.005	<0.2	2.2	<0.1	<0.005	3.34	<0.5	<0.5	0.36	0.009	7390	<0.2
08CO-03	<0.005	<0.2	2.1	<0.1	<0.005	3.26	<0.5	<0.5	0.35	<0.005	6870	<0.2
08CO-04	<0.005	<0.2	2.2	<0.1	<0.005	3.46	<0.5	<0.5	0.4	0.008	7380	<0.2
08CO-05	<0.005	<0.2	2.1	<0.1	<0.005	3.49	<0.5	<0.5	0.4	0.01	7700	<0.2
08CO-06	<0.005	<0.2	2.2	<0.1	<0.005	3.4	<0.5	<0.5	0.4	0.009	7640	<0.2
08CO-07	<0.005	<0.2	2	<0.1	<0.005	3.4	<0.5	<0.5	0.4	0.007	7470	<0.2
08CO-08	<0.005	<0.2	2.1	<0.1	<0.005	3.46	<0.5	<0.5	0.43	0.008	7620	<0.2
08CO-09	<0.005	<0.2	2	<0.1	<0.005	3.44	<0.5	<0.5	0.41	0.01	7670	<0.2
08CO-10	<0.005	<0.2	2.1	<0.1	<0.005	3.6	<0.5	<0.5	0.44	0.01	7780	<0.2
08CO-11	<0.005	<0.2	2	<0.1	<0.005	3.39	<0.5	<0.5	0.38	0.01	7700	<0.2
08CO-12	<0.005	<0.2	1.9	<0.1	<0.005	3.32	<0.5	<0.5	0.38	0.008	7420	<0.2
08CO-13	<0.005	<0.2	2.1	<0.1	<0.005	3.49	<0.5	<0.5	0.41	0.01	7680	<0.2
08CO-14	<0.005	<0.2	2.2	<0.1	<0.005	3.62	<0.5	<0.5	0.43	0.01	7900	<0.2
08CO-15	<0.005	<0.2	2.1	<0.1	<0.005	3.65	<0.5	<0.5	0.44	0.009	7790	<0.2
08CO-16	0.31	0.28	1.9	<0.1	0.073	5.42	<0.5	<0.5	7.3	0.48	8070	<0.2
08CO-17	0.65	2	1.6	<0.1	0.15	8.39	<0.5	<0.5	13.5	1	7940	<0.2
08CO-18	1.29	0.75	2	<0.1	0.3	20.3	<0.5	<0.5	25.8	2.03	12400	<0.2
08CO-19	<0.005	<0.2	0.5	<0.1	<0.005	<0.1	<0.5	<0.5	0.03	<0.005	233	<0.2
08CO-20	<0.005	<0.2	1.7	<0.1	<0.005	0.19	<0.5	<0.5	0.18	0.005	1620	<0.2
08CO-21	0.009	<0.2	2.1	<0.1	<0.005	1.24	<0.5	<0.5	0.34	0.01	2560	<0.2
08CO-22	<0.005	<0.2	<0.5	<0.1	<0.005	<0.1	<0.5	<0.5	0.04	<0.005	47.8	<0.2
08CO-23	<0.005	<0.2	1.2	<0.1	<0.005	<0.1	<0.5	<0.5	0.05	0.005	55.2	<0.2
08CO-24	0.008	<0.2	3.3	<0.1	<0.005	0.3	<0.5	<0.5	0.16	0.01	1760	<0.2
08CO-25	<0.005	<0.2	<0.5	<0.1	<0.005	<0.1	<0.5	<0.5	<0.01	<0.005	1.3	<0.2
08CO-26	0.5	0.67	2.1	<0.1	0.12	7.01	<0.5	<0.5	11.9	0.75	8940	<0.2
08CO-pw1-0	1.26	1.75	2.1	<0.1	0.29	15.4	<0.5	0.55	28.2	1.86	11300	<0.2
08CO-pw1-5	1.93	0.26	2	<0.1	0.46	12.2	<0.5	<0.5	40.8	2.96	11200	<0.2
08CO-pw1-10	0.5	<0.2	2.6	0.2	0.11	1.5	<0.5	<0.5	12	0.63	11300	<0.2
08CO-pw1-15	2.32	<0.2	2	<0.1	0.49	1.91	<0.5	<0.5	63.5	2.74	12100	<0.2
08CO-pw1-20	0.01	<0.2	3.1	<0.1	<0.005	2.69	<0.5	<0.5	0.46	0.02	8090	<0.2
08CO-pw1-25	<0.005	<0.2	3.2	<0.1	<0.005	2.97	<0.5	<0.5	0.14	0.008	248	<0.2
08CO-pw1-30	0.006	<0.2	2.6	<0.1	<0.005	0.5	<0.5	<0.5	0.26	0.009	4630	<0.2
08CO-pw1-40	<0.005	<0.2	3.2	<0.1	<0.005	0.84	<0.5	<0.5	0.14	0.007	15	<0.2
08CO-pw1-50	<0.005	<0.2	3.3	<0.1	<0.005	<0.1	<0.5	<0.5	0.05	<0.005	18.4	<0.2
08CO-pw2-0	0.02	<0.2	1.9	<0.1	<0.005	0.67	<0.5	<0.5	0.57	0.01	1610	<0.2
08CO-pw2-5	0.01	<0.2	2.2	<0.1	<0.005	0.59	<0.5	<0.5	0.5	0.01	1720	<0.2
08CO-pw2-10	0.01	<0.2	2.2	<0.1	<0.005	0.46	<0.5	<0.5	0.34	0.01	1800	<0.2
08CO-pw2-15	0.009	<0.2	2.2	<0.1	<0.005	0.14	<0.5	<0.5	0.38	0.008	2460	<0.2
08CO-pw2-20a	0.005	<0.2	2.3	<0.1	<0.005	0.2	<0.5	<0.5	0.21	0.007	2360	<0.2
08CO-pw2-20b	<0.005	<0.2	2.2	<0.1	<0.005	0.2	<0.5	<0.5	0.21	0.006	1400	<0.2
08CO-pw2-25	0.006	<0.2	2.3	<0.1	<0.005	0.46	<0.5	<0.5	0.2	0.01	1750	<0.2
08CO-pw2-30	0.01	<0.2	2.3	<0.1	<0.005	0.79	<0.5	<0.5	0.26	0.02	834	<0.2
08CO-pw2-40	0.007	<0.2	2.3	<0.1	<0.005	0.54	<0.5	<0.5	0.15	0.009	351	<0.2
08CO-pw2-50	0.008	<0.2	2.2	<0.1	<0.005	0.41	<0.5	<0.5	0.26	0.02	429	<0.2
08CO-pw2-60	0.01	<0.2	2.1	<0.1	<0.005	0.14	<0.5	0.89	0.32	0.02	464	<0.2
08CO-pw3-0	<0.005	<0.2	1.3	<0.1	<0.005	<0.1	<0.5	<0.5	0.02	<0.005	946	<0.2
08CO-pw3-5	<0.005	<0.2	1.3	<0.1	<0.005	<0.1	<0.5	<0.5	0.03	<0.005	900	<0.2
08CO-pw3-10	<0.005	<0.2	1.4	<0.1	<0.005	<0.1	<0.5	<0.5	0.04	<0.005	902	<0.2
08CO-pw3-15	<0.005	<0.2	1.4	<0.1	<0.005	<0.1	<0.5	<0.5	0.04	<0.005	869	<0.2
08CO-pw3-25	<0.005	<0.2	1.3	<0.1	<0.005	0.11	<0.5	<0.5	0.04	<0.005	619	<0.2
08CO-pw3-30	<0.005	<0.2	1.4	<0.1	<0.005	0.38	<0.5	<0.5	0.12	0.01	60.1	<0.2
08CO-pw3-40	<0.005	<0.2	1.5	<0.1	<0.005	0.16	<0.5	<0.5	0.14	0.008	5.6	<0.2
08CO-pw3-50	0.007	<0.2	2.1	<0.1	<0.005	0.14	0.7	<0.5	0.19	0.01	6.5	<0.2

Appendix C. (continued on the next page) Bulk chemistry values from ICP-AES and ICP-MS for unfiltered samples from the Tunnel, Waste Rock Pile and Wetland.

