ENVIRON

Preliminary Risk Screening of Metals Discharged from the Elkoro Mine Adit into the West Fork Jarbidge River, Nevada

Prepared For:
USFWS Bull Trout Recovery Team

Prepared By:
Jeffrey P. Fisher, Ph.D.

ENVIRON International Corporation
Seattle, WA

ABSTRACT

The potential ecotoxicological effects of an adit discharge into the West Fork Jarbidge River from the abandoned Elkoro Mine were examined as part of a broader study evaluating the feasibility of bull trout habitat restoration options in the drainage. Sampling consisted of the collection of water and sediment samples upstream, within and downstream of the adit, and the deployment of multiplate samplers with coincident temperature loggers to measure macroinvertebrate colonization and diversity and temperature variance, respectively. This preliminary report summarizes the analytical results from a subset of the water samples collected and all of the sediment samples. The mulitplates for examining macroinvertebrate colonization and diversity and the temperature monitoring devices installed in the late autumn sampling period of 2006 are still deployed and will be retrieved in the late summer of 2007.

The adit contributes a significant loading of arsenic, manganese, iron, zinc and sulfate to the West Fork Jarbidge River, based on comparison of water samples from reference stations upstream. Although mercury was detected above water quality criteria in the drainage above and below the adit, the adit does not appear to contribute mercury loading to the river. Principal risk drivers to bull trout health and habitat from the Elkoro adit are associated with the discharge of iron and, to a lesser extent, sulfate, based on comparisons to water and sediment quality screening criteria. Potential effects from these constituents are more likely attributed to the habitat impairment they cause on substrate condition and food web dynamics, as opposed to direct toxicity, but biological sampling must be completed to confirm this supposition. Loadings of zinc and manganese from the adit, while significantly above baseline concentrations in the basin, did not result in exceedances of water quality criteria at the baseflows and hardness measured. Other metal constituents analyzed from the adit discharge were either at concentrations less than measured in samples from elsewhere in the river, below detection limits, or well below risk screening guidelines. Sediment concentrations of iron are extremely high in the adit, representing nearly 50% of the dry weight of the sediments sampled. Sediment iron concentrations exceeded effects thresholds in all adit samples and in two of three sediment samples taken from the adit mixing zone downstream. Other constituents of concern in the sediments of the adit that exceeded sediment effects thresholds included arsenic, manganese, silver and zinc; these latter results mirrored somewhat the results of the water sampling.

INTRODUCTION

The Jarbidge River bull trout *Salvelinus confluentus* is recognized as a distinct population segment (DPS) of the species by the US Fish and Wildlife Service (USFWS) due to its geographic and reproductive isolation from the rest of the Snake River basin for over 100 years. The population was listed as endangered by the USFWS on August 10, 1998, but reclassified to threatened on April 8, 1999. Numerous factors have contributed to the depressed status of this population, including impacts in the Jarbidge basin from historic mining, dams impeding access to historically accessible habitat, agricultural water diversions that reduced otherwise accessible aquatic habitat and habitat quality, and livestock grazing and road building that contributed to sedimentation and other water quality problems (McNeill et al. 1997). As part of the Jarbidge Recovery Plan for the Jarbidge Bull Trout DPS (Fed Reg. 69:126), the Jarbidge bull trout recovery team (JBTRT) is exploring habitat restoration options near the town of Jarbidge that could benefit the species. In examining these options the JBTRT recognized the need to further understand the potential effects of an adit discharge from the historic Elkoro Mine that flows continuously into the West Fork Jarbidge River within the reach of river that flows through the town, a short distance upstream of the reach envisioned for habitat restoration.

Past water quality studies over a broader region in the basin examined water quality from the adit and downstream of the adit, as well as two other upstream locations associated with other past mine actions unrelated to the Elkoro mine adit discharge. In this past sampling the detection limits were not adequate to determine if chronic standards, the applicable metric from which to gauge potential effects from a continuous discharge, were exceeded for cadmium, lead silver and mercury. Further, no analyses of aluminum, TDS or sulfate were conducted, nor were chromium and arsenic speciation examined. Thus, the principal objective of this study was to determine whether metals or metalloids were entering the river at concentrations from the adit that could potentially limit the use of downstream areas under consideration for habitat restoration. The potential limitations considered through the sampling summarized here focused on determining whether the adit currently discharges metal and/or metalloid constituents at concentrations that could be directly toxic to the bull trout, as interpreted by the exceedance of state or federal water quality criteria (NAC 445A.144 or EPA 822-Z-99-001) or other relevant sediment toxicity reference values (e.g., MacDonald et al. 2000), or through indirect means, via the discharge of constituents that might affect food web dynamics (e.g., macroinvertebrate production/ diversity) but otherwise not cause direct toxicity—in this case, macroinvertebrate colonization and diversity.

METHODS & RATIONALE

Water Sample Collection and Processing

Water sampling was conducted at six stations on the West Fork Jarbidge River from November 30 to December 1, 2006 (Figure 1). Conventional water quality parameters of dissolved oxygen, pH, temperature and conductivity were measured *in situ* at each station using a YSI model 660 EDS data sonde. The data sonde was calibrated prior to deployment by Rapid Creek Research (Boise, Idaho), from whom the instrument was rented. pH calibrations were conducted in the field immediately prior to use with a two-point calibration buffer system (pH 7.0 and pH 4.0). Station location waypoints were determined with a Garmin^{tm} Legend Cx Global Positioning System device with an accuracy of 2 meters under optimum conditions (Table 1).

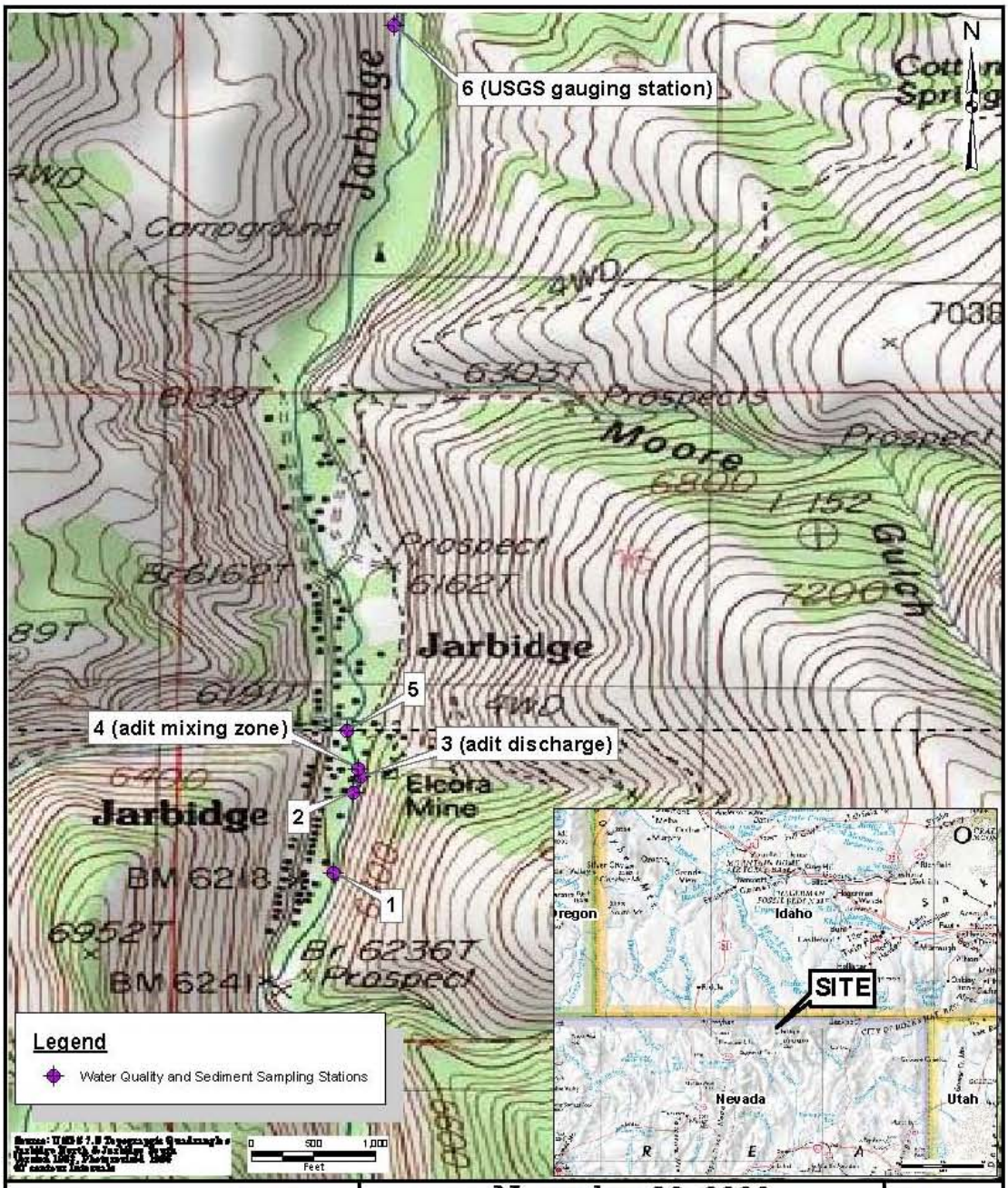
Water samples were collected in triplicate 1 gallon polyethylene jugs at each sample station (Table 1). Prior to collection, each sample collection jug was pre-rinsed three times with deionized water and then rinsed three times with river water at the sampling station. Field personnel wore polyethylene gloves, and these were changed between sample stations. Of the triplicate samples collected at each station, two of the samples were analyzed for dissolved metals and metalloids and the remaining sample was archived, with the exception of Station 4—where all three samples were analyzed. An archive sample was not collected at Station 4 because this station, immediately downstream and within the mixing zone of the adit discharge (station 3), was hypothesized to exhibit the greatest variation in concentrations across the channel among the station locations where triplicate samples were collected (Figure 2). Dissolved metals and metalloids (arsenic) were analyzed in all samples collected that were not archived. Water samples were archived as a cost savings measure to allow early interpretation of data from the duplicate samples, and a decision point from which further analysis could be determined to be warranted.

In addition to the analyses of dissolved metals performed on all samples collected that were not archived, two samples, one from the reference station just upstream of the adit (station 2), and one within the adit discharge (station 3) were also analyzed for total metals. These analyses were performed in order to gauge the ratio of total to the dissolved forms of the metals at these stations. Finally, to gain an understanding of metal speciation, aliquots of samples from four stations were analyzed for arsenic speciation, and all samples were analyzed for chromium speciation (hexavalent chromium).

Samples for dissolved metals were transferred to laboratory-provided vessels following collection and immediately placed on ice packs, with the exception of the samples from which arsenic speciation was sought. Arsenic speciation field kits were provided in the field, requiring field filtration through resin-filled syringes directly into laboratory-provided vessels. Each sample vessel provided by the laboratory was rinsed three times with a portion of the 1 gallon stock sample prior to the final sample transfer of the unfiltered sample. Following transfer, the samples were immediately stored in a cooler with ice packs. All samples were delivered to Analytical Laboratories (Boise, Idaho) within 30 hrs, the maximum holding period for one of the analytes (hexavalent chromium) prior to the addition of a preservation reagent.

Table 2 summarizes the analytical procedures used for each metal and metalloid analyzed, and the method detection limits (MDLs). With a few exceptions, water samples for total and dissolved metals were processed in accordance with standard operating procedures applied by Analytical Laboratories (Boise, Idaho) for EPA methods 200.7 and 200.8, as specified in Appendix A. However, hexavalent chromium was analyzed by method SM 3500 CR-D. Samples of mercury, silver, lead, and copper were analyzed at lower detection limits than these methods could reliably achieve in order to ensure detection limits below water quality criteria. Because Analytical Laboratories does not regularly apply these methods, subsamples of each sample collected were processed by methodologies that achieve these lower detection limits by Frontier Geosciences (Seattle, WA). At the laboratory, samples were filtered through a 0.45 micron filter prior to acid preservation. Other standard operating procedures applied by the lab to ensure quality control are provided in Appendix A. All samples were processed within EPA recommended holding times.

Sample results were screened against the chronic dissolved metals water quality criteria of the State of Nevada in NAC 445A.144, or against federal criteria if Nevada had not specified a criterion for the analyte (EPA 822-Z-99-001). When no state or federal criteria were specified, (e.g., manganese), conservative screening values obtained from the scientific literature were considered as specified in the results (Table 3). If dissolved criteria were not specified, total recoverable metals criteria were used. For the risk screening purposes of this study, a hardness value of 5 mg/l for hardness-dependent criteria was assumed, although this value is slightly lower than the lowest hardness value measured in the field during this sampling (Table 3—8.4 mg/L as calcium and magnesium carbonates at station 1).



