

6KRO

STATE OF MONTANA
NATURAL RESOURCE DAMAGE PROGRAM

QUALITY ASSURANCE/QUALITY CONTROL REPORT
NATURAL RESOURCE DAMAGE ASSESSMENT OF THE
UPPER CLARK FORK RIVER SITES

JANUARY 1995





Digitized by the Internet Archive
in 2012 with funding from
LYRASIS Members and Sloan Foundation

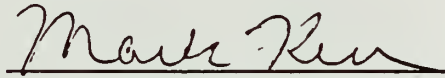
<http://archive.org/details/qualityassuracne00shor>

**QUALITY ASSURANCE/QUALITY CONTROL REPORT
UPPER CLARK FORK RIVER BASIN**

The following persons participated in the writing of this report:

A handwritten signature in cursive script, reading "Diane L. Short". The signature is written in dark ink and is positioned above a horizontal line.

Diane L. Short

A handwritten signature in cursive script, reading "Mark A. Kerr". The signature is written in dark ink and is positioned above a horizontal line.

Mark A. Kerr

A handwritten signature in black ink, reading "Diane L. Short". The signature is fluid and cursive, with a horizontal line drawn underneath the entire name.

Diane L. Short
Diane Short and Associates
1667 Cole Boulevard
Building 19, Suite 400
Golden, Colorado 80401

Mark A Kerr

Mark A. Kerr
Natural Resource Damage Litigation Program
State of Montana
Department of Justice
Old Livestock Building
1310 East Lockey Avenue
PO Box 210425
Helena, Montana 59620-1425

**QUALITY ASSURANCE/QUALITY CONTROL REPORT
SURFACE WATER SAMPLING**

TABLE OF CONTENTS

TABLE OF CONTENTS	i
LIST OF ACRONYMS	iii
LIST OF TABLES	iv
I INTRODUCTION	1
II FIELD QA/QC	1
A. Sample Bottle Preparation	2
B. Sampling Date and Time	2
C. Sampling Team	2
D. Sampling Locations	2
E. Physical Description of Sampling Location	2
F. Sample Collection Methods	2
G. Field Preparation Methods	3
H. Sample Numbers	3
I. Sample Preservation	3
J. Sample Shipping Information	4
K. Field Instrument Calibrations and Field Measurements	4
L. QC Samples	6
L1. Bottle Blanks	8
L2. Trip Blanks	8
L3. Filter Blanks	8
L4. Decontamination Blanks	8
L5. Field Replicates	11
L6. Field Splits	11
L7. Standard Reference Material	11
III LABORATORY QA/QC	15
A. Data Qualifiers	15
B. Sample Holding Times	16
C. Sample Preparation Methods	16
D. Analytical Methods and Detection Limits	16
E. Instrument Calibration	17
F. Calibration Blanks	18
G. Preparation (Method) Blanks	19
H. ICP Interference Check Samples	19
I. Interelement Correction Factors	19
J. Spikes	20
K. Duplicates	20

L.	GFAA Quality Control.	20
M.	Laboratory Splits (Duplicates).	21
N.	Sample Reanalyses.	25
IV	CUSTODY AND DOCUMENT CONTROL.	26
A.	Field Custody.	26
B.	Sample Delivery.	26
C.	Laboratory Custody.	26
D.	Sample Tracking.	27
E.	Document Control.	27
F.	Document Review.	27
G.	Identity of Sample Collector	27
V	RESULTS - DATA QUALIFICATION.	27
VI	PRECISION, ACCURACY, REPRESENTATIVENESS, COMPLETENESS AND COMPARABILITY.	34
A.	Precision.	34
B.	Accuracy.	34
C.	Representativeness	34
D.	Completeness.	35
E.	Comparability.	35
VII	REFERENCES.	36

LIST OF ACRONYMS

CCV	Continuing Calibration Verification
CFR	Clark Fork River
CLP	Contract Laboratory Program
COC	Chain-of-Custody
CRDL	Contract Laboratory Detection Limit
DOC	Dissolved Organic Carbon
EPA	Environmental Protection Agency
GFAA	Graphite Furnace Atomic Absorption
ICB	Initial Calibration Blank
ICP	Inductively-Coupled Plasma Emission Spectrometry
IDL	Instrument Detection Limit
LCS	Laboratory Control Sample
MDL	Method Detection Limit
MSA	Method of Standard Additions
MT TR	Montana Total Recoverable
NBS	National Bureau of Standards
ND	Not Detectable
NM	Not Measured
NRDA	Natural Resource Damage Assessment
NRDP	Natural Resource Damage Program
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
SBC	Silver Bow Creek
SC	Specific Conductance
SOP	Standard Operating Procedure
SOW	Statement of Work
TR	Total Recoverable
TSS/SC	Total Suspended Solids/Specific Conductance Splitting

LIST OF TABLES

1a.	Results of Field Duplicate Measurements (Dissolved Oxygen)	7
1b.	Results of Duplicate Measurements (water temperature)	7
2a.	Results of Trip Blank Analyses (Metals)	9
2b.	Results of Trip Blank Analyses (Non-Metal Analytes)	9
3.	Results of Filter Blank Analyses, Dissolved Concentrations	10
4.	Results of Decontamination Sample Analyses	10
5a.	Results of Field Replicate Sample Analyses (Metals)	12
5b.	Results of Field Replicate Sample Analyses (Non-Metals)	13
6a.	Results of Field Split Sample Analyses (metals)	14
6b.	Results of Field Split Sample Analyses (non-metals)	15
7.	Detection Limits for Surface Water Sample Analysis	17
8.	Samples Analyzed by Method of Standard Additions (MSA)	21
9.	Results of Laboratory Split Sample Analyses, EPA Total Recoverable	22
10.	Results of Laboratory Split Sample Analyses, MT Total Recoverable	23
11.	Results of Laboratory Split Sample Analyses, Dissolved Concentrations in Parts Per Billion	24
12.	Sample Reanalysis - Duplicate Digested Samples	25
13.	Sample Reanalysis Due to Suspected Sample Contamination	25
14.	EPA Total Recoverable and Montana Total Recoverable Metals Concentrations in Silver Bow Creek and the Clark Fork River	28
15.	EPA Total Recoverable and Montana Total Recoverable Metals Concentrations in the Big Hole River, Rock Creek, and Ruby River	29
16.	EPA Total Recoverable and Montana Total Recoverable Metals Concentrations in Silver Bow Creek, Yankee Doodle Creek, Blacktail Creek, Bison Creek and Flint Creek	30
17.	Dissolved Hazardous Substance Concentrations in Silver Bow Creek and the Clark Fork River	31
18.	Dissolved Metals Concentrations in the Big Hole River, Rock Creek and the Ruby River	32
19.	Dissolved Metals Concentrations in Silver Bow Creek, Yankee Doodle Creek, Blacktail Creek, Bison Creek and Flint Creek	33

QUALITY ASSURANCE/QUALITY CONTROL REPORT SURFACE WATER SAMPLING

I. INTRODUCTION

The purpose of this report is to evaluate and summarize the quality assurance (QA) and quality control (QC) associated with the collection and analysis of surface water samples and data for the Clark Fork Basin Natural Resource Damage Assessment (NRDA). This report also evaluates the collection of periphyton samples described in Assessment Plan, Part III (NRDP, 1994). Results of surface water assessment activities are summarized in Appendix A to Aquatic Resources Injury Assessment Report, Upper Clark Fork River Basin (Lipton et. al., 1995). QA/QC guidance was provided by the Natural Resource Damage Program (NRDP) Quality Assurance Project Plan (QAPP) (NRDP, 1992).