Field No.	Ag ug/L	Al ug/L	As ug/L	Ba ug/L	Be ug/L	Bi ug/L	Ca mg/L	Cd ug/L	Ce ug/L	Co ug/L	Cr ug/L	Cs ug/L	Cu ug/L	Dy ug/L	Er ug/L	Eu ug/L	Fe ug/L	Ga ug/L	Gd ug/L
08CO-01-RA	<1	92.7	<1	12.1	0.8	< 0.2	87.9	18.5	0.88	8.43	<1	0.19	143	0.066	0.04	0.02	824	0.1	0.091
08CO-02-RA	<1	86.4	<1	11.4	0.8	< 0.2	83.6	17.8	0.87	8.08	<1	0.17	138	0.067	0.03	0.01	807	0.1	0.079
08CO-03-RA	<1	95.6	<1	11.8	0.8	< 0.2	83.8	18.1	1.08	8.2	<1	0.18	156	0.081	0.04	0.02	1060	0.1	0.094
08CO-04-RA	<1	88.8	<1	11.6	0.8	< 0.2	85	18.3	0.91	8.13	<1	0.18	145	0.07	0.04	0.01	846	0.1	0.091
08CO-05-RA	<1	92.4	<1	11.9	0.7	< 0.2	84.2	18.2	0.94	8.16	<1	0.18	145	0.066	0.04	0.02	877	0.1	0.087
08CO-06-RA	<1	90.8	<1	11.6	0.7	< 0.2	83.1	18.1	0.88	8.17	<1	0.18	143	0.069	0.04	0.01	821	0.1	0.079
08CO-07-RA	<1	89.5	<1	11.6	0.8	< 0.2	83.4	17.8	0.88	7.99	<1	0.18	141	0.063	0.04	0.01	820	0.1	0.076
08CO-08-RA	<1	103	<1	13	0.8	< 0.2	82.2	18.7	1.41	8.7	<1	0.18	200	0.11	0.055	0.02	1580	0.1	0.13
08CO-09-RA	<1	93.9	<1	11.9	0.8	< 0.2	85.1	18.5	0.94	8.44	<1	0.18	150	0.073	0.04	0.02	913	0.1	0.09
08CO-10-RA	<1	125	<1	12.7	0.8	< 0.2	87.2	18.9	1.18	8.7	<1	0.21	160	0.088	0.05	0.02	1120	0.1	0.11
08CO-11-RA	<1	112	<1	12.2	0.8	< 0.2	86.3	18.6	1.48	8.39	<1	0.19	177	0.12	0.058	0.02	1560	0.1	0.13
08CO-12-RA	<1	267	<1	13.4	1.1	< 0.2	86.2	20.5	11	8.7	<1	0.21	670	0.79	0.42	0.18	13400	0.26	1.03
08CO-13-RA	<1	146	<1	13.4	0.8	< 0.2	86.8	19	2.04	8.89	<1	0.24	191	0.13	0.073	0.03	1900	0.1	0.17
08CO-14-RA	1.11	592	<1	26.6	0.9	< 0.2	86	19.1	6.33	8.58	<1	1.03	180	0.27	0.11	0.089	3240	0.36	0.44
08CO-15-RA	<1	98.6	<1	12.3	0.8	< 0.2	85.8	18.8	1.05	8.77	<1	0.19	151	0.074	0.04	0.02	938	0.1	0.091
08CO-16-RA	2.46	988	<1	20.4	0.8	0.61	46.8	30	27.8	1.62	<1	0.25	992	1.45	0.64	0.47	1760	0.54	2.31
08CO-17-RA	2.3	1550	1	43	1	0.47	34.8	33.1	80.1	10.4	<1	0.42	1020	3.22	1.37	1.1	4370	1.4	5.22
08CO-18-RA	<1	3180	<1	15.9	2.7	< 0.2	41	47.3	163	14.1	<1	0.1	1920	6.25	2.66	2.1	1320	2.6	10.1
08CO-19-RA	<1	25.2	<1	12.3	<0.05	< 0.2	14.8	0.54	0.05	<0.02	<1	< 0.02	2.3	0.006	< 0.005	< 0.005	58	< 0.05	0.008
08CO-20-RA	<1	46.4	<1	7.87	0.1	< 0.2	59.3	3.26	0.01	<0.02	<1	0.03	4.1	0.02	0.006	0.007	<50	< 0.05	0.03
08CO-21-RA	<1	133	<1	7.05	0.2	< 0.2	66.8	5.48	1.95	0.33	<1	0.08	34.4	0.12	0.04	0.04	146	< 0.05	0.2
08CO-22-RA	<1	7.9	<1	8.95	<0.05	< 0.2	5.47	0.22	0.02	<0.02	<1	0.03	<0.5	0.006	0.005	< 0.005	<50	< 0.05	0.01
08CO-23-RA	<1	105	<1	31.4	<0.05	< 0.2	33	0.15	0.42	0.48	7.9	0.03	3.4	0.05	0.02	0.02	2360	< 0.05	0.075
08CO-25-RA	<1	<2	<1	1.2	<0.05	< 0.2	<0.2	<0.02	< 0.01	<0.02	<1	< 0.02	<0.5	< 0.005	< 0.005	< 0.005	<50	< 0.05	< 0.005
08CO-26-RA	<1	1640	<1	20.6	1.3	< 0.2	48.7	32.9	54	9.3	<1	0.11	1020	2.53	1.08	0.78	2480	0.94	4
08CO-pw1-0-RA	<1	3080	<1	18.1	2.3	< 0.2	42.4	35.3	161	13.9	<1	0.12	1260	6.09	2.52	1.92	2620	2.6	9.82
08CO-pw2-0-RA	<1	64.3	<1	7.6	0.2	< 0.2	65.6	2.8	1.14	<0.02	<1	0.04	33.6	0.13	0.05	0.05	<50	< 0.05	0.25
08CO-pw3-0-RA	<1	48.4	<1	13.2	0.09	< 0.2	39.4	2.26	0.02	<0.02	<1	< 0.02	6.5	< 0.005	< 0.005	< 0.005	<50	< 0.05	< 0.005

Appendix C. (continued on the next page) Bulk chemistry values from ICP-AES and ICP-MS for unfiltered samples from the Tunnel, Waste Rock Pile and Wetland.