ENVIRON

November 30, 2006
Sampling Events
West Fork Jarbidge River
Jarbidge, Nevada

Figure
1

Drafter: DML Date: 07/25/07 Contract Number: Approved: Revised:

FILE: G:\West Fork Jarbidge\Figures\Figure 1

Figure 2. West Fork Jarbidge River with adit discharge (station 3) cascading into 'mixing zone' of river (station 4, foreground), and lower end of historic tailings upstream of adit along left bank (station 2).

Table 1. Conventional water quality sampling results, West Fork Jarbidge River, 11-30-06 and 12-01-06*.

Station Location Description	lat/long	Station	Channel Position	Approx. Time	Temp. (°C)	Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg/L)	Conductivity (mS/cm^3)	pH
Upstream Control, By School House	41° 87'186"/115° 43'077"	1	left	1635	0.07	93.5	13.65	0.04	6.99
Upstream Control, By School House	41° 87'186"/115° 43'077"	1	center	1630	0.08	92.6	13.51	0.04	7.03
Upstream Control, By School House	41° 87'186"/115° 43'077"	1	right	1640	0.07	93.6	13.65	0.04	6.99
Upstream Control, Downstream End of Elkoro Mine tailings	41° 87'363"/115° 42'995"	2	left	1355	0.08	93.4	13.62	0.045	7.09
Upstream Control, Downstream end of tailings	41° 87'363"/115° 42'995"	2	center	1410	0.07	93.6	13.64	0.044	7.07
Upstream Control, Downstream end of tailings	41° 87'363"/115° 42'995"	2	right	1425	0.07	93.5	13.67	0.045	7.02
In Adit Discharge	41° 87'398"/115° 42'979"	3	left	1230	20.45	90.6	8.04	0.24	6.94
In Adit Discharge	41° 87'398"/115° 42'979"	3	center	1300	23.5	92.1	7.83	0.262	6.92
In Adit Discharge	41° 87'398"/115.42'979"	3	right	1330	23.66	90.9	7.7	0.266	6.9
In Mixing Zone of Adit within river (30 ft downstream of adit)	41° 87'416"/115° 42'982"	4	left	1155	3.29	93	12.49	0.073	7.03
In Mixing Zone of Adit within river (30 ft downstream of adit)	41° 87'416"/115° 42'982"	4	center	1230	1.14	93.7	13.24	0.05	6.95
In Mixing Zone of Adit within river (30 ft downstream of adit)	41° 87'416"/115° 42'982"	4	right	1250	0.25	91.3	13.27	0.041	7.03
30 ft upstream of bridge behind Outdoor Inn (380 ft downstream of adit discharge)	41° 87'500"/115° 43'008"	5	center	1000	1.63	93.1	13.02	0.057	6.84
Downstream, at USGS gauging station	41° 89'055"/115° 42'904"	6*	left	0730	1.02	94.9	13.46	0.06	6.87
Downstream, at USGS gauging station	41° 89'055"/115° 42'904"	6*	center	0740	0.99	92.3	13.15	0.058	6.9
Downstream, at USGS gauging station	41° 89'055"/115° 42'904"	6*	right	0745	0.98	91.7	13.03	0.058	6.89

Table 2. Analytical methods, detection limits, and laboratory used for metals and metalloids analyzed in West Fork Jarbidge River water samples.

Analyte	Method Detection Limit Dissolved: Total (µg/L)	Method	Laboratory[1]	Date Completed
Aluminum	100:120	EPA 200.7	AL:FGS[2]	12/5/2006:6/4-25/07
Arsenic (low level—III and V forms combined)	1:1	EPA 200.8	AL	12/12/06
Arsenic III	1:NM[3]	EPA 200.8	AL	12/12/06
Arsenic V	1 :NM[3]	EPA 200.8	AL	12/12/06
Cadmium (low)	0.5:0.5	EPA 200.8	AL	12/12/06
Chromium (low level—all forms combined)	2:2	EPA 200.8	AL	12/12/06
Chromium 6^+ (hexavalent)	10:NM[3]	SM 3500 CR-D	AL	12/1/06
Copper	0.10:0.10	FGS-054	FGS	12/30/06
Iron	50:50	EPA 200.7	AL	12/5/06
Lead	0.04:0.04	FGS-054	FGS	12/30/06
Manganese	50:50	EPA 200.7	AL	12/5/06
Mercury	0.0005:NM[3]	EPA 1631 E	FGS	12/30/06
Nickel	1:1	EPA 200.8	AL	1/16/07
Selenium	5:5	EPA 200.8	AL	12/12/06
Silver	0.02:0.02	FGS-054	FGS	12/30/06
Zinc	5:8	EPA 200.7	AL:FGS[2]	2/7/07:6/4-25/07
Hardness	2:NA[4]	SM 2340	AL	12/12/06
Sulfate	1:NA[4]	EPA 300.0	AL	12/7/06
Sulfide	0.05:NA[4]	SM 4500-S2 D	AL	12/5/06
Total Dissolved Solids	25:NM[4]	SM 2540C	AL	12/5/06

1: AL: Analytical Laboratories, Boise, Idaho; FGS: Frontier Geosciences, Seattle, WA
2: Samples for this metal were reanalyzed by FGS due to potential sample contamination from filters used at the laboratory (zinc), or because AL initially used an analytical method that yielded a higher MDL than was requested by this researcher (aluminum), requiring reanalyses of archived samples at FG; 3: total recoverable concentration not measured—only samples 2a and 3a were analyzed for total recoverable metals to examine the ratio; 4: not applicable.

Sediment Sampling

Triplicate surface sediment samples were collected using a stainless steel scoop from three locations on November 30, 2006. Samples were collected: (1) upstream of the adit, at the downstream base of the historic Elkoro tailings pile, (2) within the adit at its confluence with the West Fork Jarbidge River, and (3) from the West Fork Jarbidge River downstream of the adit, within the mixing zone. Scoops were cleaned with a surfactant prior to use and rinsed with deionized water. Scoops used upstream of the adit were separated from those used downstream to ensure no cross contamination. Samplers wore polyethylene gloves. Surficial sediments were collected to a maximum sediment depth of approximately 6 cm. Fine sediments were targeted for sample

collection but were not adequately available. However, the three stations sampled were considered sufficient to determine if subsequent sampling was warranted.

Sediment samples were analyzed for moisture content and digested by method SW 846-3050. Total metals in the digestate were analyzed by EPA methods 200.7, 200.8 as reflected in Table 2, with the exception of mercury, silver and sulfate, which where analyzed by EPA methods 245.1, 272.1 and 300.0, respectively. Sediment sample results were screened against guidelines for freshwater sediments developed under consensus in Canada (MacDonald et al. 2000) and other sediment metrics, as neither the State of Nevada nor the U.S. government have promulgated freshwater sediment criteria.

Macroinvertebrate Sampling

Hester-Dendy multiplate sampling devices were deployed in triplicate at stations 2, 4 and 5. Devices were deployed by anchoring stainless steel rods into the substrate and locking the multiplates into pre-drilled holes in the rods with polyethylene lock ties. Multiplates were positioned atop the substrate surface across the channel in riffle sections. A single multiplate was deployed in the mine adit, above the bankfull width simply to explore what type of invertebrates might colonize these heated waters, and to take advantage of the co-placement of a temperature logger in this location. These samples are not processed and therefore results are not presented in this preliminary report.

Remote Temperature Logging

Temperature loggers were deployed in duplicate attached to two of the three multiplate samplers deployed at the stations outlined above. These were preprogrammed to collect data daily for a five month period. In actuality, these units were deployed for approximately nine months before retrieval and only two stations provided usable data. These data are appended to this report (Appendix B).

RESULTS

Analytical results obtained from the metals and metalloid analyses in water and sediment samples are outlined in Tables 3 and 4.

Quality Control and Assurance

Samples were processed in accordance with procedures outlined in Appendix A for EPA methods 200.7 and 200.8. All samples were processed within EPA-approved holding times. Discrepancies in sample analyses at AL were identified from an initial review of results received from the laboratory in mid-February 2007 for aluminum and zinc, as discussed below. Additionally, concentrations of total recoverable copper and magnesium in sample 3a were higher than that measured in the dissolved form from

this sample, requiring a flagging of the results for these analytes from this sample (Table 3). These discrepancies are further discussed below. None of these discrepancies invalidated the results interpretations, but subsequent analysis was required by FG, and these results were not received until mid-July.

Laboratory Discrepancies

Aluminum

The method detection limit reported for aluminum by Analytical Laboratories (AL) upon the receipt of the first analytical results was slightly above the water quality criterion. The method used by AL in these initial analyses (EPA 200.7) was not the method that was quoted or authorized (EPA 200.8), requiring subsequent reanalysis by Frontier Geosciences from archived samples, and these data are what are now reflected in Table 3.

Copper

Copper was not detected in the 'total recoverable metals sample' analyzed from sample 3a, yet was detected at 0.11 µg/L in the filtered (dissolved) aliquot from the same sample. This discrepancy resulted in this sample being flagged (Table 3).

Manganese

Manganese was detected in the 'total recoverable metals sample' analyzed from sample 3a at a slightly lower concentration than the total recoverable concentration (560 vs. 593 µg/L). This discrepancy resulted in this sample being flagged (Table 3).

Zinc

Initial filter contamination by the primary laboratory (AL) invalidated dissolved metal results for zinc, requiring subsequent analysis from 'left over' archived samples maintained in storage at the laboratory employed for trace analyses (FG).

Table 3. Metals and metalloids in West Fork Jarbidge River surface water samples collected 11/30 and 12/1/06.

DISSOLVED METAL ANALYTE	STATION LOCATION AND SAMPLE IDENTIFICATION													
	Screening Criteria (ug/L)[1]	1a	1b	2a[2]	2b	3a[2]	3b	4a	4b	4c	5a	5b	6a[3]	6c[3]
Aluminum (µg/L)	87[4]	41.9	40.5	70.4:120	45.3	BDL:BDL	32.1	33.5	33.7	43.3	37.5	34.6	60.3	57.3
Arsenic (low) (µg/L)	150[5]	BDL[6]	BDL	BDL:BDL	BDL	31:40	18	4	4	2	2	2	1	1
Arsenic III (µg/L)	ND	ND[7]	BDL	ND:NA	ND	2:NA	ND	ND	BDL	ND	ND	ND	ND	BDL
Arsenic V (µg/L)	ND	ND	BDL	ND:NA	ND	29:NA	ND	ND	4	ND	ND	ND	ND	1
Cadmium (low) (µg/L)	0.09	BDL	BDL	BDL:BDL	BDL	BDL:BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Chromium (III and VI combined) (µg/L)	15.1	BDL	BDL	BDL:BDL	BDL	BDL:BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Chromium VI+ (µg/L)	11	BDL	BDL	BDL:NA	BDL	BDL:NA	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Copper (µg/L)	0.78	0.2	0.21	0.31:0.31	0.21	0.11:BDL[8]	0.11	0.29	0.24	0.24	0.27	0.25	0.29	0.29
Iron (µg/L)	1,000	BDL	BDL	BDL:110	BDL	7,080:9,120	6,660	364	79	77	310	238	BDL	BDL
Lead (low) (µg/L)	0.125	BDL	BDL	0.063:0.108	BDL	0.04:BDL	BDL	BDL	BDL	BDL	0.068	BDL	BDL	BDL
Manganese (µg/L)	600[9]	BDL	BDL	BDL:BDL	BDL	593:560[7]	595	93	90	BDL	BDL	BDL	BDL	BDL
Mercury (ng/L)	0.012	1.86	1.77	1.78:NM	1.75	BDL:NM	BDL	1.48	1.39	1.66	1.48	1.42	1.28	1.18
Nickel (µg/L)	10.6	BDL	BDL	BDL:BDL	BDL	BDL:BDL	BDL	BDL	2	BDL	2	BDL	BDL	BDL
Selenium (µg/L)	5	BDL	BDL	BDL:BDL	BDL	BDL:BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Silver (µg/L)	0.02	BDL	BDL	BDL:BDL	BDL	BDL:BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zinc (µg/L)	7.1	7.4	7.22	8.07:8.63	7.29	56.3:61.8	55.5	16.1	16	11.2	13.3	13.2	34.2	32.8
Sulfate (mg/L)	1060[10]	6	6	6:NA	7	96:NA	94	20	19	12	13	13	14	14
Sulfide (mg/L)	2.0	BDL	BDL	BDL:NA	BDL	BDL:NA	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
TDS (mg/L)	ND	32	34	28:NA	24	140:NA	170	48	20	28	16	34	16	8
Hardness (mg/L)	ND	8.4	8.4	8.8:NA	8.6	72.2:NA	73	18	18.4	12.8	13.6	13.4	13	13

1: State of Nevada dissolved water quality criteria were used for screening, unless otherwise specified. 2:These samples were analyzed for both dissolved and total metal fractions and results are expressed as dissolved:total metal, total recoverable results for aluminum were performed by Analytical Laboratories, but a processing error by this laboratory required reanalysis of the dissolved fraction of this metal by Frontier Geosciences, from an archived subsample in these samples; 3: all stations were sampled on the afternoon of 11/30/06 with the exception of this station, which was sampled in the early morning of 12/1/06; 4: EPA 822-Z-99-001; 5: NAC 445A.144; 6: BDL: below detection limit; 7: ND = no data; 8: quality control discrepancy—dissolved metal concentration exceeds total recoverable concentration. 9: no state or federal criteria, this value represents the LOEC for chronic exposure to aquatic life as documented by the WHO in Cicads (2004); 10: BC Research 1998

Table 4. Sediment concentrations of metals in the West Fork Jarbidge River, 11-30-06, relative to sediment screening levels and method detection limits.