The organization of this report generally follows the data validation outline presented in Section 11.0 of the QAPP. Section II describes Sample Collection and Field QA/QC, including deviations from sampling protocols and standard operating procedures (SOPs) referenced in the Assessment Plan, Part II (NRDP, 1992) and Assessment Plan, Part III (NRDP, 1994), or described in the Lipton et. al. (1995). (Modifications to the Assessment Plan and research protocols contained therein are summarized in NRDL, 1995). Section III describes and evaluates Laboratory QA/QC. Section IV summarizes Custody and Document Control. Section V presents results of data qualification. Section VI discusses Precision, Accuracy, Representativeness, Completeness and Comparability.

II. SAMPLE COLLECTION AND FIELD QA/QC

QC samples are used to evaluate sample contamination and the replicability of sample collection methods. QC samples for evaluating sample contamination included bottle blanks, trip blanks, filter blanks, and field decontamination (rinseate) blanks. Grab samples, duplicates and splits were collected to validate sample collection and processing methods.

Samples were assigned a six-digit field number, consisting of a three-digit random number followed by a three-digit date code that represented the month and date of sample collection (i.e. 929-505). Sample numbers were recorded in the field logbook, on sample tracking forms, and chain-of-custody (COC) records.

There are no Environmental Protection Agency (EPA) control limits nor corrective actions for field QC samples, with the exception of field blanks. EPA (1985) and Viar & Co. (1988) consider field QC as supporting evidence in the overall assessment of a data set or sampling event. Field QC is not the basis of accepting or rejecting data, but rather acts as additional evidence in support of those conclusions arrived at by an evaluation of the complete data set. Therefore, except in the case of gross errors, poor performance on field QC samples does not invalidate data.

The following items were reviewed for sample collection and preparation, and field QA/QC:

A. Sample bottle preparation

Bottles for most surface water samples were prepared following NRDP SOP 9.0 (Preparation of Sampling Apparatus). Bottles for dissolved organic carbon (DOC) were rinsed with concentrated sulfuric acid and distilled/deionized water. Bottles for periphyton samples were not washed or rinsed prior to use.

B. Sampling date and time

Sampling dates and times were recorded in the field logbook and on chain-of-custody (COC) records. Inconsistencies between the field logbook and COC records have been corrected.

C. Sampling team

The signature of the field team leader appears at the bottom of each page in the field logbook. The field assistant's name appears in the initial entry for each sampling event.

D. Sampling locations

Sampling locations were recorded in the field logbook and on sample tracking forms. Inconsistencies between the field logbook and sample tracking forms have been corrected.

E. Physical description of sampling location

Sampling locations were not physically described in the field logbook: Sampling locations are identified on topographic maps included in the Administrative Record.

F. Sample collection methods

Samples were collected pursuant to NRDP SOP 3.0 (cross-section depth and width-integrated sample compositing) and NRDP SOP 6.0 (collection of field quality control samples).

Samples were collected, and identified on sample tracking forms, as complete cross-section composite, partial cross-section composite, or grab samples.

The following deviations from SOPs were recorded in the field logbook:

- May 11: at the first three sampling sites (Clark Fork River at Bearmouth, Beavertail Hill, and Turah) the dissolved metals sample bottle was rinsed with unfiltered stream water. Since the bottles were subsequently rinsed 3 times with the filtered sample before collecting the filtrate, contamination would have been highly unlikely.
- May 12: approximately 500 mls of sample for total suspended solids (TSS), specific conductance (SC) and total recoverable (TR) metals analyses (Big Hole River at Kalsta Ranch) were collected instead of 800 mls, due to a shortage of sample. The sample size was sufficient for laboratory analyses.

G. Field preparation methods

Field preparation included sample splitting (subsampling) and filtering.

Sample splitting adhered to NRDP SOP 4.0. Sample filtration adhered to NRDP SOP 5.0. No deviations from SOPs were noted in the field logbook.

H. Sample numbers

Sample numbers were recorded in the field logbook, on sample tracking forms and COC records. These documents were compared to identify any inconsistencies or omissions in the recording of sample numbers. Inconsistencies in the recording of sample numbers have been corrected. It is noted that a sample was recorded on the dissolved metals sample tracking form as a "Trip Blank", with sample number 791-415. This sample was not recorded in the field logbook. Because trip blanks were not analyzed for dissolved metals, the origin of this sample is unexplained.

I. Sample preservation

Samples were preserved following the QAPP. Deviations from the recommended sample preservation procedure are noted below:

- April 6 (Bison Creek at Elk Park): TR metals sample was overpreserved (twice the recommended amount of preservative was added);
- April 24 (Ruby River below Ruby Reservoir): sample preservation was not recorded;
- April 24 (Bison Creek at Elk Park): sample preservation was not recorded; and
- May 11 (Rock Creek near Stonehenge): sample preservation was not recorded.

- August 9 (periphyton collection): field decontamination samples were not preserved.

Overpreservation of the TR metals sample on April 6 would have no effect on the EPA TR concentration, as additional acid is used in the sample digestion process. Overpreservation may have affected the MT TR concentration by solubilizing more of the sediment-bound metals. Given the objective of the MT TR analyses (to demonstrate that the method results in a lower analyte concentration than the EPA TR method), the overpreservation was ultimately inconsequential. In unpreserved samples, metals may adsorb to the sample bottle and bias low the reported concentration. In addition, any directly aspirated samples (MT TR method) would not have been acidified, and low values would have been obtained since metals would not have been solubilized.

J. Sample shipping information

No samples were shipped via commercial carrier. All samples were hand-delivered from the field to the laboratory.