Field No.	Ge ug/L	Ho ug/L	K mg/L	La ug/L	Li ug/L	Lu ug/L	Mg mg/L	Mn ug/L	Mo ug/L	Na mg/L	Nb ug/L	Nd ug/L	Ni ug/L	P mg/L	Pb ug/L	Pr ug/L	Rb ug/L	Sb ug/L	Sc ug/L
08CO-01-RA	< 0.05	0.01	1.07	0.6	5.2	< 0.1	13.2	11400	< 2	3.38	< 0.2	0.37	29.2	< 0.01	7	0.09	2.61	<0.3	0.9
08CO-02-RA	< 0.05	0.01	1.02	0.59	4.8	< 0.1	11.9	10800	< 2	3.02	< 0.2	0.38	27.8	< 0.01	6.7	0.1	2.48	<0.3	0.9
08CO-03-RA	< 0.05	0.02	1.03	0.71	5.1	< 0.1	11.7	11100	< 2	3.02	< 0.2	0.46	28.1	< 0.01	8.6	0.12	2.54	<0.3	0.9
08CO-04-RA	< 0.05	0.01	1.02	0.6	5	< 0.1	11.8	11100	< 2	3.02	< 0.2	0.38	28.2	< 0.01	7	0.1	2.52	<0.3	1
08CO-05-RA	< 0.05	0.01	1.02	0.63	4.8	< 0.1	11.9	11100	< 2	3.07	< 0.2	0.4	28.2	< 0.01	7.3	0.1	2.49	<0.3	0.9
08CO-06-RA	< 0.05	0.01	1.02	0.58	4.7	< 0.1	12	11100	< 2	3.07	< 0.2	0.38	27.9	< 0.01	6.8	0.1	2.5	<0.3	0.9
08CO-07-RA	< 0.05	0.01	1.02	0.59	4.9	< 0.1	12.1	11100	< 2	3.11	< 0.2	0.35	27.8	< 0.01	6.8	0.1	2.45	<0.3	0.9
08CO-08-RA	< 0.05	0.02	1	0.93	4.6	< 0.1	12	11500	< 2	3.06	< 0.2	0.58	27.4	< 0.01	8	0.15	2.47	<0.3	0.9
08CO-09-RA	< 0.05	0.01	1.04	0.63	4.9	< 0.1	12.4	11400	< 2	3.18	< 0.2	0.4	28.5	< 0.01	7	0.1	2.53	<0.3	0.9
08CO-10-RA	< 0.05	0.02	1.07	0.77	5.6	< 0.1	13	11800	< 2	3.32	< 0.2	0.52	29.2	< 0.01	12.8	0.13	2.68	<0.3	1
08CO-11-RA	< 0.05	0.02	1.06	0.92	4.9	< 0.1	12.9	11400	< 2	3.29	< 0.2	0.62	29.3	< 0.01	11.2	0.16	2.57	<0.3	1
08CO-12-RA	0.07	0.15	1.05	6.16	5.4	< 0.1	12.7	11700	< 2	3.27	< 0.2	4.93	29.1	0.02	87.9	1.24	2.66	<0.3	1.2
08CO-13-RA	< 0.05	0.02	1.06	1.18	5	< 0.1	12.6	11800	< 2	3.24	< 0.2	0.85	29.2	< 0.01	18.4	0.22	2.72	<0.3	1
08CO-14-RA	< 0.05	0.04	1.31	3.63	5.4	< 0.1	12.6	11400	< 2	3.2	< 0.2	2.74	29.4	0.1	493	0.72	5.18	<0.3	1.2
08CO-15-RA	< 0.05	0.01	1.06	0.68	5.2	< 0.1	12.7	11800	< 2	3.25	< 0.2	0.46	29	< 0.01	7.5	0.11	2.56	<0.3	1
08CO-16-RA	0.08	0.24	0.9	15.1	3	< 0.1	10.8	5320	< 2	2.24	< 0.2	15.4	29.5	0.02	247	3.88	3.11	<0.3	1.1
08CO-17-RA	0.2	0.51	0.92	37	2.5	0.1	10.4	7020	< 2	1.89	< 0.2	37.4	30	0.07	365	9.65	3.64	<0.3	1.4
08CO-18-RA	0.34	0.96	0.86	69.4	4.1	0.2	11.3	10600	< 2	1.78	< 0.2	76.9	44.4	0.01	628	19.6	3.97	<0.3	1.4
08CO-19-RA	< 0.05	< 0.005	0.2	0.05	< 0.1	< 0.1	2.73	19.3	< 2	1.28	< 0.2	0.05	0.9	< 0.01	0.2	0.01	0.52	<0.3	< 0.6
08CO-20-RA	< 0.05	< 0.005	0.92	0.47	3.4	< 0.1	9.92	4.2	< 2	2.76	< 0.2	0.19	3.8	< 0.01	<0.05	0.06	2.44	<0.3	0.7
08CO-21-RA	< 0.05	0.02	0.93	1.74	4.5	< 0.1	11.6	760	< 2	2.91	< 0.2	1.38	9.2	< 0.01	5.8	0.35	2.58	<0.3	0.8
08CO-22-RA	< 0.05	< 0.005	0.31	0.04	< 0.1	< 0.1	0.98	0.6	< 2	0.85	< 0.2	0.06	<0.4	< 0.01	0.1	0.01	0.68	<0.3	< 0.6
08CO-23-RA	< 0.05	0.007	1.27	0.33	0.1	< 0.1	7.46	1130	< 2	11.8	< 0.2	0.45	3.2	0.02	7.5	0.1	1.21	<0.3	0.6
08CO-25-RA	< 0.05	< 0.005	<0.03	< 0.01	< 0.1	< 0.1	<0.01	<0.2	< 2	<0.01	< 0.2	< 0.01	<0.4	< 0.01	<0.05	< 0.01	< 0.01	<0.3	< 0.6
08CO-26-RA	0.1	0.41	1	27.8	3.8	< 0.1	12.7	7610	< 2	2.52	< 0.2	26	37	0.02	251	6.79	2.93	<0.3	1.1
08CO-pw1-0-RA	0.32	0.95	0.84	77	4.5	0.2	12.6	10000	< 2	2.08	< 0.2	7.18	44.4	0.02	391	18.6	3.36	<0.3	1.5
08CO-pw2-0-RA	< 0.05	0.02	0.89	3.43	3.2	< 0.1	11.6	11.2	< 2	2.88	< 0.2	1.91	4.9	< 0.01	0.94	0.53	2.13	<0.3	0.8
08CO-pw3-0-RA	< 0.05	< 0.005	0.53	0.04	1.4	< 0.1	7.41	2.7	< 2	2.35	< 0.2	0.02	3	< 0.01	0.4	< 0.01	1.24	<0.3	0.6

Appendix C. (Continued) Bulk chemistry preferred values from ICP-MS for unfiltered samples from the Tunnel, Waste Rock Pile and Wetland.