Total Metal (mg/kg) Dry Weight	TEC[1]	PEC[2]	MDL[3]	2a	2b	2c	3a	3b	3c	4a	4b	4c
Aluminum	NS[4]	NS[4]	1	2033	2740	2649	905	1000	743	2643	2766	3293
Arsenic	9.8	33	0.1	2.1	1.2	1.8	2914.5	2834.5	2201.2	182.0	85.5	7.6
Cadmium	0.99	5.0	0.05	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Chromium	43	110	0.2	0.2	0.2	0.4	0.7	BDL	BDL	0.3	0.4	0.5
Copper	32	150	0.1	1.8	2.0	2.5	0.7	BDL	BDL	2.2	2.7	2.4
Iron	20,000[5]	40,000[6]	0.5	8100.0	7641.9	9194.9	453947.4	462837.8	428994.1	43142.1	29432.6	9244.3
Lead	36	130	0.2	9.6	7.9	9.6	2.1	2.0	1.2	9.7	5.2	11.7
Manganese	460[5]	1100[6]	0.5	285.6	70.2	64.9	259.5	1003.4	7810.7	134.7	228.1	206.5
Mercury	0.18	1.1	0.02	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Nickel	23	49	0.2	BDL	0.4	BDL	4.0	4.1	4.4	0.8	BDL	0.7
Selenium	NS	NS	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Silver	1.6	2.2	0.05	0.20	0.52	0.21	4.77	3.21	3.02	0.42	0.40	0.34
Zinc	120	460	0.05	28.00	37.45	36.64	220.39	243.58	437.87	56.61	49.76	33.74
Sulfate	NS	NS	10	BDL	BDL	BDL	395	405	385	32	20	31

1: Threshold effect concentration, as defined in MacDonald et al. 2000a; 2: Probable effect concentration (MacDonald et al. 2000); 3: method detection limit; 4: NS = none specified; 5: threshold effect level as identified in Persaud et al. 1993; 6: probable effect level as specified in Persaud et al. 1993.

DISCUSSION

The following discussion compares results of the water analyses to water quality criteria or toxicity thresholds identified in the literature that are not promulgated into law, as identified in Table 3. Similarly, the sediment analyses are discussed in relation to the sediment quality guidelines identified in Table 4; no sediment quality criteria are formally promulgated by the State of Nevada. Although significant literature exists to consider additional potential effects, the purpose of the contracted study was to clarify potential exceedances of metal constituents in water and sediment relative to these criteria and guidelines, and an exhaustive interpretation of literature on each analyte was not budgeted. Hence, the discussion and conclusions that follow focus expressly on how the analytical results compare with the screening guidelines identified. Exceedances identified may highlight the need for additional study and interpretation.

Water Analysis Interpretation

Constituents of No Concern from the Elkoro Mine Adit Discharge

Aluminum

Aluminum is not considered a priority pollutant by the USEPA (EPA 822-Z-99-001). The recommended chronic criteria for aluminum of 87 µg/L identified in Table 3 is based on aquatic life criterion derived using the 1985 guidelines for the total recoverable metal (EPA 440/5-86-008). Initial analyses of aluminum by Analytical Laboratories were erroneously performed using EPA method 200.7, which cannot achieve method detection limits at water quality criteria, and none of the samples analyzed by this method reflected detectable dissolved aluminum (data not shown). For this reason, the initial results for dissolved aluminum were not usable and the laboratory was requested to reanalyze, at their expense, the archived samples that had been maintained by the laboratory that was conducting analyses at ultra-low concentrations for several of the other analytes (Frontier Geosciences). The subsequent results received in mid-July showed all samples below the water quality criteria, except the initial total recoverable sample analysis from sample 2a (120 µg/L). Of the 12 samples with detectable aluminum, the dissolved fraction averaged 44.2 µg/L (12.2 s. dev.). Aluminum in the adit discharge was the lowest measured either undetectable (sample 3a) or 32.1 µg/L (3b). These results indicate the adit is not a significant source of dissolved aluminum to the West Fork Jarbidge River.

Aluminum toxicity is generally associated with low pH waters in which it can be solubilized (dissolved), and the pH range of *all* the sample stations measured (6.84 to 7.09) was essentially neutral and well above the biologically significant acidic range of approximately pH 5.0 and below, where aluminum toxicity has manifest (Langdon 1988). The aluminum concentrations measured in the West Fork Jarbidge River during this study, with consideration of pH; do not suggest a biological risk to bull trout recovery.

Arsenic

Arsenic is considered a priority pollutant by the EPA, and the EPA and Nevada recommended chronic and acute water quality criteria for dissolved arsenic are 150 and 340 µg/L, respectively

(EPA 822-Z-99-001). These criteria were derived for trivalent arsenic, but are applied to total arsenic. To my knowledge, chronic toxicity values are available for trivalent and hexavalent arsenic only (from fathead minnow tests), and the chronic value for hexavalent arsenic is 0.29 times that of the trivalent arsenic.

Data reflected in Table 3 indicate that the Elkoro Mine adit is a minor source of arsenic to the Jarbidge River. Arsenic was below detection limits in sample stations upstream of the adit, and measurable in the undiluted adit waters at Station 3 at an average of 24.5 µg/L (range 18 to 31 µg/L). Arsenic speciation was evaluated in samples 3a, 4b and 6c and the more toxic trivalent arsenic was found only in the adit discharge, at only 6.5% of the total (2 µg/L). Trivalent arsenic was below detection limits in samples downstream of the adit.

All measured values for total dissolved arsenic are below chronic water quality criteria for the State of Nevada. Further, there is a progressive decrease in the concentration of arsenic downstream (Table 3). These data indicate dissolved arsenic is not a contaminant of concern from the adit discharge to bull trout and other aquatic life in this examined reach of the West Fork Jarbidge River.

Cadmium

Dissolved cadmium was not detectable in any sample (MDL 0.5 µg/L) and was not detected in either of the two samples analyzed for total metals (Table 3). Cadmium water quality criteria are hardness dependent. Using the chronic cadmium criterion calculation, as specified under Nevada's water quality standard and EPA 822-Z-99-001, the criterion at stations 1 and 3 would equate to 0.3565 µg/L and 1.767 µg/L, respectively, the latter of which would fall within the range of detectability applied by the laboratory. Given that no cadmium was detectable in the two samples analyzed for total recoverable cadmium (i.e., *see* Table 3, samples 2a and 3a) it is highly unlikely that either background or adit concentrations of cadmium represent a biological concern to bull trout or other aquatic life in the reach of the West Fork Jarbidge River examined in this study. Further analyses of archived samples may be warranted with methods developed by Frontier Geosciences simply to confirm the baseline concentrations of this metal, but the evidence does not support its inclusion as contaminant of concern from the adit.

Chromium

Previously unexposed rainbow trout populations have exhibited avoidance reactions to hexavalent chromium at concentrations as low as 28 µg/L whereas previously exposed populations tolerated higher concentrations (Anestius and Neufeld 1986). Dissolved concentrations of chromium were below detection limits at all sites sampled for both the hexavalent form and trivalent+hexavalent (combined) forms. Method detection limits (2 µg/L) were well below the State of Nevada water quality criteria for this metal (e.g. 15.11 ppb for dissolved chromium at hardness of 5 mg/L; 11 µg/L for hexavalent chromium--irrespective of hardness). The screening level analysis here used the 5 mg/L hardness metric initially to provide a conservative comparison among sample station results. The chromium criteria at all sites would be slightly higher than indicated in Table 3, based on the range of hardness values

detected (8.4 to 73 mg/L). Chromium is therefore not considered a contaminant of concern from the Elkoro mine adit.

Copper

Copper toxicity to salmonid fishes has been exhaustively researched over the past 30 years. Hardness dependent lethal concentrations have been recorded in ranges of 9 to 57 µg/L (*see* Hecht et al. 2007), depending on life stage and duration of chronic exposures (96 hours and longer). Beyond these mortality metrics, a variety of behavioral effects have been recorded at sublethal levels of exposure that affect predator avoidance, swimming performance, and migratory behaviors (Table 5). These effects have been recorded at exposure durations as little as 20 minutes.

The most recent research results indicate the sublethal effects of copper are likely attributed to impairments in the olfactory system of salmonids (Hecht et al. 2007). Olfactory receptors detect chemical cues that are important for foraging, predator avoidance, navigating migration routes, recognizing kin, participating in reproduction, and avoiding pollution. Exposure may destroy olfactory neurons and recent electophysiological measurements (electo-olfactograms) have confirmed this hypothesis. Such changes may particularly affect fitness through reduced predator avoidance (Hecht et al. 2007); in this paper, benchmark concentrations (BMC) were calculated for dissolved copper from 0.18 – 2.1 µg/L that corresponded to reductions in predator avoidance behavior from approximately 8 – 57%.

Dissolved copper was not detected in the range of these effects concentrations in the adit discharge (0.11 µg/L) in the current study. Samples upstream and downstream of the adit discharge ranged from 0.20 to 0.31 ppb. Concentrations detected in all stations were well below the chronic water quality criteria (e.g., 0.78 ppb, at 5 mg/L calcium carbonate), but stations upstream and downstream of the adit had dissolved copper concentrations within the lowest effect range for olfactory changes reported by Hecht et al. (2007). Copper concentrations measured in the adit were one half to one third of that measured in upstream sample stations indicating the adit does not represent a significant source of dissolved copper to the West Fork Jarbidge River. Total recoverable copper measured in sample 3a from the adit (50 µg/L, Table 3) suggests there may be a trace amount of copper liberated from the adit that is sediment bound or otherwise chelated. However, dissolved copper concentrations measured at downstream stations were within the range measured in the stations upstream of the adit, suggesting this source of copper was not appreciably released to the water column at the time the sampling was conducted. (Further, sediment samples from any of the stations did not indicate significant copper contamination, as discussed in the subsequent section).

From the existing chemistry data it is not possible to ascertain whether dissolved copper represents a contaminant of concern more broadly in the West Fork Jarbidge River, relative to the effects concentrations summarized by Hecht et al. (2007), but it would seem unlikely given the relatively low concentrations detected that were well below water quality criteria. Notwithstanding, the existing evidence suggests that copper does not represent a contaminant of concern from the Elkoro adit.

Lead

Dissolved lead was detectable in only 3 samples, one upstream of the adit, one within the adit, and one downstream of the adit (Table 3). Frontier Geosciences achieved a MDL of 0.04 µg/L, well below the chronic criteria for lead of 0.125 µg/L, at an assumed hardness of 5 mg/L (NAC 445.144A). The concentration detectable in one adit sample (0.04 µg/L) was less than the samples with detectable lead upstream at Station 2 (0.063 µg/L) or downstream at Station 5 (0.068 µg/L). These results suggest lead is neither a contaminant of concern in baseline waters of the West Fork Jarbidge River, nor in waters currently discharging from the Elkoro Mine adit.