K. Field instrument calibrations and field measurements

Field instruments included:

- Marsh-McBirney Model 2100 flowmeter (primary unit Serial No. 9040)
- Marsh-McBirney Model 2100 flowmeter (backup unit Serial No. 8320)
- Marsh-McBirney Model 2100 flowmeter (loaner unit Serial No. 90135)
- Hach One portable pH meter
- DH-48 depth integrating sampler (primary unit)
- DH-48 depth-integrating sampler (backup unit)
- red alcohol thermometer, 1°C graduation (primary unit, no correction factor)
- red alcohol thermometer, 1°C graduation (backup unit, -1°C correction factor)
- continuous recording water temperature data loggers (Onset Instrument Corporation)

The pH meter was calibrated using pH 7 and pH 9 standards, rather than pH 4 and pH 7 standards specified in FPM SOP 5.2.2. Standards of pH 7 and pH 9 better bracketed the pH values commonly measured in surface waters of western Montana. Calibration was verified by measurement of pH 7 and/or pH 9 standards after calibration, and was often rechecked during and at the end of the day.

Field thermometers were calibrated against NBS (National Bureau of Standards) certified thermometers. Temperature corrections were recorded on the thermometer and applied to field measurements, as appropriate.

Flowmeter calibration is performed by the manufacturer. A calibration "check" is made in the field to verify that the flowmeter batteries are adequately charged and properly installed (per FPM SOP 5.1.1). This check was made before taking flowmeters into the field, and at the beginning of each sampling day.

Equipment problems noted in the field logbook include:

- April 5: primary flowmeter was not calibrating, backup unit was used for the rest of April 5 and April 6;
- April 6: pH meter did not calibrate properly; April 5 calibration was used and verified against pH standards;
- April 15-16: backup flowmeter used (primary flowmeter returned for manufacturer servicing);
- April 23-24: manufacturer-loaned flowmeter used (primary flowmeter in manufacturer servicing);
- May 2-3: backup DH-48 used (primary unit left in field on April 24); used backup flowmeter (primary unit would not calibrate); primary thermometer broke, used backup thermometer;
- May 11: used backup flowmeter (primary flowmeter returned for servicing); used backup DH-48 (primary DH-48 had not been recovered yet); lost DH-48 gasket at first site, replaced gasket; pH meter temperature compensator fluctuated, noted where pH readings were with and without temperature compensation; noted near end of day that DH-48 gasket appeared to leak at times, overfilling bottle or filling bottle too quickly;
- May 12: primary DH-48 was recovered at first sampling location, and was used remainder of day; and
- May 20-21: backup flowmeter was used (primary flowmeter in manufacturer servicing).

The primary flowmeter had been serviced and calibrated by the manufacturer prior to the first sampling date. The backup flowmeter had not been serviced for several years. Due to problems with the primary unit and its return to the manufacturer for servicing, the backup unit was used for all sampling dates except April 23-24, for which a manufacturer loaner unit was used. The backup unit was sent for servicing and calibration after sampling ended. The flowmeter calibration was found to be well within the expected precision of the flow-gauging method (approximately $\pm 15\%$).

Samples collected with the backup DH-48 and replacement gasket on May 11 (Clark Fork

River, Flint Creek, and Rock Creek sites) may have been affected by the leaking gasket (the amount of TSS in the sample may be under or overrepresented because of the entry of water into the bottle around the gasket). Given that the TSS concentrations for these sites were low (between 2 and 8 mg/l), it is unlikely that leaking substantially affected the representativeness of the samples. Additionally, duplicate composite samples collected at Flint Creek showed agreement within an acceptable relative percent difference range ($\pm 35\%$) for all constituents measured, and similar acceptable agreement between the composite and grab samples was evident.

L. QC samples

Field QC includes taking duplicate field measurements. Duplicate measurements were made for dissolved oxygen and water temperature. Results of duplicate measurements for dissolved oxygen are summarized in Table 1a. Results of duplicate measurements of water temperature are presented in Table 1b.

QC samples collected for laboratory analysis are identified in the field logbook and on sample tracking forms. All QC samples were collected at one randomly selected sampling site each sampling trip. Inconsistencies between the field logbook and sample tracking forms in recording QC sample information have been corrected.

Field blanks (bottle, trip, filter and decontamination) are used to evaluate sample contamination. They are assessed and qualified the same as preparation blanks (see section IV-G). For any blanks greater than two times the instrument detection limit (IDL), results less than five times the amount in any associated samples are qualified UJB#, where "#" is the value of the highest blank associated with the sample.

Analysis of samples from the first two sampling events indicated potential zinc contamination. The source was determined to be the polysulfone bottles caps, which were found to leach zinc on contact with an acid solution. Elevated zinc concentrations in several field blanks possibly resulted from these caps. The laboratory determined that contamination was not actually in the sample, but around the threads of the bottle top where the caps were seated. This potential contaminant source was most relevant to the EPA TR samples, for which an aliquot is poured from the sample bottle for digestion. New aliquots of samples were redigested after discovery of the contaminant source. Polyethylene bottle caps were used in subsequent sampling events. It is noted that analytical data from these two sampling events have been qualified only to the extent that zinc concentrations in field blanks exceeded QC limits.

Table 1a.
Results of field duplicate measurements (dissolved oxygen).

Date	Sample	Concentration (mg/l)
08/05/94	Sample	6.70
	Duplicate	6.70
08/09/94	Sample	6.10
	Duplicate	6.10
08/11/94	Sample	7.90
	Duplicate	7.95

Table 1b.
Results of field duplicate measurements (water temperature)¹

Clark Fork River			Duplicate		
08/24/94	18:00:00	20.57	08/24/94	18:00:00	20.73
08/25/94	19:12:00	20.08	08/25/94	19:12:00	20.24
08/26/94	20:00:00	18.79	08/26/94	20:00:00	19.11
08/27/94	21:12:00	19.59	08/27/94	21:12:00	19.76
08/28/94	22:00:00	18.47	08/28/94	22:00:00	18.79
08/29/94	23:12:00	16.54	08/29/94	23:12:00	16.86
08/31/94	00:00:00	16.22	08/31/94	00:00:00	16.38
09/01/94	01:12:00	14.96	09/01/94	01:12:00	15.12
09/02/94	02:00:00	14.80	09/02/94	02:00:00	14.96
09/03/94	03:12:00	15.59	09/03/94	03:12:00	15.75
09/04/94	04:00:00	13.71	09/04/94	04:00:00	13.87
09/05/94	05:12:00	12.16	09/05/94	05:12:00	12.32
09/06/94	06:00:00	12.63	09/06/94	06:00:00	12.78
09/07/94	07:12:00	14.02	09/07/94	07:12:00	14.18
09/08/94	08:00:00	14.18	09/08/94	08:00:00	14.33
09/09/94	09:12:00	14.49	09/09/94	09:12:00	14.64
09/10/94	10:00:00	12.01	09/10/94	10:00:00	12.16
09/11/94	11:12:00	12.94	09/11/94	11:12:00	13.09
09/12/94	12:00:00	14.33	09/12/94	12:00:00	14.49

1. Results presented as date, time, and temperature (°C) for the daily maximum temperature recorded.

L1. Bottle blanks

Bottle blanks for water samples were analyzed at the frequency specified in the QAPP (one per bottle lot) prior to the first sampling run. Analytical results for bottle blanks were less than detectable. No bottle blank was analyzed for periphyton collection.