Field No.	Se ug/L	SiO_2 mg/L	Sm ug/L	SO_4 mg/L	Sr ug/L	Ta ug/L	Tb ug/L	Th ug/L	Ti ug/L	Tl ug/L	Tm ug/L	U ug/L	V ug/L	W ug/L	Y ug/L	Yb ug/L	Zn ug/L	Zr ug/L
08CO-01-RA	< 1	12.3	0.07	231	1100	0.22	0.01	< 0.2	1.5	<0.1	< 0.005	4.15	<0.5	< 0.5	0.71	0.02	7580	< 0.2
08CO-02-RA	< 1	11.3	0.07	214	1070	0.24	0.01	< 0.2	1.4	<0.1	0.005	4.15	<0.5	< 0.5	0.71	0.03	7110	< 0.2
08CO-03-RA	< 1	11.5	0.09	217	1080	0.2	0.02	< 0.2	1.7	<0.1	0.005	4.31	<0.5	< 0.5	0.82	0.03	7250	< 0.2
08CO-04-RA	< 1	11.4	0.06	218	1080	0.2	0.01	< 0.2	1.6	<0.1	< 0.005	4.23	<0.5	< 0.5	0.75	0.03	7350	< 0.2
08CO-05-RA	< 1	11.3	0.06	216	1080	0.2	0.01	< 0.2	1.6	<0.1	< 0.005	4.25	<0.5	< 0.5	0.76	0.03	7360	< 0.2
08CO-06-RA	< 1	11.4	0.07	217	1080	0.1	0.01	< 0.2	1.5	<0.1	< 0.005	4.19	<0.5	< 0.5	0.72	0.03	7380	< 0.2
08CO-07-RA	< 1	11.4	0.06	215	1070	0.1	0.01	< 0.2	1.4	<0.1	< 0.005	4.13	<0.5	< 0.5	0.73	0.02	7300	< 0.2
08CO-08-RA	< 1	11.3	0.11	214	1050	0.06	0.02	< 0.2	1.3	<0.1	0.007	4.8	<0.5	< 0.5	1.08	0.04	7410	< 0.2
08CO-09-RA	< 1	11.5	0.08	223	1080	0.1	0.01	< 0.2	1.5	<0.1	0.005	4.37	<0.5	< 0.5	0.77	0.03	7530	< 0.2
08CO-10-RA	< 1	12	0.09	227	1120	0.1	0.01	< 0.2	2.5	<0.1	0.005	4.57	<0.5	< 0.5	0.88	0.03	7690	< 0.2
08CO-11-RA	< 1	12	0.11	226	1110	0.1	0.02	< 0.2	2	<0.1	0.007	4.78	<0.5	< 0.5	1.03	0.04	7620	< 0.2
08CO-12-RA	< 1	13.2	0.84	226	1120	0.08	0.13	0.4	2.7	<0.1	0.05	11.7	<0.5	< 0.5	5.74	0.29	7840	< 0.2
08CO-13-RA	< 1	11.8	0.14	227	1110	0.08	0.02	< 0.2	2.8	<0.1	0.009	5.03	<0.5	< 0.5	1.18	0.05	7730	< 0.2
08CO-14-RA	< 1	13	0.46	224	1100	0.07	0.05	1.37	8.7	<0.1	0.01	5.34	0.7	< 0.5	1.56	0.08	7680	0.2
08CO-15-RA	< 1	11.9	0.08	224	1100	0.07	0.01	< 0.2	1.5	<0.1	0.005	4.44	<0.5	< 0.5	0.81	0.03	7700	< 0.2
08CO-16-RA	< 1	10.5	2.68	192	627	0.03	0.3	0.47	2.2	<0.1	0.076	5.8	<0.5	< 0.5	6.82	0.47	7890	< 0.2
08CO-17-RA	< 1	10.3	6.12	175	448	< 0.02	0.65	3.36	4.6	<0.1	0.16	9.38	<0.5	< 0.5	13.5	0.98	7900	< 0.2
08CO-18-RA	< 1	13.3	12.7	208	474	0.04	1.24	0.98	1.7	<0.1	0.3	22.2	<0.5	< 0.5	24.6	1.97	12100	< 0.2
08CO-19-RA	< 1	4.9	0.01	40	193	< 0.02	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	< 0.1	<0.5	< 0.5	0.03	< 0.005	242	< 0.2
08CO-20-RA	< 1	10.3	0.03	175	864	0.04	0.005	< 0.2	1.2	<0.1	< 0.005	0.21	<0.5	< 0.5	0.19	0.006	1700	< 0.2
08CO-21-RA	< 1	11.4	0.22	199	914	0.04	0.02	0.2	1.5	<0.1	0.006	1.75	<0.5	< 0.5	0.61	0.04	2660	< 0.2
08CO-22-RA	< 1	4.4	0.01	14	50.1	< 0.02	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	0.11	<0.5	< 0.5	0.05	< 0.005	46.9	< 0.2
08CO-23-RA	< 1	8.5	0.08	125	425	< 0.02	0.009	< 0.2	3.3	<0.1	< 0.005	0.17	<0.5	< 0.5	0.17	0.02	69.9	< 0.2
08CO-25-RA	< 1	< 0.2	< 0.01	2	< 0.5	< 0.02	< 0.005	< 0.2	< 0.5	<0.1	< 0.005	< 0.1	<0.5	< 0.5	< 0.01	< 0.005	1.1	< 0.2
08CO-26-RA	< 1	13.2	4.21	218	650	0.03	0.5	0.83	2.5	<0.1	0.13	8.16	<0.5	< 0.5	12	0.78	8730	< 0.2
08CO-pw1-0-RA	< 1	14	11.4	214	526	0.02	1.21	1.82	1.8	<0.1	0.29	16.2	<0.5	< 0.5	27.6	1.85	11500	< 0.2
08CO-pw2-0-RA	< 1	9.6	0.25	199	856	0.04	0.03	< 0.2	1.6	<0.1	< 0.005	0.72	<0.5	< 0.5	0.86	0.03	1670	< 0.2
08CO-pw3-0-RA	< 1	9.4	< 0.01	123	561	< 0.02	< 0.005	< 0.2	0.7	<0.1	< 0.005	< 0.1	<0.5	< 0.5	0.02	< 0.005	988	< 0.2

Appendix D. Bulk chemistry preferred values from ICP-AES for unfiltered samples from the Tunnel, Waste Rock Pile and Wetland.