Mercury

Mercury is considered a priority pollutant by the EPA due to its persistence, toxicity, and propensity to bioaccumulate. Ultra low detection limits were therefore sought for mercury to address concerns regarding mercury sources in the Jarbidge drainage, and the insufficient detection limits that were applied in previous sampling efforts to allow for comparisons against relevant water quality criteria (NAC 445A.144). Frontier Geosciences, which specializes in analytical techniques to achieve the lowest reproducible detection limits for metals, was contracted to achieve an MDL of 0.5 ng/L (parts per trillion [ppt]), using EPA method 1631E (Table 2). The current chronic water quality criteria for dissolved mercury is 770 ppt (NAC 445A.144). Of note, no dissolved mercury was measurable in the adit discharge; however, mercury was detectable in all other samples, with a slight increase in the samples obtained upstream versus those downstream. These data suggest mercury is not a contaminant of concern from the mine adit discharge. The average concentration of the four samples taken upstream of the adit exceeded the average from the seven samples collected downstream (e.g., 1.46 ppt, vs. 1.41 ppt) suggesting the adit discharge may be diluting background mercury in the river to a marginal extent. Alternatively, other constituents in the adit discharge could form insoluble mercuric salts (e.g., mercuric sulfate) thereby explaining the lack of detection in the dissolved fraction. Given that mercury was similarly undetectable in adit sediments (discussed further in the sediment section) this scenario seems most unlikely. Regardless, dissolved mercury in the baseline waters was more than three orders of magnitude lower than the water quality criterion, indicating essentially no risk to aquatic life.

Nickel

Similar to copper, cadmium and lead, the aquatic life criterion for nickel is hardness dependent. At an assumed hardness of 5 mg/L, the chronic criterion recognized by the State of Nevada is 10.6 µg/L (NAC 445.144A), and the laboratory achieved an MDL of 1 µg/L for the Jarbidge samples. Dissolved nickel was detected in only two of the 13 samples analyzed, both downstream of the mine adit in Stations 4 and 5 at a concentration of 2 µg/L (Table 3). However, nickel was undetected in the mine adit in either dissolved or total recoverable form (Table 3). These results indicate the Elkoro Mine adit is not a significant source of nickel to the West Fork Jarbidge River, and does not pose a risk to aquatic life.

Selenium

Selenium is considered a priority pollutant by the EPA, but it was not detectable at the MDL of 5 µg/L in any of the West Fork Jarbidge River water samples (Table 3). This MDL was equivalent to the chronic water quality total recoverable criteria concentration of 5 µg/L, and approximated the dissolved criteria of 4.61 µg/L (conversion specified in EPA 822-Z-99-001). These data do not indicate selenium is discharged into the West Fork Jarbidge River from the Elkoro Mine adit, nor do they indicate baseline levels of selenium pose biological risk to bull trout or other aquatic life in the reach of the Jarbidge River examined.

Silver

Silver is considered a priority pollutant by the EPA. An ultra-low detection limit for silver was sought to achieve an MDL that met Nevada chronic water quality criteria for the dissolved metal (0.02 µg/L at 5 mg/L calcium carbonate). Frontier Geosciences met this detection limit, but silver was not detected in any of the water samples from the adit, or upstream or downstream of the adit in the Jarbidge River (Table 3). These results indicate silver is not a contaminant of concern.

Table 5. Summary of sublethal copper toxicity metrics identified in salmonids (Source: Hecht *et al.* 2007).

Species (lifestage)	Effect	Effect concentration (µg/L)	Effect statistic	Hardness (mg/L)	Exposure duration
	Sensory and behavioral effects				
Coho salmon (juvenile)	Reduced olfaction and compromised alarm response	0.18 - 2.1	EC_{10} - EC_{50}	120	3 hours
Chinook salmon (juvenile)	Avoidance in laboratory exposures	0.75	LOEC	25	20 minutes
Rainbow trout (juvenile)	Avoidance in laboratory exposures	1.6	LOEC	25	20 minutes
Chinook salmon (juvenile)	Loss of avoidance ability	2	LOEC	25	21 days
Atlantic salmon (juvenile)	Avoidance in laboratory exposures	2.4	LOEC	20	20 minutes
Atlantic salmon (adult)	Spawning migrations in the wild interrupted	20	LOEC	20	indefinite
Chinook salmon (adult)	Spawning migrations in the wild apparently interrupted	10 – 25	LOEC	40	indefinite
Coho salmon	Delays and reduced downstream migration of dCu-exposed juveniles	5	LOEC	95	6 day
Rainbow trout	Loss of homing ability	22	LOEC	63	40 weeks
	Ecosystem effects				
	Ecosystem function: Reduced photosynthesis	2.5	LOEC	49	~ 1 year
	Ecosystem structure: loss of invertebrate taxa richness in a mountain stream	5	LOEC	49	~ 1 year

Constituents of Potential Concern from the Elkoro Mine Adit Discharge

Sulfate

Sulfate was detectable in all samples collected, ranging from 6 mg/L upstream of the adit, to 70 mg/L within the adit waters, with intermediate concentrations detected downstream (Table 3). Sulfate is not considered a priority pollutant and no water quality criteria are specified for this analyte. Mortality tests conducted with a variety of freshwater species with sodium sulfate have recorded 96 hr LC50's ranging from 56 mg/L in striped bass, to over 13,000 mg/L in bluegill as sulfate (*see* http://www.pesticideinfo.org/List_AquireAll.jsp?Rec_Id=PC34430&Taxa_Group=Fish). Unfortunately, results on coldwater fishes addressing sulfate toxicity are relatively lacking. BC Research Inc.(1998) performed 7-day salmonid embryo viability tests (e-test) using the rainbow trout, *Onchorhynchus mykiss*, and a 7-day survival and growth test using the fathead minnow *Pimephales promelas.* For rainbow trout embryo viability, a NOEC and LOEC of 1060 and 3500 mg/L SO_4 were reported, respectively. A 7-day EC_{25} and EC_{50} for viability of 1280 and 1477 mg/L SO_4, respectively, were also reported for the trout embryos. For the fathead minnow test, a NOEC and LOEC for survival of 510 and 1060 mg/L SO_4, respectively, were reported, and for growth, a NOEC and LOEC of 1060 and 3650 mg/L SO_4, respectively, were reported. The absolute lowest effect concentrations identified in the literature has been reported for aquatic mosses by Frahm (1975), where mortality was reported at 100 mg/L in *Fontinalis antipyretica*.

The sulfate concentrations recorded in the current study were over two orders of magnitude lower than the toxic concentrations identified in salmonids by BC Research, and significantly less than the other metrics discussed above. These comparisons suggest sulfate is essentially non-toxic as a water soluble (dissolved) constituent, and results obtained from the adit likely pose no biological risk in the water column. However, elevated sulphate levels of approximately 71 mg/L sulphate (range of 27.7 to 189 mg/L) may stimulate large sulphur bacteria growths that coat streambeds and alter the macroinvertebrate community http://www.env.gov.bc.ca/wat/wq/BCguidelines/sulphate/sulphate-04.htm#TopOfPage. Based on the concentrations of sulfate currently discharging from the Elkoro adit, and visual evidence of rock staining and bacterial growth on the rocks downstream of the adit, indirect effects on Jarbidge Bull trout through alterations in macroinvertebrate food sources are possible. Because data remain to be collected from the multiplates deployed in the river to address potential macroinvertebrate effects from the adit discharge, we cannot conclude whether such effects are occurring. However, the uncertainty associated with the potential effects of sulfate for this endpoint support the classification of sulfate as a metal of potential concern.

Manganese

Manganese is an essential mineral for life and is not considered a priority pollutant by the EPA and there are no aquatic life standards designated. However, the adit clearly serves as a source of manganese load to the Jarbidge River. Dissolved manganese averaged 594 µg/L in two samples from the mine adit discharge, and was detectable within the mixing zone in Station 4

(left bank and mid-channel) at an average of 91.5 µg/L (Table 3). No further detections were reported downstream or upstream.

The British Columbia government has proposed chronic manganese aquatic life criteria for waters of low hardness (0 to 24 mg/L calcium carbonate) of 600 , and 800 µg/L for waters with hardness in the range detected in the adit—50 to 74 mg/L (http://www.env.gov.bc.ca/wat/wq/BCguidelines/manganese/update-07.html). Tests conducted at near-neutral pH values with three different species of salmonids (brown trout, coho salmon, and rainbow trout) yielded 96-hr LC50 values ranging from 2.4 to 3.8 mg/L (Davies and Brinkham 1994; Reimer 1999; Birge 1978—as cited in Cicads 2004). No observable effect concentrations (NOECs) were assumed at 10-fold dilutions of these measurements by the World Health Organization (WHO) (Cicads 2004).

Early-life-stage tests were conducted by Stubblefield et al (1997) to determine the toxicity of manganese to brown trout (*Salmo trutta*) and to evaluate the extent to which water hardness affects the chronic toxicity of Mn. Water hardness significantly affected Mn chronic toxicity, with toxicity decreasing with increasing hardness (range tested was 30 to 450 mg/L as $CaCO_3$). Decreased survival was the predominant effect noted in the 30-mg/L hardness experiment, while significant effects on growth (as measured by changes in body weight) were observed in both the 150- and 450-mg/L hardness experiments. The twenty-five percent inhibitory concentration (IC25) values for survival and growth were 4.67, 5.59, and 8.68 mg Mn/L (as Mn) at hardness levels of approximately 30, 150, and 450 mg/L as $CaCO_3$, respectively.

The detected concentrations in the adit discharge exceed the NOEC proposed by the WHO for aquatic life, but are significantly below the effects concentrations reported in brown trout by Stubblefield et al. (1997). Dilution within the mixing zone in Station 4 is exceedingly rapid, as evidenced by the roughly 85% dilution measured in the two samples from Station 4 where manganese was detected, and these concentrations were well below aquatic life thresholds and effect concentrations established in the literature. This collective evidence does not support the inclusion of manganese as a contaminant of concern at this time, and biological effects to Jarbidge River bull trout and other aquatic life are considered unlikely. However, the loadings of manganese to the system through the adit are significant, and potential indirect effects on food web dynamics downstream of the adit support the inclusion of this metal as a metal of potential (albeit unlikely) concern.

Zinc

Dissolved zinc was detected in all samples, with concentrations from the mine adit averaging 55.90 µg/L (sd 0.57), relative to concentrations from upstream reference stations averaging 7.5 µg/L (sd 0.39), and downstream stations averaging 19.54 (sd 9.69) Notably, sampling results suggest an additional source of zinc may be entering the river further downstream, as sample results in stations 4 and 5 fell significantly below station 6 at the USGS gauging station (Table 3).

Relative to the dissolved criteria at an assumed low hardness of 5 mg/L, all of the measurements of dissolved zinc would exceed the chronic water quality criterion of 7.12 µg/L. However, at the minimum and maximum hardness values detected (8.4 mg/L at Station 1 and 73 mg/L in the

adit), the chronic dissolved criteria for zinc would be 14.49 and 90.06 µg/L at stations 1 and 3, respectively. Thus, zinc in the adit would not exceed the chronic criteria, and half of the samples upstream of the adit would exceed the lower criteria. None of the samples analyzed at station 4 would exceed the dissolved chronic criteria of 28 µg/L that would apply to the lowest hardness measured there (18 mg/L), and none of the samples at station 5 would exceed the dissolved zinc criteria of 21 ppb that would be applicable to the lowest hardness measured at this station (13 mg/L). Samples at the furthest station downstream exceeded the applicable dissolved chronic criteria by over two fold—a hazard quotient of 2.19.

Zinc was found to alter critical swimming performance at 50 µg/L when the hardness was set at 20 mg/L (Alsop et al. 1999). The concentrations observed within the adit approximate this effect concentration for zinc, but only at the lower hardness values more consistent with measurements downstream; thus, such effects *in situ* are unlikely, particularly given acclimation to chronic exposure that likely occurs in the basin. The existing results do not suggest zinc is a contaminant of concern from the mine adit at the hardness values within the adit discharge, nor do the current data suggest significant biological risk to bull trout within the reach examined. However, the adit is clearly a source of zinc to the drainage and the cumulative effects of this source in concert with other sources that appear to be present in the drainage cannot be ascertained from the existing data. For this reason, zinc is considered a constituent of potential concern from the adit discharge.

Constituents of Concern

<u>Iron</u>

Iron may cause cellular injury in several ways, including damage to DNA and membrane structure or alterations in intracellular Ca2+ homeostasis in fish. Dalzell and McFarlane (1999) found that the 96-h LC_{50} on brown trout from a commercial iron (III) sulphate was 28 mg total Fe/L (0·05 mg soluble Fe/L). The 96-h LC_{50} for analar grade iron (III) sulphate was 47 mg total Fe/L (0·24 mg dissolved Fe/L). Lethal and sublethal exposure to both grades of iron resulted in accumulation on the gill, which appears to be the main target for iron toxicity. Respiratory disruption due to physical clogging of the gills is suggested as a possible mechanism for iron toxicity.