L2. Trip blanks

A trip blank consisted of a sample bottle containing distilled/deionized water that was transported to and preserved in the field, and returned to the laboratory with other samples for analysis. EPA TR and MT TR metals, TSS, SC were analyzed (for dissolved metals concentrations, filter blanks also served the purposes of trip blanks). For water sampling, trip blanks were collected at the frequency specified in the QAPP (once per sampling event for each of six sampling events). No trip blanks were analyzed for periphyton collection.

Results of trip blanks are summarized in Table 2. Trip blanks generally showed undetectable concentrations of cadmium, copper, and lead. Three EPA TR zinc concentrations exceeded the control limit of 2X IDL (sample dates 4/6, 4/24, and 5/11). The largest zinc concentration (19 ppb) had a corresponding MT TR zinc concentration of 2 ppb. This suggests that the high zinc concentration may have resulted from contamination of the sample during laboratory processing.

L3. Filter blanks

Filter blanks were collected by filtering distilled/deionized water carried into the field in a clean bottle. Because filter blank sample bottles are transported to the field and returned to the laboratory with all other sample bottles, analytical results can also serve the purpose of a trip blank. Filter blanks were analyzed for dissolved metals.

Filter blanks results (Table 3) generally showed undetectable analyte concentrations. Two samples (sample dates 4/6 and 4/15) contained zinc concentrations greater than 2X the IDL.

L4. Decontamination blanks

Decontamination (rinseate) blanks measure the effectiveness of sampling equipment decontamination. Decontamination blanks consisted of a distilled/deionized water rinse of decontaminated sampling equipment (DH-48, sampling bucket, sample splitting ladle, funnel). Decontamination blanks were analyzed for EPA TR and MT TR metals.

Results of decontamination blanks are presented in Table 4. Analyte concentrations are generally undetectable. The first blank (sample date 4/6) contained EPA TR and MT TR copper and zinc concentrations greater than 2X IDL. Two other EPA TR zinc concentrations (sample dates 4/15 and 5/3) also exceeded 2X IDL. The MT TR lead (sample date 4/24) concentration also exceeded 2X IDL.

Table 2a.
Results of trip blank analyses (metals)^{1,2}
(concentrations in ug/l)

Date	Sample Number ³	Cadmium (ug/l)		Copper (ug/l)		Lead (ug/l)		Zinc (ug/l)	
		EPA TR	MT TR	EPA TR	MT TR	EPA TR	MT TR	EPA TR	MT TR
04/06/92	NM/0497	ND	ND	ND	ND	1.3	ND	18.5	2.0
04/15/92	0727/0685	ND	NM	ND	ND	ND	NM	1.5	NM
04/24/92	NM/0844	ND	ND	ND	ND	ND	ND	3.0	ND
05/03/92	0963/0994	ND	NM	ND	ND	ND	NM	1.5	NM
05/11/92	1228/1207	ND	ND	ND	ND	ND	ND	ND	ND
05/20/92	1429/1439	ND	NM	1.8	NM	ND	NM	3.5	NM

1. Abbreviations: NM (not measured), ND (concentration below detection limits), EPA TR (EPA total recoverable), MT TR (Montana total recoverable)
2. Detection limits: cadmium (0.2 ug/l); copper, lead and zinc (1 ug/l); TSS (1 mg/l)
3. Sample number TSS, SC/sample number TR metals

Table 2b.
Results of trip blank analyses (non-metal analytes)^{1,2}

Date	Analyte ³	Sample Number	Concentration
04/15/92	TSS	0727	ND
	SC	0727	26
05/03/92	TSS	0963	ND
	SC	0963	30
05/11/92	TSS	1228	ND
	SC	1228	5
	DOC	1151	<0.5
05/20/92	TSS	1429	ND
	SC	1429	3
08/11/94	DOC	105616	<0.5
	DOC	105617	0.5

1. Abbreviations: ND (concentration below detection limits)
2. Detection limits: TSS (1 mg/l); DOC (0.5 mg/l)
3. TSS (total suspended solids); SC (specific conductance); DOC (dissolved organic carbon)

Table 3.
Results of filter blank analyses, dissolved concentrations^{1,2}

Date	Sample Number	Ca (mg/l)	Mg (mg/l)	Cadmium (ug/l)	Copper (ug/l)	Lead (ug/l)	Zinc (ug/l)
04/06/92	0510	ND	ND	ND	ND	ND	4
04/15/92	0704	ND	ND	ND	ND	ND	3
04/24/92	0861	ND	ND	ND	ND	ND	ND
05/03/92	0975	ND	ND	ND	ND	ND	ND
05/11/92	1210	ND	ND	ND	ND	ND	ND
05/20/92	1456	ND	ND	ND	ND	ND	ND

1. Abbreviations: ND (concentration below detection limits).

2. Detection limits: cadmium (0.2 ug/l); copper, lead and zinc (1 ug/l); calcium and magnesium (1 mg/l)

Table 4.
Results of decontamination sample analyses
(concentrations in ug/l)^{1,2,3}

Date	Sample Number	Cadmium		Copper		Lead		Zinc	
		EPA TR	MT TR	EPA TR	MT TR	EPA TR	MT TR	EPA TR	MT TR
04/06/92	0496	ND	ND	7.4	5.0	2.0	1.1	14.5	9.0
04/15/92	0679	ND	NM	1.1	NM	1.3	NM	3.0	NM
04/24/92	0835	ND	ND	1.8	1.8	ND	9.3	ND	ND
05/03/92	1002	ND	NM	ND	NM	ND	NM	2.8	NM
05/11/92	1191	ND	ND	ND	ND	ND	ND	1.5	ND
05/20/92	1440	ND	NM	ND	NM	ND	NM	2.0	NM
08/11/94	105633	NM	ND	NM	ND	NM	ND	NM	ND
08/14/94	105632	NM	ND	NM	ND	NM	ND	NM	ND

1. Abbreviations: NM (not measured), ND (concentration below detection limits).

2. Detection limits (surface water): cadmium (0.2 ppb); copper, lead and zinc (1 ppb)

Detection limits (periphyton): cadmium (5 ppb); copper (10 ppb); lead (50 ppb); zinc (5 ppb).

3. Samples collected in 1992 associated with surface water sample collection. Samples collected in 1994 associated with periphyton sample collection.