Field No.	Ag ug/L	Al ug/L	As ug/L	B ug/L	Ba ug/L	Be ug/L	Ca mg/L	Cd ug/L	Co ug/L	Cr ug/L	Cu ug/L	Fe ug/L	K mg/L	Li ug/L	Mg mg/L	Mn ug/L	Mo ug/L	Na mg/L	Ni ug/L	P mg/L	Pb ug/L	Sb ug/L	Se ug/L	SiO_2 mg/L	SO4 mg/L	Sr ug/L	V ug/L	Zn ug/L
08CO-01-RA	<5	149	<50	<5	12.6	<10	89.9	19.8	<10	<10	139	838	1.13	7.84	17.2	11500	<20	4.22	33.2	<0.5	<50	<50	< 200	13.8	257	1060	<10	6610
08CO-02-RA	<5	150	<50	<5	12.6	<10	89.4	19.8	10.7	<10	146	881	1.14	6.96	17.1	11500	<20	4.26	32.7	<0.5	<50	<50	< 200	13.8	257	1070	<10	6620
08CO-03-RA	<5	150	<50	<5	12.7	<10	90.3	19.1	<10	<10	153	1090	1.13	7.95	16.7	11600	<20	4.16	31.6	<0.5	<50	<50	< 200	13.5	250	1070	<10	6450
08CO-04-RA	<5	140	<50	<5	13.1	<10	85.2	18.3	<10	<10	156	872	1.08	7.15	16.5	11300	<20	4.4	32.8	<0.5	<50	<50	< 200	13.8	256	1090	<10	6480
08CO-05-RA	<5	145	<50	<5	13.6	<10	90.2	18.6	<10	<10	161	936	1.14	7.57	17	11900	<20	4.49	32.9	<0.5	<50	<50	< 200	14.3	264	1140	<10	6650
08CO-06-RA	<5	142	<50	<5	13.4	<10	89.9	19	<10	<10	162	885	1.07	8.38	16.8	11900	<20	4.47	33.4	<0.5	<50	<50	< 200	14.2	262	1140	<10	6690
08CO-07-RA	<5	140	<50	<5	13.5	<10	86.9	18.6	10.4	<10	161	886	1.14	6.04	16.7	11600	<20	4.56	32.2	<0.5	<50	<50	< 200	14	259	1130	<10	6640
08CO-08-RA	<5	165	<50	<5	15.3	<10	90.9	19.4	12	<10	225	1720	1.17	6.84	16.5	12700	<20	4.58	35.9	<0.5	<50	<50	< 200	14.2	259	1170	<10	6820
08CO-09-RA	<5	144	<50	<5	13.6	<10	87.6	18.9	<10	<10	162	952	1.09	7.23	16.7	11900	<20	4.47	32.5	<0.5	<50	<50	< 200	14.1	261	1130	<10	6590
08CO-10-RA	<5	175	<50	<5	13.5	<10	88	18.2	<10	<10	165	1100	1.12	7.79	16.3	11900	<20	4.37	34.4	<0.5	<50	<50	< 200	14	255	1120	<10	6440
08CO-11-RA	<5	159	<50	<5	13.4	<10	85.3	18	<10	<10	185	1560	1.07	7.17	16.2	11300	<20	4.5	31.3	<0.5	<50	<50	< 200	13.8	254	1130	<10	6460
08CO-12-RA	<5	350	<50	<5	14.9	<10	84.4	19.9	11.4	<10	662	12700	1.1	7.27	16.3	11600	<20	4.5	30.4	<0.5	93.3	<50	< 200	15.3	253	1120	<10	6680
08CO-13-RA	<5	221	<50	<5	15	<10	90.8	19.6	11	<10	204	1920	1.2	8.23	16.7	12400	<20	4.55	33.8	<0.5	<50	<50	< 200	14.7	267	1170	<10	6660
08CO-14-RA	<5	1680	<50	<5	40	<10	88.1	18.8	10.7	<10	189	3470	2.06	8.43	16.4	12000	<20	4.63	35.1	<0.5	452	<50	< 200	18.6	257	1190	<10	6650
08CO-15-RA	<5	142	<50	<5	13.6	<10	85.9	18.3	10.5	<10	157	953	1.09	8.22	16.1	12000	<20	4.5	32.6	<0.5	<50	<50	< 200	13.9	255	1140	<10	6540
08CO-16-RA	<5	1320	<50	<5	23.8	<10	51.9	31	<10	<10	1030	1850	1	5.75	14	5850	<20	3.14	34.1	<0.5	230	<50	< 200	13	229	702	<10	6880
08CO-17-RA	<5	1980	<50	<5	50	<10	39.6	34	11.4	<10	1050	4460	1.09	5.67	13.2	7870	<20	2.62	34	<0.5	335	<50	< 200	12.6	208	503	<10	6880
08CO-18-RA	<5	4230	<50	<5	18.9	<10	45	49.6	16.6	<10	1990	1390	1.05	5.66	15.4	11400	<20	2.65	48.7	<0.5	593	<50	< 200	17	254	515	<10	10400
08CO-19-RA	<5	32	<50	<5	13.8	<10	16	<5	<10	<10	<10	79.1	0.213	<5	2.99	21	<20	1.54	<10	<0.5	<50	<50	< 200	5.56	46	213	<10	213
08CO-20-RA	<5	66	<50	<5	8.83	<10	63.7	<5	<10	<10	<10	<20	1.06	5.38	12.5	<10	<20	3.79	<10	<0.5	<50	<50	< 200	12.1	204	937	<10	1500
08CO-21-RA	<5	169	<50	<5	8.28	<10	73.8	5.11	<10	<10	32.9	173	1.1	6.46	13.9	821	<20	4.02	10	<0.5	<50	<50	< 200	12.7	225	1030	<10	2320
08CO-22-RA	<5	<20	<50	<5	10.7	<10	6.18	<5	<10	<10	<10	<20	0.288	<5	1.05	<10	<20	1.09	<10	<0.5	<50	<50	< 200	4.49	13.7	61.5	<10	40.8
08CO-23-RA	<5	114	<50	25.2	35.4	<10	33.7	<5	<10	<10	<10	2390	1.42	<5	7.87	1190	<20	13.8	<10	<0.5	<50	<50	< 200	8.34	129	448	<10	62.9
08CO-25-RA	<5	<20	<50	<5	1.28	<10	<0.1	<5	<10	<10	<10	<20	<0.1	<5	<0.1	<10	<20	<0.1	<10	<0.5	<50	<50	< 200	<0.1	< 1	<1	<10	<20
08CO-26-RA	<5	1800	<50	<5	23.5	<10	52.8	32.3	11	<10	1000	2430	1.21	5.05	14.6	8100	<20	3.29	39.6	<0.5	227	<50	< 200	14	245	707	<10	7380
08CO-pw1-0-RA	<5	3450	<50	<5	19.9	<10	44.4	33.7	14.5	<10	1210	2480	0.9	6.12	14.7	10400	<20	2.69	49.4	<0.5	335	<50	< 200	15.6	239	554	<10	9170
08CO-pw2-0-RA	<5	87.4	<50	<5	8.66	<10	70.7	<5	<10	<10	311	<20	1.12	<5	14.1	12.3	<20	3.85	<10	<0.5	<50	<50	< 200	10.9	225	952	<10	1480
08CO-pw3-0-RA	<5	62.4	<50	<5	16	<10	45.6	<5	<10	<10	<10	<20	0.664	<5	8.64	<10	<20	3.19	<10	<0.5	<50	<50	< 200	10.2	142	680	<10	915

Appendix E. Bulk chemistry values from ICP-AES for filtered (0.1µm) samples from the Tunnel, Waste Rock Pile and Wetland.