Although not considered a priority pollutant by the EPA, iron concentrations currently discharging from the Elkoro Mine adit exceed the recommended chronic criterion for iron for the protection of aquatic life (1,000 µg/L) by nearly seven-fold (average of two samples = 6,870 µg/L). Iron staining on the rocks is grossly visible downstream of the adit to below Station 5, nearly to the first bridge crossing over the Jarbidge River upon entry into the town. Iron oxide deposition on the rocks may be affecting invertebrate production, but the analysis of colonized multiplates upstream and within the affected reach has not been completed. Notably, iron concentrations downstream of the adit remain elevated to at least Station 5, but were never measured at a concentration that exceeded water quality criteria. These results suggest the vast majority of iron discharged into the West Fork Jarbidge River via the Elkoro Mine adit precipitates out of solution extremely rapidly to such an extent that dissolved iron is unlikely to represent a toxic risk in the reach of the West Fork Jarbidge River downstream of the town that is

envisioned for habitat restoration. However, iron is likely compromising habitat quality and suitability of the substrate to support invertebrate food sources important for bull trout within the mixing zone of the adit and downstream to (at least) station 5 where staining is visibly evident.

Based on the results of Dalzell and McFarlane (1999) in particular, the dissolved iron concentrations observed within and downstream of the adit to station 5 could represent a risk to bull trout if they were to occupy the affected reach for an extended duration, particularly with the concomitant increases of sulfate. From the existing data it is not clear if the iron discharged from the adit could behaviorally isolate bull trout populations above and below the adit (via chemical avoidance), but this outcome would seem unlikely given the relatively short reach affected by elevated iron concentrations, and the range in flows that occur in the Jarbidge that undoubtedly redistribute bull trout populations annually. Avoidance of the reach, if occurring, would be more likely attributed to the secondary effects of the iron discharge on habitat quality.

Constituents of Uncertain and/or Unknown Risk

Sulfide

Hydrogen sulfide can be highly toxic to aquatic life and terrestrial life forms, and the chronic criteria has been established at 2 µg/L. The MDL applied by the laboratory was not sufficient to meet this detection limit, and sulfide was not detectable in the adit waters or any of the other samples analyzed at the MDL possible (50 µg/L). Potential risks from the introduction of hydrogen sulfide into the Jarbidge River from the Elkoro Mine adit cannot be determined with the available information.

Sediment Analysis Interpretation

Neither the state of Nevada or the EPA has promulgated freshwater sediment standards. Therefore, to screen the potential risks from metals in Jarbidge sediments, sediment concentrations were compared against consensus-based sediment screening levels identified in MacDonald et al. (2000) as the threshold effect concentration (TEC) or probable effect concentration (PEC), or to the lowest effect level (LEL) and severe effect levels (SELs) identified by Persaud et al. (1993). These screening values are not accepted by the U.S. government as a matter of law because many factors can affect sediment toxicity that are not reflected simply in the absolute concentration of a sediment analyte; however, they are widely used in screening analyses as a first measure to gauge potential problems. Exceedances of the PEC or SEL in particular may warrant focused sediment bioassays, and/or further biological study in field examinations. As demonstrated in Table 4, the MDL was below the screening levels for all analytes.

Sediment Constituents of No Concern from the Elkoro Mine Adit

Se, Hg, Cd, Al, Cr, and Pb

Sediment analytes that did not exceed the TEC or LEL were considered constituents of no concern in this screening level analysis. No evidence collected from the sediment samples

analyzed would suggest that selenium, mercury or cadmium represent sediment constituents of concern in either the Elkoro adit or West Fork Jarbidge River sediments examined in this study, as these metals were not detectable in any of the samples. As demonstrated in Table 4, concentrations of aluminum, chromium and lead in sediments upstream and downstream of the adit exceeded those from the adit, but none of the samples exceeded TEC guidelines. Thus, selenium, mercury, cadmium, aluminum, chromium and lead are concluded to be of no concern in sediments potentially contaminated from the adit discharge (or otherwise) in the localized reach examined.

Sediment Constituents of Potential Concern from the Elkoro Mine Adit

Analyte concentrations that exceeded the TEC or LEL but fell below the PEC or PEL criteria were considered constituents of potential concern in this study. Zinc was the only constituent that fell into this category, with concentrations in the adit sediments exceeding the TEC, (Table 4).

Zinc

Sediment zinc concentrations averaged 300.61 mg/kg dry weight (sd 119.43) from the adit. Based on the average sediment zinc concentration in the adit, the hazard quotient, the measured sediment concentration divided by the sediment guideline, would be 2.5 relative to the TEC. In considering the water quality sample from station 3a, 91% of the measurable zinc was present in dissolved form (Table 3). Clearly, the adit represents a source of zinc and a portion of which appears to adsorb and concentrate in the adit's sediments. Sediment zinc concentrations drop below the TEC quickly in the mixing zone (Station 4), although it is notable that the concentrations across the channel exhibit far less variance for this analyte than the constituents of concern discussed below (average 46.7 mg/kg, sd 11.7).

Sediment Constituents of Concern from the Elkoro Mine Adit

Analytes that exceeded the higher PEC or PEL sediment guidelines were considered constituents of concern in this screening level analysis. In this case, one or more sample from stations 3 or 4 exceeded the PEC for arsenic, manganese, silver, and iron.

Arsenic

Sediment arsenic concentrations exceeded the PEC substantially in adit sediments and exceedances of the PEC were also observed in samples collected in the mixing zone along the left bank and mid-channel (4a and 4b). Arsenic averaged 2,650.1 mg/kg (sd 390.8) in adit sediments. Hazard quotients for sediment arsenic in the adit ranged from 66.7 to 88.3, relative to the PEC. Arsenic drops abruptly in sediments within the mixing zone of Station 4, with concentrations measured in sediments along the opposite bank of the adit (4c) only four percent of that measured along the left bank (nearly consistent with the reference sediment samples collected upstream at Station 2) and concentrations along the left bank representing 7 percent of the average arsenic concentration in the adit sediments. Like zinc, clearly, the adit represents a

source of arsenic, a significant portion of which appears to adsorb and concentrate in the adit's sediments. In considering the exploratory water quality sample from station 3a, 22% of the measurable arsenic was present in particulate-bound form (Table 3), likely accounting for much of the sediment exceedances for this analyte through settlement of these particulates (Table 3).

Manganese

Manganese concentrations detected in the Elkoro adit sediments exhibited the greatest standard deviation around the mean of all the constituents of concern measured (mean 3,024.4, sd 4,161.8). This result was surprising given the visible consistency of sediments that have accreted atop the adit discharge (Figure 2). However, the laboratory reported no complications in the processing of these samples and we have no reason to discard the analyses. The average manganese concentration yields a hazard quotient of 2.75 relative to the PEC justifying its inclusion as a sediment constituent of concern.

Iron

Based on visual evidence in the stream, and the results of water quality sampling, the reported levels of iron in the sediments obtained from the adit were not surprising (mean 448,593 mg/kg, sd 17,546). Based on the results in Table 4, it appears that nearly half of the sediments accreted at the adit outlet, before entering the river, are composed of iron. The average sediment concentration of iron at the adit yields a hazard quotient of 11 relative to the PEL (there is no PEC identified for iron). Particulate bound iron appears to constitute approximately 22 percent of the iron discharged from the adit, based on the exploratory analysis of total recoverable metals from sample 3b (Table 3). Over time, these particulates have accreted at the outlet to the adit, and downstream. The extreme iron concentrations in adit sediments and large hazard quotient relative to the PEC justify the inclusion of iron as a sediment constituent of concern.

Silver

Silver concentrations in adit sediments averaged 3.67 mg/kg (range 3.02 to 4.77), well in excess of the PEC of 2.2 mg/kg (a hazard quotient of 1.67). Sediment concentrations in the mixing zone at station 4 did not exceed either the TEC or PEC suggesting very limited downstream transport of silver contamination from the adit.

CONCLUSIONS

Sediment and water analyses from within, upstream and downstream of the abandoned Elkoro Mine adit were examined to determine the potential risk of toxic metals to bull trout and other aquatic life in the West Fork Jarbidge River. No results obtained for any analyte, in either water or sediment unequivocally suggest that aquatic biota are at significant *unavoidable* toxicological risk from metals discharged through the adit because trout populations are not restricted or confined within zones where sediment or water concentrations of metal analytes exceeded risk water quality criteria or sediment screening thresholds. That is, there are no physical restrictions preventing them from avoiding exposure by staying out of the adit discharge zone. Uncertainties remain with respect to the significantly elevated iron, arsenic, zinc, manganese and silver measurable in sediments above risk screening thresholds, and dissolved iron and zinc measurable in the water column above Nevada water quality criteria in the adit's waters. In particular, iron and sulfate discharged via the adit appear to be negatively affecting substrate quality downstream of the adit through iron oxide precipitation and bacterial growth. Analyses of multiplate colonization and/or other invertebrate sampling could provide evidence of such effects; however, these effects may be more related to physical habitat impairment, rather than a potential chemically-induced alteration of fitness because water and sediment quality exceedances generally did not extend downstream of the adit's mixing zone (station 4). Sediment quality further downstream could not be confirmed (Station 5) because of a lack of appropriate-sized substrate for sampling. Nonetheless, should bull trout inhabit the affected reach; it would be unlikely they would be intoxicated based on the data collected in this study. The decreased suitability of the reach due to the heavy iron precipitation would also likely dissuade their use.

None of the data analyzed in this preliminary study would suggest that habitat improvements under consideration further downstream, below the first West Fork Jarbidge River bridge leading into the town of Jarbidge (and below the area sampled in this study) would be affected by the adit discharge. Field reconnaissance revealed that this reach does not exhibit the extensive rock staining and iron precipitate and no water quality measurement exceeded screening criteria at the closest sampling station to this reach (Station 5), approximately ¼ to ½ mile upstream. Habitat restoration actions considered within the reach affected by staining that was largely sampled in this study (Figure 1) would not be advisable until the adit discharge was remediated to reduce the loading of iron to the system, and confirm whether other constituents of potential concern in the water (zinc and manganese) and sediment (arsenic, manganese) represent biological concern *in situ*.

REFERENCES

Alsop, D.H., J. C. McGeer, D. G. McDonald, and C. M. Wood. 1999. Costs of chronic waterborne zinc exposure and the consequences of zinc acclimation on the gill/zinc interactions of rainbow trout in hard and soft water. Environmental Toxicology and Chemistry, 18: 1014–1025 |

BC Research Inc. 1998. Brenda Mines Sulphate and Molybdenum Toxicity Testing. Prepared for Noranda Mining and Exploration Inc., Brenda Mines Div. Project No: 2-11-825/826.

Birge, WJ. 1978. Aquatic toxicology of trace elements of coal and fly ash. *In*: Thorp, JH, JW Gibbons eds. *Energy and environmental stress in aquatic systems.* Augusta, GA, US Department of Energy, pp (US Dept. of Energy Symposium Series 48: Conf-771114).

Cicads [Concise International Chemical Assessment Document]. 2004. Manganese and its compounds: environmental aspects. Vol. 63. 83 pp.

Davies, PH, SF Brinkman. 1995. Acute and chronic toxicity of manganese to brown trout in hard water. Fort Collins, CO, Colorado Division of Wildlife.

EPA 822-Z-99-001. National Recommended Water Quality Criteria for non-priority toxic pollutants. U.S. EPA Office of Water. April 1999.

Frahm, J.P. 1975. Toxicity Tolerance Studies Utilizing Periphyton. (Toxitoleranzversuche an Wassermoosen). Gewasser Und Abwasser 57/58:59-66 (GER). (AQUIRE K_2SO_4 Reference number 7922).

Hecht, S.A., D. H. Baldwin, C. A. Mebane, T. Hawkes, S. J. Gross, and N. L. Scholz. 2007. An overview of sensory effects on juvenile salmonids exposed to dissolved copper: Applying a benchmark concentration approach to evaluate sublethal neurobehavioral toxicity. Technical White Paper. NOAA, Northwest Science Center.

McNeill, M.E., J. Frederick, B. Whalen. 1997. Jarbidge River Watershed Analysis. Jarbidge Ranger District, Humboldt-Toiyabe National Forest.

NAC 445A.144. State of Nevada standards for toxic materials applicable to designated waters.

MacDonald, D.D., C.G. Ingersoll and T.A. Berger. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives of Environmental Contamination and Toxicology, 39:20-31.

Persaud, D., R. Jaagumagi and A. Hayton. 1993. Guidelines for the protection and management of aquatic sediment quality in Ontario. Water Resources Branch, Ontario Ministry of the Environment, Toronto. 26 pp.

Reimer, PS. 1999. Environmental effects of manganese and proposed freshwater guidelines to protection of aquatic life in British Columbia. MSc. Thesis, University of British Columbia.