L5. Field replicates

Field replicates are used to assess field and laboratory precision. Although duplicate samples were collected as close in time as possible, there is inherently a time factor which cannot be quantified when duplicate samples are not collected simultaneously. For duplicates collected within a short period of time, the time factor would not likely be significant. The relative percent difference (RPD) can be used to assess field duplicate data. Control limits for field duplicates is RPD $\leq 35\%$ or duplicate difference of $\leq 2 \times \text{CRDL}$ (contract laboratory detection limit) if both results are less than $5 \times \text{CRDL}$. For low-level results that were commonly measured in surface water samples, $\leq 2 \times \text{IDL}$ is more meaningful than a calculation of $\leq 2 \times \text{CRDL}$. If either of the values is less than the IDL, the value is not calculable.

Per the CLP data validation guidance, data are not technically qualified for exceeding a $2 \times \text{IDL}$ duplicate difference. Data have been qualified only for data assessment purposes in monitoring homogeneity of these sample analyses. No data are outside the CRDL limit defined in the EPA guidance. Data that have been qualified for RPD limit deviations are also data under the $5 \times \text{CRDL}$ limit and would not be qualified referencing the EPA guidance. No EPA CLP duplicate deviations have occurred in analysis of these data.

A total of seven duplicates (six composites and one grab) were collected during each of six sampling events. The 6 duplicate composites for 74 total composite ambient samples met the QAPP target frequency of 1 per 20. The one duplicate grab for 13 total grab ambient samples also met the QAPP target of 1 per 20.

Results of field duplicate analyses are summarized in Table 5. All duplicates were analyzed for EPA TR cadmium, copper, lead and zinc. Three duplicates were analyzed for MT TR metals. Dissolved analyses were made on all but one duplicate. All 56 duplicate analyses met target RPD limits. The results indicate that field and laboratory precision is acceptable.

L6. Field splits

Field splits are used to assess field subsampling technique, and sample homogeneity. Splits were collected from the field duplicate sample. All splits were analyzed for EPA TR metals. Two splits were analyzed for MT TR metals. One split sample was analyzed for dissolved metals. Results are assessed in the same manner as field duplicates. Field splits were collected on all but the first sampling event. The frequency of 5 split samples for 87 composited samples was within the QAPP target frequency of 1 per 20.

Results of field splits are presented in Table 6. Of the 28 analyses made on split samples, four were outside of the target RPD limits. The results indicate that field subsampling technique is generally statistically acceptable (greater than 85 percent of all splits were within control limits). Because the results of field splits do not necessarily reflect sample-specific effects in the associated samples of a sampling event, no sample qualification has resulted for duplicates which were outside target RPD limits.

Table 5a.
Results of field replicate sample analyses (metals)^{1,2}
Concentrations in ug/l (surface water) and mg/kg dry weight (periphyton)

Date	Sample Number	Cadmium			Copper			Lead			Zinc		
		EPA TR	MT TR	Diss	EPA TR	MT TR	Diss	EPA TR	MT TR	Diss	EPA TR	MT TR	Diss
Surface water ³													
04/06/92 - Sample	0499/0511	ND	ND	ND	7	5	5	1	ND	ND	20	20JD40	16
Duplicate	0491/0512	ND	ND	ND	6	3	4	1	ND	ND	27	14	19
04/15/92 - Sample	0684/0710	0.2	NM	ND	26	NM	7	2	NM	ND	30	NM	11
Duplicate	0690/0701	ND	NM	ND	24	NM	ND	3	NM	ND	29	NM	12
04/24/92 - Sample	0848/NC	ND	ND	NC	2J*3	1	NC	2	2	NC	8	7	NC
Duplicate	0840/NC	ND	ND	NC	8	1	NC	2	2	NC	11	5	NC
05/03/92 - Sample	0999/0985	ND	NM	ND	2	NM	ND	5	NM	ND	13	NM	ND
Duplicate	0997/0980	ND	NM	ND	3	NM	ND	6	NM	ND	15	NM	1
05/11/92 - Sample	1206/1225	ND	ND	ND	3	3	1	4	4	ND	11	9	ND
Duplicate	1202/1209	ND	ND	ND	ND	1	ND	4	3	ND	10	9	ND
05/20/92 - Sample	1438/1465	ND	NM	ND	4	NM	3	ND	NM	ND	5	NM	4
Duplicate	1451/1460	ND	NM	ND	5	NM	3	ND	NM	ND	6	NM	2
05/21/92 - Sample	1436/1468	0.3	NM	ND	8	NM	3	ND	NM	ND	6	NM	1
Duplicate	1449/1454	ND	NM	ND	7	NM	3	1	NM	ND	5	NM	ND
Periphyton													
08/09/94 - Sample	105625		<0.93			<9.30			<9.30			50.00	
Triplicate	105626		<1.00			<10.50			<10.50			35.00	
Triplicate			<1.00			<9.60			<9.60			41.00	
08/09/94 - Sample	105618		2.59			126.00			17.80			398.00	
Triplicate	105619		2.01			128.00			15.20			356.00	
Triplicate	105620		2.37			110.00			17.70			422.00	
08/11/94 - Sample	105622		1.06			27.10			<10.60			99.40	
Triplicate	105623		<1.01			27.00			<10.10			101.00	
Triplicate	105624		<1.04			33.00			<10.40			106.00	

- Abbreviations: NM (not measured), ND (concentration below detection limits).
- Detection limits (surface water): Cadmium (0.2 ppb); copper, lead and zinc (1 ppb).
Detection limits (periphyton): cadmium (5 ppb); copper (10 ppb); lead (50 ppb); zinc (5 ppb).
- Sample number is total recoverable sample/dissolved sample; NC = not collected

Table 5b.
Results of field replicate sample analyses (non-metals)^{1,2}

Date	TSS (mg/l)		SC (umhos at 25° C)		DOC (mg/l)	
	Sample Number	Concentration	Sample Number	Concentration	Sample Number	Concentration
04/06/92 - Sample	0534	4.4	0534	121	NC	NC
Duplicate	0529	4.4	0529	131	NC	NC
04/15/92 - Sample	0721	8.0	0721	574	NC	NC
Duplicate	0728	7.9	0728	553	NC	NC
04/24/92 - Sample	0876	88.2	0876	556	NC	NC
Duplicate	0878	88.7	0878	548	NC	NC
05/03/92 - Sample	NC	NC	0954	277	NC	NC
Duplicate	NC	NC	0970	204	NC	NC
05/11/92 - Sample	1237	7.1	1237	191	1153	2.5
Duplicate	1243	5.9	1243	194	1154	2.4
05/20/92 - Sample	NC	NC	1419	606	NC	NC
Duplicate	NC	NC	1418	602	NC	NC
05/21/92 - Sample	1413	5.8	1413	199	NC	NC
Duplicate	1428	5.5	1428	199	NC	NC
08\10\94 - Sample	NC	NC	NC	NC	105610	3.7
Duplicate	NC	NC	NC	NC	105611	3.3