Site No.	Ag	Al	As	B	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	Sb	Se	SiO_2	SO4	Sr	V	Zn
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	ug/L	mg/L	ug/L	ug/L	mg/L	ug/L	mg/L	ug/L	ug/L	ug/L	mg/L	mg/L	ug/L	ug/L	ug/L
08CO-01-.1FA	<5	104	<50	<5	14.2	<10	99.9	20.6	<10	<10	97.3	25.5	1.28	9.95	18.1	13400	<20	4.92	37.3	<0.5	<50	<50	< 200	15.5	290	1220	<10	6550
08CO-02-.1FA	<5	110	<50	<5	13	<10	91.5	18.8	<10	<10	42.8	32.4	1.19	7.04	16.7	12300	<20	4.48	35.3	<0.5	<50	<50	< 200	14.3	268	1110	<10	6510
08CO-03-.1FA	<5	120	<50	<5	13.3	<10	92.5	18.7	<10	<10	63.9	43.3	1.25	7.24	16.8	12400	<20	4.53	32	<0.5	<50	<50	< 200	14.2	265	1130	<10	6590
08CO-04-.1FA	<5	123	<50	<5	13.4	<10	89.4	18.6	10.5	<10	69.6	49.3	1.23	6.78	16.7	12100	<20	4.52	33.4	<0.5	<50	<50	< 200	14.3	266	1100	<10	6550
08CO-05-.1FA	<5	133	<50	<5	13.3	<10	93.2	19.3	<10	<10	117	55.7	1.23	8.17	16.9	12600	<20	4.66	32.8	<0.5	<50	<50	< 200	14.4	270	1130	<10	6720
08CO-06-.1FA	<5	123	<50	<5	13.1	<10	90.1	19.6	<10	<10	84.6	56.1	1.23	7.31	16.8	12200	<20	4.41	33.2	<0.5	<50	<50	< 200	14	264	1070	<10	6580
08CO-07-.1FA	<5	129	<50	<5	13.2	<10	89.6	18.9	<10	<10	83.3	62	1.14	5.47	16.6	12200	<20	4.42	34	<0.5	<50	<50	< 200	14	263	1080	<10	6210
08CO-08-.1FA	<5	129	<50	<5	13.3	<10	92	19.7	<10	<10	125	63.1	1.14	7.59	16.7	12700	<20	4.35	33.2	<0.5	<50	<50	< 200	14.2	265	1080	<10	6590
08CO-09-.1FA	<5	133	<50	<5	13.2	<10	94.6	19.9	<10	<10	92.3	77.6	1.17	7.19	17.2	13200	<20	4.28	35.5	<0.5	<50	<50	< 200	14.3	269	1070	<10	6690
08CO-10-.1FA	<5	130	<50	<5	13.2	<10	91.7	18.9	<10	<10	91	61.1	1.26	7.05	16.7	12600	<20	4.28	34.8	<0.5	<50	<50	< 200	14	262	1050	<10	6620
08CO-11-.1FA	<5	131	<50	<5	13.1	<10	89.4	19.4	<10	<10	84.1	45.3	1.21	7.63	17	12100	<20	4.36	34.1	<0.5	<50	<50	< 200	14.2	266	1040	<10	6530
08CO-13-.1FA	<5	128	<50	<5	13.2	<10	91.1	18.8	<10	<10	88.3	67.9	1.17	6.06	16.6	12500	<20	4.31	32.2	<0.5	<50	<50	< 200	13.9	260	1060	<10	6550
08CO-15-.1FA	<5	131	<50	<5	13.3	<10	91	19.6	10.8	<10	122	57.6	1.26	6.8	16.7	12900	<20	4.31	35.1	<0.5	<50	<50	< 200	14.3	264	1050	<10	6550
08CO-16-.1FA	<5	1380	<50	<5	13.8	<10	56.8	33.6	<10	<10	1070	225	0.914	5.17	14.8	6350	<20	3.04	36.5	<0.5	77.9	<50	< 200	13.3	239	666	<10	7070
08CO-17-.1FA	<5	2030	<50	<5	14.1	<10	39	36.6	12	<10	1050	822	0.8	<5	13.7	7770	<20	2.52	35.9	<0.5	114	<50	< 200	12.5	214	438	<10	6740
08CO-18-.1FA	<5	4610	<50	<5	17.4	<10	47.7	53.8	17.8	<10	2080	488	0.958	6.96	16	12100	<20	2.49	55.5	<0.5	587	<50	< 200	17.6	265	476	<10	10500
08CO-19-.1FA	<5	<20	<50	<5	14.3	<10	17.1	<5	<10	<10	<10	33.9	0.107	<5	3.29	23	<20	1.56	<10	<0.5	<50	<50	< 200	6.11	50.8	203	<10	217
08CO-20-.1FA	<5	62	<50	<5	8.92	<10	69.4	<5	<10	<10	<10	<20	1.16	<5	12.8	<10	<20	3.64	<10	<0.5	<50	<50	< 200	12.7	212	881	<10	1490
08CO-21-.1FA	<5	56.1	<50	<5	7.38	<10	75.2	5.49	<10	<10	19.9	<20	0.968	<5	14.2	836	<20	3.59	<10	<0.5	<50	<50	< 200	12.7	224	866	<10	2270
08CO-22-.1FA	<5	<20	<50	<5	9.81	<10	6.34	<5	<10	<10	<10	<20	0.349	<5	1.07	<10	<20	0.922	<10	<0.5	<50	<50	< 200	4.49	13.6	51.6	<10	35.3
08CO-25-.1FA	<5	<20	<50	<5	<1	<10	<0.1	<5	<10	<10	<10	<20	<0.1	<5	<0.1	<10	<20	<0.1	<10	<0.5	<50	<50	< 200	<0.1	< 1	<1	<10	<20
08CO-26-.1FA	<5	1900	<50	<5	20.5	<10	53.1	36	10.6	<10	1040	1840	0.889	5.25	15	8140	<20	2.84	41.8	<0.5	192	<50	< 200	14	245	595	<10	7340
08CO-pw1-0-.1FA	<5	3900	<50	<5	17.8	<10	48.9	37.9	15.1	<10	1260	1470	0.724	7.54	15.6	11300	<20	2.48	50.5	<0.5	305	<50	< 200	16.3	247	503	<10	9330
08CO-pw2-0-.1FA	<5	80.2	<50	<5	8.12	<10	73	<5	<10	<10	24	<20	0.99	<5	14.7	<10	<20	3.37	<10	<0.5	<50	<50	< 200	11.1	227	772	<10	1470
08CO-pw3-0-.1FA	<5	55.6	<50	<5	14.5	<10	46.3	<5	<10	<10	<10	<20	0.618	<5	9.17	<10	<20	2.79	<10	<0.5	<50	<50	< 200	10.3	142	540	<10	894

Appendix F. (continued on next page) Bulk chemistry values from ICP-MS for filtered (0.1µm) samples from the Tunnel, Waste Rock Pile and Wetland.