Soucek, D.J. 2007. Comparison of hardness and chloride-regulated acute effects of sodium sulfate on two freshwater crustaceans. Environmental Toxicology and Chemistry, 26:773-779.

Stubblefield, WA, SE Brinkman, PH Davies, TD Garrison. 1997. Effects of water hardness on the toxicity of nanganese to developing brown trout (*Salmo trutta*). Environmental Toxicology and Chemistry, 16:2082-2089.

WebSite: UWFWS Bull Trout Recover Team. http://www.fws.gov/nevada/protected_species/fish/jarbidge/index.html

Appendix A—Quality Control and Assurance
Standard Operating Procedures of Analytical Laboratories

I. EPA Methods 200.7 and SW 846 6010

1. Introduction

1.1. This method is used to determine the concentration of dissolved and total recoverable trace elements in ground water, surface water, drinking water, storm runoff, and wastewater. Also the total recoverable elements in sediment, sludge's, and soils. These are determined through the use of inductively coupled plasma emission spectroscopy.

2. Summary of Methods

2.1. Samples are prepared using a variety of metal prep methods. The prepared samples are analyzed by ICP-OES. The concentration of each metal is determined by generating a calibration curve with standards of known concentrations.

3. Apparatus

3.1. Varian Vista-MPX CCD Simultaneous ICP-OES (Serial # EL03128004)
- 3.1.1. Sturman-Master Double-pass Spray Chamber
- 3.1.2. Radial Configuration
- 3.1.3. V Groove Nebulizer

3.2. Vista-MPX software version 4.0, Build 425.
3.3. Varian SPS-5 Auto sampler (Serial # 2041107)
3.4. Lytron MCS – (Molecular Cooling System) Water chiller (Serial # 746270-01)
3.5. ICP tubing Blue-Blue (CPI P/N 4062-465)
3.6. ICP tubing Gray-Gray (CPI P/N 4062-451)
3.7. Dell personal Computer
3.8. Disposable test tubes 18x150mm (VWR #47729-582 or equivalent)
3.9. Disposable syringe 10ml (BD #309604)
3.10. Syringe filter with 0.45µm Nylon membrane (Pall #4438T or equivalent)
3.11. Filter Mate push filter (Environmental Express #SC0401)
3.12. Disposable watch glass (Environmental Express #SC505)
3.13. Digestion vessel, 68ml, with screw cap (Environmental Express #SC475)
3.14. Class A Volumetric glassware

4. Reagents

4.1. 1000 µg/ml and 10,000 µg/ml Standard Reference Material (SRM).

4.1.1. The following is a list of part numbers for the different metals. Equivalent standards may be used.

4.1.2. Elements in italics are 10,000 µg/ml concentration, others are 1000 µg/ml

Metals	Supplier/Part #	Metals	Supplier/Part #
Al	CPI 4400-100011	Mo	CPI 4400-1000342
As	CPI 4400-100023	*Na*	CPI 4400-10M521
B	CPI 4400-100074	Ni	CPI 4400-1000361
Ba	CPI 4400-100041	Pb	CPI 4400-1000281
Be	CPI 4400-100051	Sb	CPI 4400-100023
Ca	CPI 4400-10M91	Se	CPI 4400-1000491
Cd	CPI 4400-100081	*Si*	CPI 4400-10M504F
Co	CPI 4400-1000131	Sn	CPI 4400-1000613
Cr	CPI 4400-1000121	Sr	CPI 4400-1000531
Cu	CPI 4400-1000141	Ti	CPI 4400-1000622
Fe	CPI 4400-1000261	Tl	CPI 4400-1000581
K	CPI 4400-10M411	V	CPI 4400-1000651
Mg	CPI 4400-10M311	Zn	CPI 4400-1000681
Mn	CPI 4400-1000321		

4.2. Trace Level Grade Acid HNO_3 (Fisher #A509-212 or equivalent)

4.3. Metals Grade Acid HCl (Mallinckrodt #Mk5587 or equivalent)

4.4. Triton X-100 (Spectrum #CAS 9002-93-1)

4.5. High Purity Deionized water

4.6. Initial Calibration Verification (ICV).

4.6.1. The following is a list of metals and concentrations of the QC standards: Equivalent quality control samples may be used.

Metals	Concentration	Supplier/Part #
Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Tl, Ti, V, Zn, Li, Sr,	100µg/ml	Environmental Express ICQ100-21
K Al, B, Na, Ba, Ag Si	1000µg/ml 100µg/ml 50µg/ml	Environmental Express ICQ100-7

5. Sampling and Storage

5.1. Initial preservation of samples is required. Use 1.5ml of HNO_3 per liter of sample and must ensure that pH is less then 2.0. There is a 16-hour waiting time after preservation.

5.2. Samples are stored in metals fridge or on the metals shelf.

6. **Safety**
   6.1. Proper eye wear and gloves should be used when working with acid.
7. **Interferences**
   7.1. The following are interferences associated with this method:
      7.1.1. High concentration of metals.
      7.1.2. Spectral interference.
      7.1.3. Matrix interference.
8. **Preparation of Solutions**
   8.1. Lab Reagent Blank (LRB): 1.5ml HNO_3 / L DI water
   8.2. Calibration Blank (ICB/CCB): 5ml HNO_3 + 5ml HCl / L DI water
   8.3. Initial Calibration Verification (ICV): 1.0 mg/L concentration for all metals except for K = 10 mg/L and Si = 0.50 mg/L.
      8.3.1. 10mL of both ICP solutions, 5ml HNO_3 and 5ml of HCl / L DI water.
   8.4. CRI will be made up in the same grouping as the four multi-element standards, refer to section 8.7.1. The following is the concentration that is required.

Metal	mg/L	Metal	mg/L	Metal	mg/L	Metal	mg/L
Al	0.20	Co	0.02	Mo	0.10	Sn	0.20
As	0.20	Cr	0.10	Na	0.20	Sr	0.010
B	0.10	Cu	0.02	Ni	0.04	Ti	0.20
Ba	0.10	Fe	0.10	Pb	0.10	Tl	0.20
Be	0.010	K	0.5	Sb	0.20	V	0.10
Ca	0.20	Mg	0.20	Se	0.20	Zn	0.010
Cd	0.010	Mn	0.10	Si	0.20		

      8.4.1. Create a CRI x 100 solution using the SRM listed in section 4.1.
      8.4.2. CRI working solution: Take 10ml of this solution, 5ml HNO_3, and 5ml HCl / L DI water
   8.5. ICP Tuning Solution: 500 mg/L of K, and 50 mg/L of every other metal
      8.5.1. Stock Tuning solution: Using the SRM 25ml of the following, Al, As, Ba, Cd, Cr, Co, Cu, K, Mn, Mo, Ni, Pb, Se, Sr, Zn and 5mL HNO_3 / 500ml DI water.
      8.5.2. Then take 5ml of stock tuning solution and 5 mL HNO_3 into 500ml DI water. This solution is the working solution.
   8.6. Spiking solution will be made up in the same grouping as the four multi-element standards, refer to section 8.7.1.
      8.6.1. 10ml of each relevant SRM and 2ml HNO_3 / 100ml DI water.
      8.6.2. The resulting concentrations are: 100 mg/L for Sec 3, TCLP, and Sec 2. 500 mg/L for Minerals, and 100, 500 mg/L for B and Si respectively.
   8.7. Multi Standard # 3
      8.7.1. Four sets of multi-element standards are used.
         8.7.1.1.Sec 3: Al, As, Ba, Cd, Cr, Cu, Mn, Fe, Ni, Pb, Se, Zn (10 mg/L)
         8.7.1.2.Sec 2: Sb, Be, Mo, Co, Ti, Tl, V (10 mg/L)
         8.7.1.3.Minerals: Ca, Mg, Na, K (100 mg/L)
         8.7.1.4.B Si: B, Si (10,100 mg/L respectively)
      8.7.2. To 1 Liter volumetric flask, add 500 mL DI water with 5ml HNO_3, and 5ml HCl.

8.7.3. Using separate 10ml volumetric pipettes add 10ml of each SRM listed in section 8.7.1. to the flask.
8.7.4. Bring to volume with DI water and mix well.
8.7.5. Record lot #'s of standards in Standard Prep Log along with date and prep steps.

8.8. Multi Standard # 2
8.8.1. To 1 Liter volumetric flask add DI water, 4ml HNO_3, 4ml HCl, and 200ml of Multi standard # 3.
8.8.2. Bring to volume with DI water and mix well.

8.9. Multi Standard # 1
8.9.1. To 1 Liter volumetric flask add 5ml HNO_3, 5ml HCl and 40ml of Multi standard # 3.
8.9.2. Bring to volume with DI water and mix well.

9. Sample Preparation Procedure

9.1. Samples that have visible solids or turbidity greater than 1.0 NTU after 16 hours of preservation need to be digested prior to running. The pH is verified < 2 SU by pH paper after the 16-hour minimum time.
9.1.1. Check turbidity with turbidimeter according to turbidity SOP.

9.2. When a Dissolved Metals Test is requested and cannot be filtered in the field, the samples will need to be filtered, and then preserved. This includes samples where the elements of interest are already in solution. This can be done following the Metals filtering SOP.

9.3. Sample digestions are performed using the following procedures:
9.3.1. Deicers, sludges, solids, soils, multiphasic liquids, oils, and food samples are digested using EPA method 3050A.
9.3.2. Samples from certain clients with special MDL requirements need to be concentrated using the concentration variation of EPA method 200.9.
9.3.3. All other liquids should be digested using EPA method 200.9.
9.3.4. See the corresponding SOP for further details on all of these methods.

10. Samples, QC, Blank, and Standards Set up

10.1. Label test tubes with sample number and dilution, if any.

10.2. Testing requires about 10ml of each sample.

10.3. If a dilution is necessary, it can be prepared in the test tube prior to analysis.
10.3.1. Add the accurate amount of sample and dilute with LRB.
10.3.2. Swirl test tube thoroughly to mix.

10.4. Prepare a sample and blank spike for every run, sample matrix, or every 10 samples, whichever is more often.
10.4.1. Add 100µl of the 100 mg/L spiking solution to the test tube.
10.4.2. Add 10ml of sample or blank (CCB).
10.4.3. Swirl test tube thoroughly to mix.

10.5. Run a duplicate sample for about every 10 samples. This is a separate tube with 10ml of the sample that is being duplicated.

10.6. For standards, use the Multi standards; refer to sections 8.7-8.9.
10.6.1. Use fresh standards for every run; dump old standards in an acid waste container.
10.6.2. Use about 10ml for every generation of a calibration curve.

10.7. For the Blank, use 10ml of ICB.

10.8. For CCV, use 10ml of Multi standard #2 (2.0 mg/L solution)

10.9. For QCS, outside standard, use 10ml of QCS solution (1.0 mg/L solution)
10.10. Prep Blank, use 10ml of LRB
10.11. For CRI, use 10ml of low standard check, CRI solution
10.12. For CCB, use about 10ml of Calibration blank
10.13. Once tubes are filled and mixed, place the racks in the appropriate places in the autosampler

11. Analysis Procedure

11.1. Check Argon pressure, which should be > 80 psi.
11.2. Check to make sure plasma exhaust, vent at the top of the instrument, is on.
11.3. Turn on water chiller, switch in the back. Check the water level; refer to section 15.3 for filling.
11.4. Turn on autosampler by the switch in the front
11.5. Make sure ICP is on.
11.6. Turn computer on.
11.7. Open ICP Expert from the desktop.
11.7.1. Prior to igniting the plasma, make sure that:
11.7.1.1. Torch and bonnet are in place
11.7.1.2. Argon tubes are connected
11.7.1.3. Spray chamber is in place
11.7.1.4. Peristaltic pump tubing is connected
11.7.1.4.1. Waste tube = blue – blue
11.7.1.4.2. Sample tube = gray – gray
11.7.2. Ignite the plasma. This is the "Plasma on" icon at the top of the program. With the plasma and pump on, allow about 15 – 20 minutes warm up time before running analysis.
11.8. Click the "Worksheet" icon on the ICP expert opening page
11.8.1. Select "Open" and find Templates file folder
11.8.2. Open the list of metals that will be run.
11.8.3. Immediately save the worksheet
11.8.3.1. Use "Save As" function and save under the folder of the current month and year.
11.8.3.2. Save the file as: the metal/metals that are being studied and the date, for example: AlBaCd 2-9-05
11.9. <u>Sequence Tab</u>: To set up samples.
11.9.1. Go to "Sequence Editor" and adjust the number of samples in the run.
11.9.1.1. To alter the number of samples between recalibration, check the "Recalibrate Box" and adjust the number. Generally one should recalibrate every 20 samples.
11.9.1.2. To change the number of samples between each QC run, click the "Rate Generated QC" tab, then right click on the line directly under Rate QC Blocks. Left click on properties and change the number.
11.9.2. Type the sample numbers in the blank rows of the template
11.9.3. Type in any weights, final volumes, and/or dilutions associated with the sample in the columns to the right of the sample label.