1. Abbreviations: NC (not collected).

Table 6a.
Results of field split sample analyses (metals)
(concentrations in ug/l)^{1,2}

Date	Sample Number ³	Cadmium			Copper			Lead			Zinc		
		EPA TR	MT TR	Diss	EPA TR	MT TR	Diss	EPA TR	MT TR	Diss	EPA TR	MT TR	Diss
04/15/92 - Sample Split	0690/NC	ND	NM	NM	24	NM	NM	2	NM	NM	28	NM	NM
04/24/92 - Sample Split	0731/NC	ND	NM	NM	25	NM	NM	3	NM	NM	31	NM	NM
04/24/92 - Sample Split	0840/NC	ND	ND	NM	8J*3	1	NM	2J*1.5	2	NM	11	5	NM
05/03/92 - Sample Split	0851/NC	ND	ND	NM	2J*3	2	NM	5J*1.5	3	NM	8	7	NM
05/03/92 - Sample Split	0997/0980	ND	NM	NM	3	NM	NM	6	NM	NM	15	NM	1
05/11/92 - Sample Split	1003/0979	ND	NM	NM	3	NM	NM	5	NM	NM	17	NM	ND
05/11/92 - Sample Split	1202/NC	ND	ND	NM	2	1	NM	4	3	NM	10	9	NM
05/20/92 - Sample Split	1201/NC	ND	ND	NM	1	1	NM	3	3	NM	10	9	NM
05/20/92 - Sample Split	1451/NC	ND	NM	NM	5	NM	NM	ND	NM	NM	6	NM	NM
05/20/92 - Sample Split	1432/NC	ND	NM	NM	4	NM	NM	ND	NM	NM	5	NM	NM

1. Abbreviations: NM (not measured), ND (concentration below detection limits).

2. Detection limits: cadmium (0.2 ppb); copper, lead and zinc (1 ppb).

3. Sample number is total recoverable sample/dissolved sample; NC = not collected

Table 6b. Results of field split sample analyses (non-metals) ^{1,2}			
Date	Sample Number	TSS (mg/l)	Specific Conductance (umhos at 25° C)
04/15/92 - Sample	0728	7.9	553
Split	0719	8.4	564
04/24/92 - Sample	0878	88.7	548
Split	0881	86.7	550
05/03/92 - Sample	0970	NM	204
Split	0971	NM	203
05/11/92 - Sample	1243	5.9	194
Split	1231	6.9	194
05/20/92 - Sample	1418	NM	602
Split	1427	NM	601
1. Abbreviations: NM (not measured).			

L7. Standard Reference Material

No standard reference materials were submitted from the field to the laboratory.

III. Laboratory QA/QC

A. Data qualifiers

The following qualifiers are applied, as appropriate, to data as a result of the data validation process. More detailed descriptions of the validation process is provided in the subsections IV-D through IV-M.

- "JCX" - qualified due to lack of calibration blank frequency of 1 per 20.
- "JD#" - # is the value of the relative percent difference (RPD) when RPD is outside target QC limits of 35% RPD.
- "J*#" - # is one-half the difference between the two duplicate values when values are less than 5X the IDL. For these low values, the duplicate data difference must be <2 X IDL or MDL.
- "JS#" - # is the value of the percent recovery of the spike when the matrix spike recovery is outside of target QC limits (100% $\pm$ 25%).
- "JK#" - calibration blank is outside of target QC limits (K denotes a negative blank whose absolute value "#" is greater than 2X the IDL).

- "JL#" - # is the value of the percent recovery of the laboratory control sample (LCS) from the true value when the percent recovery is outside target QC limits (100% $\pm$ 20%) or the range defined by the supplier.
- "JC#" - # is the percent recovery of the continuing calibration verification (CCV) standard from the true value when the percent recovery is outside target QC limits (100% $\pm$ 10%).
- "UJB#" - # is the value of the highest blank affecting data. The reported value is due to contamination from field collection or laboratory preparation of the sample.

B. Sample holding times

All samples were analyzed within the required holding times.

C. Sample preparation methods

Samples were analyzed for EPA TR, MT TR, and dissolved metals. EPA TR analyses required digestion of a 50 ml aliquot of sample. Sample digestion followed EPA Method 200.2.

No laboratory sample preparation was required for MT TR and dissolved metals analyses. Aliquots for these analyses were aspirated directly from the sample bottle by the analytical instrument.

D. Analytical methods and detection limits

Both Inductively-Coupled Plasma Emission Spectrometry System (ICP) and Graphite Furnace Atomic Absorption (GFAA) analytical methods were used in the analysis of TR and dissolved metals. ICP analyses followed EPA Method 200.7. GFAA analyses followed EPA Methods 213.2 (Cd), 220.2 (Cu), 239.2 (Pb), and 289.2 (Zn). All methods are contained in the EPA Contract Laboratory Program (CLP) Statement of Work (SOW), 1990 ILMO 2.0 and referred to in the data reports as "the SOW".

All analyses for cadmium and lead were made using GFAA only. Copper and zinc were analyzed by both ICP and GFAA. The ICP analysis was generally made first to identify samples with high copper and zinc concentrations. Samples below the ICP detection limits were then reanalyzed by GFAA. Because of overlapping analytical ranges, many samples have both an ICP and a GFAA measured concentration. During the analysis of zinc, the initial ICP detection limit of 5 ppb was redetermined as 2 ppb. Therefore, many samples which were initially analyzed by ICP at the 5 ppb detection limit were reanalyzed at the 2 ppb detection limit (3ppb for EPA total recoverable zinc). Samples with zinc concentrations less than 2 ppb were subsequently reanalyzed by GFAA. Calcium and magnesium were

analyzed on filtered samples by ICP. Detection limits are summarized in Table 7.

Table 7.
Detection limits for surface water sample analysis.

Analyte	Contract Required Detection Limit (CRDL) (ug/l)	Method Detection Limit (MDL) (ug/l)	Lowest Lab Standard (ug/l)
Cadmium	5 (ICP)	0.2 (GFAA)	2.5 (GFAA)
Calcium	5,000 (ICP)	1,000 (ICP)	25.0 (ICP)
Copper	25 (ICP)	1.0 (GFAA)	10.0 (GFAA)
Lead	3 (GFAA)	1.0 (GFAA)	10.0 (GFAA)
Magnesium	5,000 (ICP)	1,000 (ICP)	25.0 (ICP)
Zinc	20 (ICP)	1.0 (GFAA)	1.0 (GFAA)

E. Instrument calibration

All ICP calibrations were performed as defined in the relevant method.