Site No.	Ag ug/L	Al ug/L	As ug/L	Ba ug/L	Be ug/L	Bi ug/L	Ca mg/L	Cd ug/L	Ce ug/L	Co ug/L	Cr ug/L	Cs ug/L	Cu ug/L	Dy ug/L	Er ug/L	Eu ug/L	Fe ug/L	Ga ug/L	Gd ug/L	Ge ug/L	Ho ug/L	K mg/L	La ug/L	Li ug/L	Lu ug/L	Mg mg/L	Mn ug/L	Mo ug/L
08CO-01-.1FA	<1	79.4	<1	11.8	0.7	< 0.2	88.4	17.2	0.1	8.5	<1	0.19	92.7	0.009	0.008	< 0.005	<50	0.1	0.008	< 0.05	< 0.005	1.12	0.14	5	< 0.1	13.9	11500	< 2
08CO-02-.1FA	<1	88.7	<1	11.9	0.6	< 0.2	88.8	17.1	0.06	8.49	<1	0.19	44.8	< 0.005	0.005	< 0.005	<50	0.1	< 0.005	< 0.05	< 0.005	1.11	0.1	5.5	< 0.1	14.2	11400	< 2
08CO-03-.1FA	<1	102	<1	12.3	0.7	< 0.2	91.8	17.8	0.09	8.84	<1	0.19	63.9	0.006	0.006	< 0.005	<50	0.1	0.005	< 0.05	< 0.005	1.16	0.14	5.5	< 0.1	14.7	11900	< 2
08CO-04-.1FA	<1	106	<1	12.4	0.7	< 0.2	91.5	17.9	0.1	8.87	<1	0.2	71.2	0.006	0.008	< 0.005	65	0.1	0.007	< 0.05	< 0.005	1.17	0.16	5.7	< 0.1	14.9	12000	< 2
08CO-05-.1FA	<1	106	<1	12.4	0.7	< 0.2	91.3	18.2	0.14	8.91	<1	0.2	116	0.01	0.01	< 0.005	58	0.1	0.01	< 0.05	< 0.005	1.16	0.19	5.6	< 0.1	14.8	12000	< 2
08CO-06-.1FA	<1	108	<1	12.6	0.8	< 0.2	92.4	18.3	0.13	9.04	<1	0.2	86.6	0.01	0.008	< 0.005	64	0.1	0.007	< 0.05	< 0.005	1.18	0.18	5.6	< 0.1	15	12200	< 2
08CO-07-.1FA	<1	109	<1	12.5	0.7	< 0.2	92.2	18.3	0.14	8.95	<1	0.2	89.6	0.01	0.01	< 0.005	74	0.1	0.01	< 0.05	< 0.005	1.17	0.19	5.8	< 0.1	15.2	12100	< 2
08CO-08-.1FA	<1	111	<1	12.4	0.7	< 0.2	90.8	18.5	0.17	9.07	<1	0.2	125	0.02	0.01	< 0.005	64	0.1	0.01	< 0.05	< 0.005	1.16	0.22	5.9	< 0.1	15.3	12100	< 2
08CO-09-.1FA	<1	107	<1	12.1	0.8	< 0.2	87.4	17.5	0.14	8.89	<1	0.2	88	0.01	0.008	< 0.005	74	0.1	0.009	< 0.05	< 0.005	1.13	0.18	5.6	< 0.1	14.4	11900	< 2
08CO-10-.1FA	<1	109	<1	12.4	0.7	< 0.2	89.6	18	0.15	9.04	<1	0.2	92.3	0.01	0.01	< 0.005	64	0.1	0.01	< 0.05	< 0.005	1.25	0.2	5.7	< 0.1	14.8	12000	< 2
08CO-11-.1FA	<1	105	<1	12	0.7	< 0.2	88.8	17.5	0.12	8.74	<1	0.19	83	0.01	0.006	< 0.005	<50	0.1	0.009	< 0.05	< 0.005	1.14	0.18	5.2	< 0.1	14.6	11700	< 2
08CO-13-.1FA	<1	114	<1	12.6	0.8	< 0.2	92.4	18.6	0.15	9.29	<1	0.2	91.7	0.01	0.01	< 0.005	74	0.1	0.01	< 0.05	< 0.005	1.19	0.2	6	< 0.1	15.4	12300	< 2
08CO-15-.1FA	<1	115	<1	13	0.7	< 0.2	91.2	18.6	0.2	9.41	<1	0.21	123	0.02	0.01	< 0.005	<50	0.1	0.02	< 0.05	< 0.005	1.19	0.24	5.3	< 0.1	14.8	12600	< 2
08CO-16-.1FA	<1	1210	<1	12.8	0.9	< 0.2	53.9	31	31.5	1.79	<1	0.15	1060	1.52	0.66	0.48	211	0.55	2.44	0.08	0.26	0.92	16.8	3.5	< 0.1	12.6	5800	< 2
08CO-17-.1FA	<1	1750	<1	12.9	1	< 0.2	38.4	33.1	86.3	11	<1	0.17	1060	3.36	1.38	1.08	865	1.4	5.38	0.2	0.55	0.78	38	2.4	0.1	11.5	7500	< 2
08CO-18-.1FA	<1	3870	<1	16.2	2.6	< 0.2	46.5	47.8	184	15.7	<1	0.08	2080	6.56	2.79	2.23	501	3	10.8	0.37	1.05	0.92	78.4	3.8	0.3	13.2	11800	< 2
08CO-19-.1FA	<1	23.9	<1	12.8	<0.05	< 0.2	15.9	0.53	0.05	<0.02	<1	< 0.02	2.5	0.007	< 0.005	< 0.005	<50	< 0.05	0.006	< 0.05	< 0.005	0.2	0.05	< 0.1	< 0.1	2.86	19	< 2
08CO-20-.1FA	<1	51.7	<1	8.26	0.1	< 0.2	64.5	3.14	< 0.01	<0.02	<1	0.04	4	0.02	0.009	0.006	<50	< 0.05	0.03	< 0.05	< 0.005	1	0.47	2.6	< 0.1	10.4	<0.2	< 2
08CO-21-.1FA	<1	39.9	<1	7.19	0.2	< 0.2	73.1	5.31	1.27	0.35	<1	0.08	24.9	0.058	0.02	0.02	<50	< 0.05	0.092	< 0.05	0.01	1	1.52	3.9	< 0.1	11.4	791	< 2
08CO-22-.1FA	<1	3.5	<1	9.15	<0.05	< 0.2	5.85	0.2	< 0.01	<0.02	<1	0.03	<0.5	0.006	< 0.005	< 0.005	<50	< 0.05	0.009	< 0.05	< 0.005	0.32	0.03	< 0.1	< 0.1	0.92	<0.2	< 2
08CO-25-.1FA	<1	<2	<1	<0.2	<0.05	< 0.2	<0.2	<0.02	< 0.01	<0.02	<1	< 0.02	<0.5	< 0.005	< 0.005	< 0.005	<50	< 0.05	< 0.005	< 0.05	< 0.005	<0.03	< 0.01	< 0.1	< 0.1	<0.01	<0.2	< 2
08CO-26-.1FA	<1	1710	<1	20.8	1.3	< 0.2	54.3	33	58.7	9.82	<1	0.09	1080	2.66	1.13	0.82	2060	1	4.18	0.2	0.44	0.96	30.9	3.4	0.1	13	8150	< 2
08CO-pw1-0-.1FA	<1	3360	<1	17.3	2.1	< 0.2	46.2	33.8	172	14.4	<1	0.09	1280	6.08	2.52	2	1560	2.8	10.1	0.35	0.99	0.79	82.6	3.6	0.2	13	10400	< 2
08CO-pw2-0-.1FA	<1	65.9	<1	8.04	0.2	< 0.2	69.9	2.75	0.67	<0.02	<1	0.04	29	0.072	0.03	0.02	<50	< 0.05	0.14	< 0.05	0.01	0.95	2.98	2.5	< 0.1	12	6.8	< 2
08CO-pw3-0-.1FA	<1	47.5	<1	14.3	0.09	< 0.2	44.5	2.24	< 0.01	<0.02	<1	< 0.02	5.4	< 0.005	< 0.005	< 0.005	<50	< 0.05	0.005	< 0.05	< 0.005	0.58	0.04	1.1	< 0.1	7.54	<0.2	< 2

Appendix F. (continued) Bulk chemistry preferred values from ICP-MS for filtered (0.1µm) samples from the Tunnel, Waste Rock Pile and Wetland.