11.9.4. The "Autosampler" tab will show the racks that are currently being used. Can change the size of the rack by right clicking on the rack and modifying as necessary.

11.9.5. Go to the "Sequence Parameter" tab before starting the analysis and turn plasma and pump off after run. Choose something else if you are planning on performing another run immediately afterwards.

11.10. Analysis Tab: To start a run

11.10.1. Samples need to be highlighted in yellow. Left click the numbers to the left of the sample or clicking "Tube" on the top left of the page will highlight all of the samples. The standards, blank, and QC will be in gray, these do not need to be highlighted.

11.10.2. To view only certain metals or wavelengths click on "View" at the top of the screen. At the very bottom of the list select "Column Properties". This shows all the metals and wavelengths that will be analyzed. Click on the ones that you either what hidden or shown and check the "Visible" and "Apply QC Error Actions" box. A check means that it will be shown. This action is only available before an analysis run is started or after the run is completed.

11.10.3. Make sure there is LRB in the auto-sampler rinse box.

11.10.4. Click on the green arrow above the analysis tab to start the run.

11.11. Methods Tab: To change instrument parameters.

11.11.1. To see the list of parameters, see Appendix 2.

12. Finishing Analysis

12.1. To adjust the baseline for any of the results click on the metal that you want adjusted. Hold Ctrl on the keyboard and center the red H on the curve by moving it to the right or the left. Click the "Recalculate" icon above the sequence tab.

12.2. To print the report go to "File" and click on "Report Settings."

12.2.1. The report will only contain the metals and wavelengths that are selected as visible.

12.2.2. The "Tabular" button will show only the final results for the samples.

12.2.3. The "All Data" button will show all the data used for all the calculations as well as calibration data. This option is typically used.

12.3. After printing the report shut down the instrument by turning off the plasma, water chiller, and autosampler. The main power to the ICP is NOT turned off.

12.4. Finally, make sure that the tubing is released from the peristaltic pump.

13. Detection Limits

13.1. For all of the detection limits see Appendix 1.

14. Reporting

14.1. For reporting the following are the acceptable tolerances. If the ICV and CCV are not within these ranges the data cannot be used and the sample will have to be re-run.

14.1.1. The initial calibration verification (ICV) must be within 10%.

14.1.2. The continuing calibration verification (CCV) must be within 10%.

14.1.3. All duplicates must be within 20%.

14.2. Every 10 samples must be bracketed by the ICV and CCV, if either of these fail before or after the samples then the data cannot be used.

15. Maintenance

15.1. Once a week, calibrate the wavelength, check the water chiller level, and clean the torch, spray chamber, and nebulizer. For help with disassembly/reassembly use the "Help" function. It has pictures and movies to show all the different parts of the instrument.

15.2. <u>Calibrate the wavelength</u>.

15.2.1. On the opening page of ICP Expert click on the "Instrument" icon

15.2.2. Select the "W/L Calib" tab

15.2.3. Place the sipper into the ICP tuning solution.

15.2.4. Turn the pump on fast using the "hand pump" icons at the top

15.2.5. Allow to run fast watch for a blue tip on the flame, then slow pump down

15.2.6. Click the "Calibrate Wavelength" tab on the right side, takes about 2 minutes to calibrate.

15.2.7. The range should be around 182.143nm to 766.491nm, click okay.

15.2.8. Remove the sipper from the ICP tuning solution.

15.3. Check the water level gauge on the front of the water chiller.

15.3.1. If it is at the add mark open the lid at the top. The two screws turn a quarter of a turn.

15.3.2. Fill with Distilled water, *not DI water*, till the gauge reads full, and replace lid.

15.4. <u>Cleaning the torch</u>

15.4.1. This is done as needed, or after every Deicer run.

15.4.2. Rotate white knob a quarter turn to loosen torch.

15.4.3. Disconnect argon tubing and tube to spray chamber, and remove torch.

15.4.4. Place in aqua regia (3:1 $HCl:HNO_3$ solution) for at least 30 minutes.

15.4.5. Remove and rinse well, place in 103°C oven to dry.

15.4.6. For reassembly reconnect all of the tubing and align the inner cone of the torch so that it is level with the bottom of the bonnet. Turn the white knob to hold the torch in place, and adjust the snout so that it is not touching the bonnet or the torch.

15.4.7. After moving the torch, must perform a torch alignment.

15.4.7.1. This is done following the same method as the wavelength calibration, section 15.2.

15.4.7.2. The difference is in section 15.2.2 select the "Torch Align" tab.

15.4.7.3. Follow 15.2.3-15.2.5 and then select "Torch Scan"

15.4.7.4. The range that is acceptable is close to –1 to +1.

15.4.7.5. After the scan click yes to save the results

15.5. <u>Cleaning the spray chamber</u>

15.5.1. This is done once a week, or after every Deicer run

15.5.2. Remove the nebulizer and drain tube, and disconnect the torch.

15.5.3. Lift the spray chamber and supporting bracket off the knobs on the sample compartment wall. Slide the spray chamber off the bracket.

15.5.4. Undo the two screws at the top and separate the spray chamber halves, *do not* touch the inner surface.

15.5.5. Place the spray chamber in an ultrasonic bath with one drop of Triton X-100 and DI water. Allow for about 20 minutes of cleaning and then turn over so all sides are adequately cleaned.

15.5.6. Rinse well with DI water and reassemble.

15.6. Cleaning the nebulizer

15.6.1. This can be done at the same time as the spray chamber.

15.6.2. Place in the same ultrasonic bath and allow 2-3 minutes for cleaning.

15.6.3. Rinse well with DI water.

15.6.4. It is important not to touch the nozzle of the nebulizer also nothing should be inserted into the tip for cleaning.

15.7. Tube replacement

15.7.1. Sample tubing (gray – gray) should be replaced once a week, or if it appears to be flattened due to being clamped for an extended period of time.

15.7.2. Waste tubing (blue – blue) should be replaced once every two weeks, or as needed.

15.7.3. All other tubing should be replaced every couple of months or as needed.

16. Waste Management

16.1. Samples are disposed of in the large carboys and neutralized.

II. ICP-MS SOP--EPA Method 200.8, Rev 5.4

17. Introduction

17.1. This method is used to determine the concentration of dissolved and total recoverable trace elements in ground water, surface water, drinking water, storm runoff, and wastewater. Also the total recoverable elements in sediment, sludge's, and soils. These are determined through the use of inductively coupled plasma mass spectrometry. The metals that are evaluated are Sb, As, Be, Ba, Cd, Cr, Cu, Ni, Pb, Se, Tl, U, and Zn.

18. Summary of Methods

18.1. The method describes the multi-element determination of trace elements by ICP-MS. Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height.

19. Apparatus

19.1. Varian ICP-MS ISPMS6 (Serial # EL04063917)

19.2. Vista-ICP-MS software version 1.1, Build 49.

19.3. Varian SPS-3 Auto sampler (Serial # 04017887)

19.4. Lytron Recirculating chiller RC030 (Serial #750675-01)

19.5. ICP tubing Blue-Blue (CPI P/N 4062-465)
19.6. ICP tubing Black-Black (CPI P/N 4062-430)
19.7. ICP tubing White-White three stop (CPI P/N 4062-540)
19.8. Dell personal Computer
19.9. Polystyrene test tubes 16x125mm (Fisher #14-956-8G or equivalent)
19.10. Disposable syringe 10ml (BD #309604)
19.11. Syringe filter with 0.45µm Nylon membrane (Pall #4438T or equivalent)
19.12. Filter Mate push filter (Environmental Express #SC0401)
19.13. Disposable watch glass (Environmental Express #SC505)
19.14. Digestion vessel, 68ml, with screw cap (Environmental Express #SC475)
19.15. Class A Volumetric glassware

20. Reagents

20.1. 10 µg/ml Standard Reference Material (SRM).

20.1.1. The following is a list of part numbers for the different metals. Equivalent standards may be used.

Metals	Supplier/Part #
Sb, As, Be, Cd, Cr, Pb, Se, Tl, Cu, Ni, Zn, Ba, U	CPI 4400-ICP-MSCS

20.2. Internal standard, 100µg/ml of each of the following metals.

20.2.1. Equivalent standards can be used.

Metals	Supplier/Part #
Bi, In, 6Li, Sc, Tb, Y	Custom Grade Standard VAS-IS-1

20.3. Metals Grade Acid HCl (Mallinckrodt #Mk5587 or equivalent)
20.4. Trace Level Grade Acid HNO_3 (Fisher #A509-212 or equivalent)
20.5. High Purity Deionized water
20.6. Tuning solution (Varian #VARTSMS or equivalent)
20.7. Quality Control Standards.

20.7.1. The following is a list of metals and concentrations of the QC standards: Equivalent quality control samples may be used.

Metals	Concentration	Supplier/Part #
Sb, As, Be, Cd, Cr, Cu, Ni, Pb, Se, Tl	100µg/ml	Environmental Express ICQ100-21
Ba	100µg/ml	Environmental Express ICQ100-7
U	1,000µg/ml	CPI S4400-1000641

21. Sampling and Storage

21.1. Initial preservation of samples is required. Use 1.5ml of trace metal HNO_3 per liter of sample and must ensure that pH is less then 2.0. There is a 16-hour waiting time after preservation.
21.2. Samples are stored in metals fridge or on the metals shelf.

22. Safety

22.1. Proper eye wear and gloves should be used when working with acid.

23. Interferences

23.1. The following are interferences associated with this method:
23.1.1. High concentration of metals leading to memory effect interferences.
23.1.2. Isobaric polyatomic ion or element interferences caused by ions of more than one atom or isotopes of different elements forming ions of the same mass-to-charge ratio as the analyte.
23.1.3. Abundance sensitivity caused when a small ion peak is being measured adjacent to a large one.
23.1.4. Matrix or physical interferences including but not limited to viscosity effects and high surface tension leading to problems with aerosol formation. These interferences can also lead to build up on the skimmer cone and torch.
23.1.5. For a more complete discussion refer to EPA 200.8

24. Preparation of Solutions

24.1. Lab Reagent Blank (LRB): 1.5ml HNO_3 / L DI water
24.2. 1% Nitric solution also called Calibration blank: 40ml HNO_3 / 4L DI water
24.3. Laboratory Fortified Matrix and Blank (LFM and LFB): These are spike solutions in the run. See sec 26.7 for preparation.
24.4. Internal Standard (IS): For Standard prep use concentrated solution, sec 20.2.
24.4.1. Working Internal Standard (IS): 5ml of concentrated solution into 50ml of 1% HNO_3.
24.5. Quality Control Sample (QCS): 5.0 and 50 ppb concentration.
24.5.1. 1ml of both QC standards and 1 ml of a 1/10 dilution of U stock into 50ml of 1% HNO_3 = 2,000 ppb
24.5.2. 5ml of 2,000 ppb into 200ml of 1% HNO_3 = 50 ppb
24.5.3. 0.5ml of 2,000 ppb into 200ml of 1% HNO_3 = 5 pp
24.5.3.1. Add 200µl of IS to each QC solution after brought up to volume.
24.6. Standards: 100, 50, 10, and 1 ppb final concentrations.
24.6.1. 5ml of standard into 50ml of 1% HNO_3 = 1,000 ppb intermediate.
24.6.2. 20ml of 1,000 ppb into 200ml of 1% HNO_3 = 100 ppb
24.6.3. 10ml of 1,000 ppb into 200ml of 1% HNO_3 = 50 ppb
24.6.4. 2ml of 1,000 ppb into 200ml of 1% HNO_3 = 10 ppb
24.6.5. 2ml of 100 ppb into 200ml of 1% HNO_3 = 1 ppb
24.6.5.1. To all of the standards except the 1000 ppb and 100 ppb, add 200µl of IS to solutions after they have been brought to volume. For the 100 ppb add 198µl of IS after it has been brought to volume and the 2ml for the 1 ppb solution has been removed.
24.7. ICP Tuning Solution: 10 ppb concentration.
24.7.1. 1ml of concentrated tuning solution into 1L of 1% HNO_3.