The GFAA three-point calibration curve and blank were analyzed as required by the SOW. The GFAA analytical chemist calibrated the instrument following the Perkin-Elmer 5500 operator's manual, which calls for using a blank and three calibration standards. The lowest standard is generally about 10X the IDL. For copper, cadmium, and zinc, the curve included the defined standard at or below the CRDL. These CRDLs, however, reference the CLP protocols for ICP analysis of these metals (except for lead).

For lead, the CRDL standard was not met. The CRDL for lead in the SOW is for the low level GFAA analysis.

For zinc, the calibration criteria are met for low level determinations. For copper and cadmium, the CRDL limits are met but the project MDLs are not verified with standards. In several cases, the reproducibility of low level sample duplicate pairs demonstrates the instrument sensitivity at the MDL. For lead, neither the CRDL or MDL lower limit standard criteria are met. There is no qualification defined in the data validation guidelines for this situation.

One CCV exceeded the CLP limit of 110%. It was reported at 116%. Dissolved zinc samples have been qualified JC116. The LCS and other standards in the data set were acceptable. It is possible that the qualified data are biased slightly high. All other data meet calibration requirements.

Calibration standards and instrument calibration are verified by analysis of laboratory control samples (LCS) prepared from EPA reference solutions. LCS samples for EPA total recoverable analyses were prepared and digested following methods used for ambient samples. LCS samples for MT total recoverable and dissolved analysis were acidified and analyzed by direct aspiration. One LCS was high, but all affected samples were undetected, indicating that there was no high bias effect. Undetected data are not qualified for high LCS recoveries. All other data meet the LCS accuracy criteria.

F. Calibration blanks

The SOW requires that ICBs and CCBs follow the ICVs and CCVs in order to verify that there is no analyte carryover from the standard (high samples) into the subsequent analysis and to confirm instrument stability from the high to low range (analytical baseline). The SOW also requires that all reported sample results be obtained from analytical runs bracketed by CV/CB pairs at a frequency of 10%, including a final CCV/CCB pair at the end of the run. The QAPP defined the frequency of the calibration standards and blanks, but not the sequence.

The raw data have been rigorously examined by the NRD project manager and by the QA reviewers. Although the run sequence as outlined in the EPA CLP SOW ILMO 2.0 was not always followed, the reviewer has evaluated the intent of that sequence - which is to ensure that no carryover or instrument drift is present to impact the accuracy of the sample data. The following is a summary of the evaluation process:

All data have been checked to ensure that 1) no carryover is evident in preceding samples which have analyte concentrations greater than the sample preceding the sample in question; 2) no carryover was present from the high standard to the CCB (with one or two exceptions which are then qualified as blank violations); and 3) QC samples verify instrument stability throughout the run.

For some of the analyses, the CCB was analyzed before the CCV or an analytical spike was analyzed after the CCB. If no carryover was present in the CCB after the high standard and no carryover was evident in the spike or duplicate QC results that followed a standard, no qualification was determined to apply to the samples bracketed by the CCB/CCV set. In cases where there could be any question regarding potential carryover or baseline drift of the of the CCV or spike into an environmental sample, the run sequence is documented in the analytical report.

In a few cases, the final CCV/CCB pair was not analyzed. If the CCV/CCB pairs run within the set have consistently been within limits, the data are considered to be acceptable. In addition, LCS samples and undetected environmental sample results and duplicates have also been examined to verify instrument stability. The review of the raw data has verified the intent of the CCV/CCB sequence to confirm instrument stability and lack of carryover.

G. Preparation (method) blanks

Preparation blanks are made up of the laboratory grade water and reagents used in the sample preparation or analytical method. These reagents are carried through all method preparation and analysis procedures. If no reagents are used, as in the MT TR direct aspiration analysis, there are no true preparation blanks, only the CCB which is laboratory water. Preparation blanks were included at the frequency specified in the QAPP.

Results in the preparation blank which are more than two times the IDL may indicate contamination in the samples associated with that preparation blank. Data which are affected by positive blank contamination are qualified "UJB#" where "#" equals the blank result. These data are fully usable as undetected values at the elevated limit. Data associated with negative blanks (whose absolute values are greater than 2 X IDL) are qualified JK#, where "#" equals the absolute value of the blank result. These qualified data may possibly be biased low or be reported falsely as undetected.

H. ICP interference check samples

The ICP interference check sample (ICS) consists of two solutions (solution A and solution B) combined and analyzed to verify interelement correction factors. The SOW requires analysis of ICSA and ICSAB solutions at the beginning and end of each sample run, or twice every 8 hours, whichever is more frequent, to monitor interferences due to high concentrations of other analytes. The laboratory analyzed one ICS sample per sample run, as specified in the QAPP. The ICS contained the required analytes of an ICSAB solution, but at diluted levels appropriate to analyte levels in the samples. Target control limits of 100 ± 25 percent were used for validating and qualifying data. No ICS samples were out of limits. Consequently, no data have been qualified.

I. Interelement correction factors

No interelement correction factors were provided by the laboratory.

J. Spikes

Matrix spikes are used to assess the effect of the sample matrix on digestion and measurement methodology. Target control limits of 100 ± 25 percent were used for validating data. Spike control limits were not met for three data sets. Copper data for the 4/23, 5/03 and 5/11/92 sets were qualified "JS64", "JS128", and "JS191" respectively. Data for the 4/23 copper samples could possibly be biased low by 35%. Positive reported results for the 5/03 and 5/11 data could possibly be biased high by 28 to 91 percent, respectively. All other data met the accuracy criteria for spike recovery.

K. Duplicates

Duplicate samples are a measure of precision. Target control limits of RPD ≤ 20 percent were used for validating duplicates. All laboratory precision limits have been met. No data have been qualified for not meeting target RPDs. Field duplicate data have been evaluated in a separate section of the report. Field duplicates met the criteria for duplicate differences to be less than the CRDL if sample values are $< 5 \times \text{CRDL}$.

L. GFAA Quality Control

Duplicate injections and analytical (post-digestion) spikes are used to assess the precision and accuracy of analytical results, and to determine the need for Method of Standard Additions (MSA). Duplicate injections were used for all GFAA analyses. Analytical spikes were prepared for the digested samples, which includes the EPA TR samples.

Because the SOW quality control criteria, in general, are written for samples prepared using the SOW methods (hot acid digested samples), guidance relevant to the analysis of undigested samples (MT TR and dissolved analyses) is not specifically defined. The SOW requires an analytical spike post-digestion for each sample in a GFAA analysis as a means of monitoring sample-specific matrix effects on the analysis. The "analytical spike" is defined in two sections (SOW, Exhibit E, page E-25 and Exhibit G, page G-1) in terms of digested samples. Additionally, "dissolved" metals are defined in the SOW (Exhibit G, page G-1) as "analyte elements which have not been digested prior to analysis".