Site No.	Na mg/L	Nb ug/L	Nd ug/L	Ni ug/L	P mg/L	Pb ug/L	Pr ug/L	Rb ug/L	Sb ug/L	Sc ug/L	Se ug/L	SiO_2 mg/L	Sm ug/L	SO_4 mg/L	Sr ug/L	Ta ug/L	Tb ug/L	Th ug/L	Ti ug/L	Tl ug/L	Tm ug/L	U ug/L	V ug/L	W ug/L	Y ug/L	Yb ug/L	Zn ug/L	Zr ug/L
08CO-01-.1FA	3.51	<0.2	0.03	30.2	<0.01	0.09	<0.01	2.37	<0.3	1.2	<1	13.2	<0.01	264	984	0.1	<0.005	<0.2	2.2	<0.1	<0.005	3.6	<0.5	<0.5	0.29	0.008	7030	<0.2
08CO-02-.1FA	3.62	<0.2	0.01	29.9	<0.01	<0.05	<0.01	2.4	0.71	1.2	<1	13.2	<0.01	266	1000	0.1	<0.005	<0.2	2.2	<0.1	<0.005	2.7	<0.5	<0.5	0.17	<0.005	7350	<0.2
08CO-03-.1FA	3.67	<0.2	0.02	31.2	<0.01	0.05	<0.01	2.49	0.57	1.2	<1	13.7	<0.01	271	1040	0.1	<0.005	<0.2	2.3	<0.1	<0.005	2.51	<0.5	<0.5	0.24	0.005	7400	<0.2
08CO-04-.1FA	3.71	<0.2	0.02	31.5	<0.01	<0.05	<0.01	2.46	0.48	1.2	<1	13.8	<0.01	270	1040	0.1	<0.005	<0.2	2.2	<0.1	<0.005	2.45	<0.5	<0.5	0.28	<0.005	7310	<0.2
08CO-05-.1FA	3.83	<0.2	0.04	31.5	<0.01	0.09	0.01	2.49	<0.3	1.2	<1	13.8	<0.01	274	1040	0.1	<0.005	<0.2	2.3	<0.1	<0.005	3.06	<0.5	<0.5	0.36	0.007	7560	<0.2
08CO-06-.1FA	3.76	<0.2	0.03	31.5	<0.01	0.05	0.01	2.5	0.32	1.2	<1	14	<0.01	279	1040	0.1	<0.005	<0.2	2.3	<0.1	<0.005	2.86	<0.5	<0.5	0.31	0.005	7600	<0.2
08CO-07-.1FA	3.77	<0.2	0.03	31.5	<0.01	0.1	0.01	2.48	0.48	1.2	<1	13.9	<0.01	276	1030	0.1	<0.005	<0.2	2.3	<0.1	<0.005	2.93	<0.5	<0.5	0.32	0.007	7590	<0.2
08CO-08-.1FA	3.74	<0.2	0.04	30.8	<0.01	<0.05	0.01	2.48	<0.3	1.2	<1	13.7	<0.01	275	1030	0.09	<0.005	<0.2	2.1	<0.1	<0.005	3.5	<0.5	<0.5	0.4	0.01	7760	<0.2
08CO-09-.1FA	3.61	<0.2	0.03	30.2	<0.01	0.09	<0.01	2.4	1.84	1.2	<1	13.3	<0.01	264	987	0.07	<0.005	<0.2	2.3	<0.1	<0.005	1.54	<0.5	<0.5	0.3	<0.005	7230	<0.2
08CO-10-.1FA	3.69	<0.2	0.04	30.7	<0.01	0.2	0.01	2.41	0.44	1.2	<1	13.6	<0.01	272	1010	0.06	<0.005	<0.2	2.3	<0.1	<0.005	2.5	<0.5	<0.5	0.33	<0.005	7460	<0.2
08CO-11-.1FA	3.65	<0.2	0.03	30.3	<0.01	<0.05	0.01	2.39	0.5	1.2	<1	13.4	<0.01	270	998	0.06	<0.005	<0.2	2.2	<0.1	<0.005	2.34	<0.5	<0.5	0.31	0.006	7330	<0.2
08CO-13-.1FA	3.84	<0.2	0.04	31.7	<0.01	0.05	0.01	2.47	0.53	1.2	<1	14	<0.01	280	1040	0.06	<0.005	<0.2	2.3	<0.1	<0.005	2.29	<0.5	<0.5	0.34	0.005	7780	<0.2
08CO-15-.1FA	3.72	0.64	0.05	31.8	<0.01	0.08	0.02	2.6	1.14	1.2	<1	14.4	0.01	260	1070	0.52	<0.005	<0.2	2.4	<0.1	<0.005	3.74	<0.5	0.98	0.41	0.01	7900	<0.2
08CO-16-.1FA	2.52	0.31	16.5	32.9	<0.01	84.5	4.14	2.47	0.62	1.4	<1	13	2.89	223	654	0.24	0.32	0.31	2	<0.1	0.076	5.57	<0.5	0.52	7.09	0.47	8580	<0.2
08CO-17-.1FA	2.02	0.22	38.9	32.2	<0.01	108	10.1	2.17	0.42	1.6	<1	12.2	6.41	197	442	0.2	0.69	2.18	1.9	<0.1	0.16	8.94	<0.5	<0.5	13.4	1.01	8260	<0.2
08CO-18-.1FA	2.02	0.21	82.9	49.5	<0.01	577	21	3.72	0.34	1.9	1.1	16.9	13.4	240	481	0.2	1.36	0.84	2.1	<0.1	0.32	21.4	<0.5	<0.5	25.4	2.03	12700	<0.2
08CO-19-.1FA	1.31	<0.2	0.04	1	<0.01	0.1	0.01	0.52	<0.3	<0.6	<1	5.6	<0.01	40	192	0.08	<0.005	<0.2	<0.5	<0.1	<0.005	<0.1	<0.5	<0.5	0.03	<0.005	244	<0.2
08CO-20-.1FA	2.9	<0.2	0.19	4.3	<0.01	<0.05	0.05	2.41	<0.3	0.9	<1	12.3	0.02	192	814	0.2	<0.005	<0.2	2.1	<0.1	<0.005	0.19	<0.5	<0.5	0.18	0.006	1660	<0.2
08CO-21-.1FA	2.94	<0.2	0.82	10	<0.01	0.93	0.22	2.47	<0.3	1	<1	13	0.11	219	866	0.2	0.01	<0.2	2.2	<0.1	<0.005	1.23	<0.5	<0.5	0.35	0.01	2620	<0.2
08CO-22-.1FA	0.83	<0.2	0.04	<0.4	<0.01	<0.05	<0.01	0.67	<0.3	<0.6	<1	4.2	<0.01	11	50	0.04	<0.005	<0.2	<0.5	<0.1	<0.005	<0.1	<0.5	<0.5	0.04	<0.005	45.3	<0.2
08CO-25-.1FA	<0.01	<0.2	<0.01	<0.4	<0.01	<0.05	<0.01	<0.01	<0.3	<0.6	<1	<0.2	<0.01	<2	<0.5	0.04	<0.005	<0.2	<0.5	<0.1	<0.005	<0.1	<0.5	<0.5	<0.01	<0.005	<0.5	<0.2
08CO-26-.1FA	2.49	<0.2	27.5	40.5	<0.01	197	7.22	2.62	<0.3	1.4	<1	14.8	4.35	246	633	0.1	0.54	0.73	2.4	<0.1	0.13	7.44	<0.5	<0.5	11.9	0.82	8990	<0.2
08CO-pw1-0-.1FA	2.11	<0.2	73.8	46.6	<0.01	317	19.3	2.71	<0.3	1.8	1.1	16.2	11.6	233	507	0.1	1.26	1.59	2.1	<0.1	0.3	14.5	<0.5	<0.5	26.8	1.82	11500	<0.2
08CO-pw2-0-.1FA	2.95	<0.2	1.12	5.4	<0.01	0.2	0.33	2.08	<0.3	0.8	<1	10.8	0.13	209	820	0.1	0.01	<0.2	2.1	<0.1	<0.005	0.58	<0.5	<0.5	0.59	0.02	1690	<0.2
08CO-pw3-0-.1FA	2.44	<0.2	0.02	3.4	<0.01	0.1	<0.01	1.27	<0.3	0.8	<1	10.2	<0.01	132	570	0.08	<0.005	<0.2	1.5	<0.1	<0.005	<0.1	<0.5	<0.5	0.02	<0.005	1040	<0.2

CURRICULUM VITA

Suzan Aranda Luna was born in Lima, Peru. She attended the Universidad National del Callao in Lima where she graduated first in her class with a Bachelor's degree in Fishing Engineering in 2004. She worked mostly in the field of aquaculture and seafood production. She and a group of colleuges started the Killamar Company in 2003, geared to developing and selling seafood derived products to those living in poverty. With a personal drive to continue helping those in economic distress, she decided to study English so as to effectively network with other international agencies willing to help this noble cause. In 2008, she joined the master program at The University of Texas at El Paso. Her research was guided by David M. Borrok, PhD with the goal to study the environmental impact of metal contamination in soil and water near the Waldorf Mine in Colorado. Using copper and zinc isotopes, she was able to analyze the level of contamination at the Waldorf Mine, and those results will soon be published in the Geochemical Journal. She received her Master of Science degree with major in Geological Science in 2010.

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