25. Sample Preparation Procedure

25.1. Samples that have visible solids or turbidity greater than 1.0 NTU after 16 hours of preservation need to be digested prior to running. The pH is verified < 2 SU by pH paper after the 16-hour minimum time.
25.1.1. Check turbidity with turbidimeter according to turbidity SOP.
25.2. When a Dissolved Metals Test is requested and cannot be filtered in the field, the samples will need to be filtered, and then preserved. This includes samples where the elements of interest are already in solution. This can be done following the Metals filtering SOP.

25.3. Sample digestions are performed using the following procedures:
25.3.1. Sludges, solids, soils, multiphasic liquids, oils, and food samples are digested using EPA method 3050A.
25.3.2. All other liquids should be digested using EPA method 200.9-11.
25.3.3. See the corresponding SOP for further details on all of these methods.

26. Samples, QC, Blank, and Standards Set up

26.1. Label test tubes with sample number.
26.2. For every 20 samples include LRB.
26.3. Add 80µl of concentrated HNO_3 to every non-digested sample test tube, LFM tube, LFB tube, and LRB tube to adjust nitric acid level to about 1%.
26.4. Add 100µl of working internal standard to every tube.
26.5. With a pipette transfer 10ml of sample or blank into the test tubes.
26.6. If an analyte is suspected of being above the calibration curve or if the matrix is suspected of becoming an interferent then a dilution should be done.
26.6.1. If a dilution is necessary, add 1ml of sample and 9ml of 1% HNO_3.
26.6.1.1. Make sure that there is working internal standard in tube.
26.7. Prepare a LFM and LFB for every 10 samples.
26.7.1. Add 50µl of the standard solution (sec 20.1.1) to the test tube.
26.7.2. Add 10ml of sample or blank (LRB).
26.8. Run a duplicate sample for every 10 samples. This is a separate tube with 10ml of the sample that is being duplicated as well as solutions from 26.3-26.4.
26.9. With parafilm, cover each sample and invert to ensure complete mixing.
26.10. For the Blank, use 10ml of 1% HNO_3.
26.11. For standards, refer to section 24.6.
26.11.1. Use fresh standards for every run; dump old standards in an acid waste container.
26.11.2. Use about 10ml for every generation of a calibration curve.
26.12. Quality Control Sample, use 10ml of QC solution (5.0 and 50.0 mg/L solution)
26.13. Use 10ml of LRB
26.14. Once tubes are filled and mixed, place the racks in the appropriate places in the autosampler

27. Analysis Procedure

27.1. Check that the following are on:
27.1.1. ICP-MS, Argon (pressure should be 80-100 psi), autosampler, water chiller, and computer.
27.2. Open ICP-MS Expert from the desktop.
27.2.1. Prior to igniting the plasma, make sure that:
27.2.1.1. Torch is in place
27.2.1.2. Argon tubes are connected
27.2.1.3. Peristaltic pump tubing is connected
27.2.1.3.1. Waste tube = blue - blue
27.2.1.3.2. Sample tube = black - black
27.2.2. Ignite the plasma. This is the "Plasma on" icon at the top of the program. With the plasma and pump on, allow about 30 minutes warm up time before running analysis.
27.3. While the instrument is warming up perform the following:

27.3.1. Place the sample tube into tuning solution.
27.3.2. Open the "Instrument Setup" tab
27.3.3. Select "Plasma Align" and hit "Start" make sure that the "Manual Sample Introduction" box is checked then select "Read"
27.3.3.1. Watch the lines for stabilization; they should reach a linear horizontal status.
27.3.4. Select "Mass Cal" and hit "Start" make sure that the "Manual Sample Introduction" box is checked then select "Read".
27.3.4.1. Print out Pb and Mg lines to show resolution between peaks is approximately 0.75 amu and peak height is 5%.
27.3.4.2. Close the dialog boxes.
27.3.5. Select "Resolution and Trim" and hit "Start" make sure that the "Manual Sample Introduction" box is checked then select "Read". When this passes, close the dialog boxes.
27.3.6. Open the "PreCalCheck" template and start the run. Make sure that there is stability in the results before performing a run with results of ten replicates having a RSD of <5%.

27.4. Click on the "Open" icon on the top. Open any of the worksheets.
27.4.1. Save as the date of the run under the folder for the month.
27.4.2. Under the "Edit" menu select delete results, and then confirm delete.
27.4.3. Type sample numbers in the labels.
27.4.4. Delete old log records by right clicking on log section and choose delete all.
27.4.5. Start run by the "Run" icon

27.5. View table one for a list of isotopes that are being analyzed and monitored during the run.

27.6. To view all the method parameters, see Appendix 2.

28. Finishing Analysis

28.1. To print the report go to "File" and click on "Report Settings."

28.2. After printing the report shut down the instrument by making sure the following is off: plasma, water chiller, and autosampler. The main power to the ICP is NOT turned off.

28.3. Finally, make sure that the tubing is released from the peristaltic pump.

29. Detection Limits

29.1. For all of the detection limits, see Appendix 1.

30. Reporting

30.1. For reporting the following are the acceptable tolerances. If these are not within these ranges the data cannot be used and the sample will have to be re-run.
30.1.1. The Quality Control Sample (QCS) must be within 10%.
30.1.2. The Internal Standard (IS) must be within 60-125%.
30.1.3. Laboratory Fortified Matrix (LFM) must be within 70-130%.
30.1.4. Laboratory Fortified Blank (LFB) must be within 85-115%.
30.1.5. LBR must be run every 20 samples and it must be less then the MDL.
30.1.6. Calibration Blank and Check Standard must be run after each calibration and after every 10 samples.
30.1.7. All duplicates must be within 20%.

30.2. The following are a list of the concentrations that are used for the reporting limits in sec 30.1.

30.2.1. QCS = 50 ppb
30.2.2. LFM and LFB = 50 ppb
30.2.3. IS = 100 ppb
30.2.4. Check Standard = 10 ppb

31. Maintenance

31.1. Cleaning the torch

31.1.1. This is done as needed.
31.1.2. Remove the clamps outside and inside the torch chamber.
31.1.3. Rotate white knob a quarter turn to loosen torch.
31.1.4. Disconnect argon tubing, and remove torch.
31.1.5. Place in aqua regia (3:1 $HCl:HNO_3$ solution) for at least 30 minutes.
31.1.6. Remove and rinse well, place in 103°C oven to dry.
31.1.7. For reassembly reconnect all of the tubing and align the inner cone of the torch so that it is level with the right hand side of the RF coil. Turn the white knob to hold the torch in place.
31.1.8. Reattach the clamps on the outside and inside of the torch chamber.

31.2. Cleaning the Skimmer cone and inside cone:

31.2.1. This is easiest to clean while the torch is being cleaned.
31.2.2. Remove the torch as in section 31.1.
31.2.3. Click on the "Actions" menu at the top of the computer. Select "Park Torch"
31.2.4. With the round grey tool remove the skimmer cone. Be careful not to drop this down into the instrument.
31.2.5. With the yellow tool remove the inner cone. DO NOT touch the tip of the cone.
31.2.6. Can scrub the skimmer cone rigorously with a cloth or sponge.
31.2.7. Place the inner cone in an ultrasonic bath with one drop of Triton X-100 and DI water. Allow for about 20 minutes of cleaning.
31.2.8. Rinse well with DI water and reassemble.

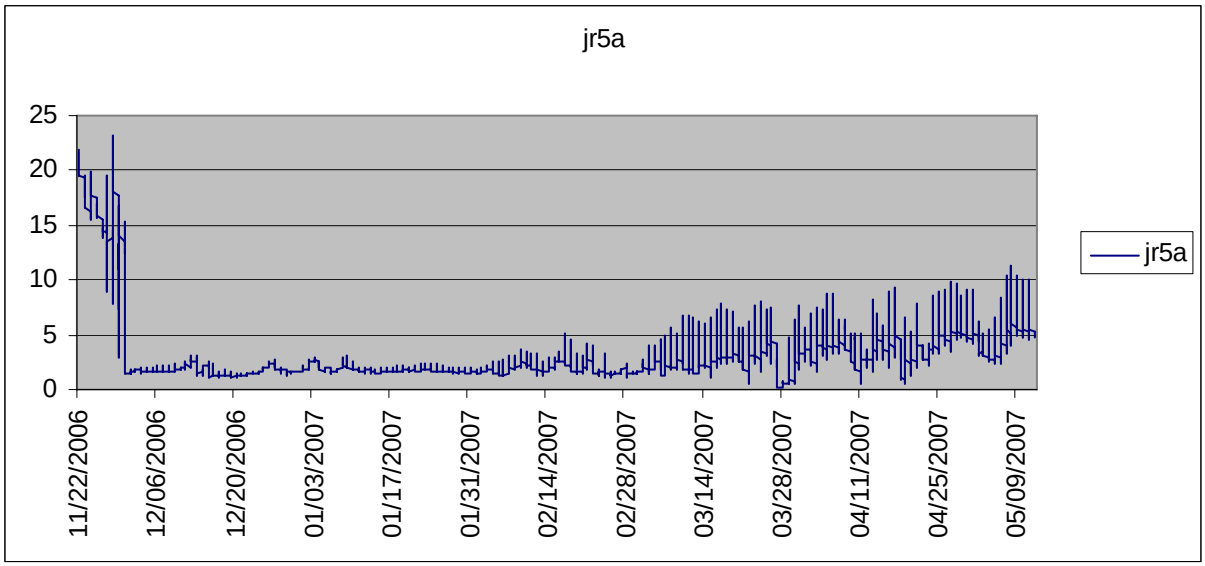
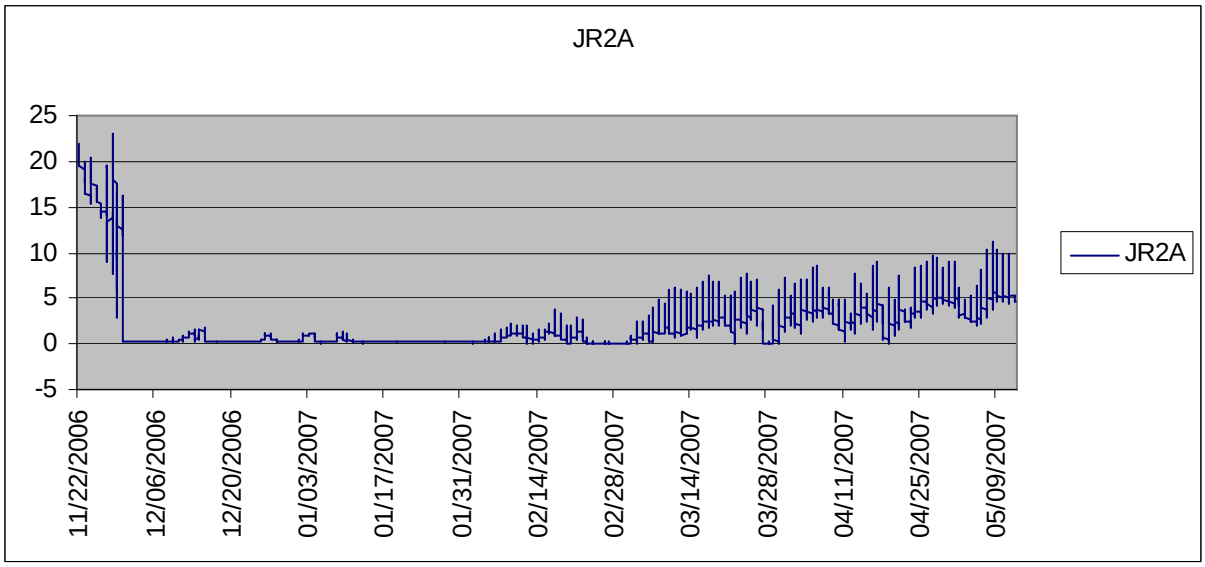
31.3. Tube replacement

31.3.1. Sample tubing (black-black) should be replaced as necessary.
31.3.2. Waste tubing (blue – blue) should be replaced as necessary.
31.3.3. All other tubing should be replaced every couple of months or as needed.

32. Waste Management

32.1. Samples are disposed of in the large carboys and neutralized.

Element of Interest	Isotope/s used for analysis	Isotope/s being monitored
Antimony	123	121
Arsenic	75	
Barium	137	135
Beryllium	9	
Cadmium	111	106, 108, 114
Chromium	52	53
Copper	63	65
Lead	206, 207, 208	
Nickel	60	62
Selenium	82	77
Silver	107	109
Thallium	205	203
Uranium	238	
Zinc	66	67, 68

Appendix B
Temperature Logger Data
West Fork Jarbidge River

Note: Station jr5a is downstream of the adit, Station jr2a is upstream of the adit discharge (*see* Figure 1 in text).