Consequently, the GFAA analytical chemist applied the analytical spike only to digested (EPA TR) samples. For undigested (MT TR and dissolved) samples, analytical spikes were performed at a normal spike frequency of 1/20 samples per the QAPP. Although not clearly defined by EPA in its guidance, this could preclude the evaluation of sample-specific matrix effects in the undigested samples. However, in matrix effects in low level water samples are expected to be minimal, especially for dissolved (filtered) samples. Careful review of the analytical spikes that were performed, which were representative of the sample matrices, showed no evidence of matrix effects. Almost all analytical spike recoveries were well

above the 85% control limit. The few samples that required MSA fully met the correlation coefficient criteria. Because representative samples verify the lack or minimal impact of matrix effects, no qualification has been added to GFAA sample results.

Table 8.
Samples analyzed by Method of Standard Additions (MSA).

Sample Number and Analyte	Site	First Analysis (ug/l)	MSA (ug/l)	Reanalysis (ug/l)
491 - cadmium	Field duplicate	0.16	0.185*	0.115
675 - copper	Big Hole River/Notch Bottom	1.35	3.15*	2.2
678 - copper	Big Hole River/ Kalsta Ranch	2.15	3.8*	3.3
680 - copper	Clark Fork River/Gold Creek	19.7	23.4	21.5*
849 - copper	Bison Creek/Elk Park	4.6	17.1*	9.7

* denotes analytical result used in the surface water assessment

Five samples exceeded the analytical spike control limit for percent recovery, and were analyzed by MSA and reanalyzed by GFAA. Although GFAA reanalyses were within control limits, MSA results were used in the aquatic resources report for all but one sample. No results were therefore qualified due to unacceptable spike recoveries. Results of MSA analyses are presented in Table 8.

M. Laboratory splits (duplicates)

Laboratory duplicates were analyzed to assess the replicability of laboratory subsampling techniques. Splits for EPA TR metals analyses involved taking two separate aliquots of sample through sample digestion and analysis. MT TR and dissolved duplicate analyses involved two successive aspirations directly from the sample bottle.

Samples have been qualified using the IDL as a limit rather than the CRDL as specified in the data validation guidance. No data are outside the EPA CLP data validation limits for samples whose values are $< 5 \times \text{CRDL}$ and whose duplicate difference is $\leq \text{CRDL}$. For this study, data have been evaluated in terms of the low level IDL to determine the actual bias to co-located samples using low-level analyses. Deviations are minimal even at these low limits, verifying the overall precision of the sampling and testing methods.

Tables 9 through 11 summarize the results of split sample analyses for EPA TR, MT TR, and dissolved metals concentrations.

Table 9.
Results of laboratory split sample analyses, EPA total recoverable concentrations in parts per billion^{1,2}

Date	Sample Number	Sample Location	Cadmium	Copper	Lead	Zinc
04/06/92	0488	QA/QC grab sample	0.3 / ND	42 / 41	4 / 3	53 / 56
04/06/92	0492	SBC near Ramsay	NM	234 / 276	NM	NM
04/15/92	0676	Ruby R above Ruby Reservoir	0.3 / ND	8 / 8	5 / 2J*1.5	8 / 5J*1.5
04/15/92	0686	Rock Creek near Stonehenge	ND / ND	ND / ND	1 / 1	NM
04/24/92	0836	Big Hole River at Notch Bottom	ND / ND	1 / 1	ND / ND	3 / 3
04/24/92	0846	CFR at Turah	ND / ND	11 / 14	2 / 2	15 / 20
05/03/92	0992	CFR at Deer Lodge	ND / ND	- 25 / 39JD44 ³	2 / 5J*1.5 ⁴	34 / 44
05/11/92	1190	CFR at Deer Lodge	ND / ND	15 / 15	1 / 1	15 / 14JD110
05/11/92	1200	CFR at Beavertail Hill	ND / ND	8 / 22JD93 ⁴	ND / 2	7 / 24
05/20/92	1431	Ruby R above Ruby Reservoir	0.2 / 1.8J*.8 ⁴	4 / 3	3 / 3	13 / 13
05/20/92	1441	CFR at Gold Creek	ND / ND	7 / 7	ND / ND	10 / 10

1. Abbreviations: NM (not measured); ND (not detectable)
2. Detection limits: cadmium (0.2 ppb); copper, lead and zinc (1 ppb)
3. Reanalysis concentration = 28 ppb; RPD based on sample reanalysis = 11
4. Reanalysis concentration = 8 ppb; RPD based on sample reanalysis = 0
5. Reanalysis concentration = 2 ppb; RPD based on sample reanalysis = NC
6. Reanalysis concentration = ND; RPD based on sample reanalysis = NC

Table 10.
Results of laboratory split sample analyses, MT total recoverable concentrations in parts per billion^{1,2}

Date	Sample Number	Sample Location	Cadmium	Copper	Lead	Zinc
04/06/92	0481	CFR at Gold Creek	0.3 / 0.3	48 / 48	6 / 6	53 / 54
04/06/92	0491	QA/QC field duplicate	ND / ND	3 / 3	ND / ND	15 / 12
04/15/92	0834	QA/QC grab sample	ND / ND	1 / 2	2 / 2	4 / 2
04/24/92	0843	CFR at Beavertail Hill	ND / ND	17 / 17	3 / 3	25 / 24
04/24/92	0850	Ruby R below Ruby Reservoir	NM	NM	NM	1 / 1
05/03/92	1190	CFR at Deer Lodge	ND / ND	14 / 14	1 / 1	15 / 13
05/11/92	1200	CFR at Beavertail Hill	ND / ND	6 / 7	ND / ND	7 / 9

1. Abbreviations: NM (not measured); ND (not detectable)

2. Detection limits: cadmium (0.2 ppb); copper, lead and zinc (1 ppb)

Table 11.
Results of laboratory split sample analyses, dissolved concentrations in parts per billion^{1,2}

Date	Sample Number	Sample Location	Cadmium	Copper	Lead	Zinc
04/06/92	0510	QA/QC filter blank	ND / ND	ND / ND	ND / ND	ND / ND
04/06/92	0515	Big Hole River at Notch Bottom	NM	NM	NM	27 / 27
04/15/92	0693	Big Hole River at Kalista Ranch	ND / ND	ND / ND	ND / ND	3 / 2
04/15/92	0694	Ruby R above Ruby Reservoir	NM	NM	NM	2 / 2
04/24/92	0842	CFR at Deer Lodge	ND / ND	8 / 7	ND / ND	6 / 6
04/24/92	0863	Big Hole River at Kalista Ranch	ND / ND	ND / ND	ND / ND	ND / ND
05/03/92	0973	Rock Creek near mouth	ND / ND	ND / ND	ND / ND	ND / ND
05/03/92	0983	Big Hole River at Notch Bottom	ND / ND	ND / ND	ND / ND	ND / ND
05/03/92	0985	Flint Creek below Douglas Creek	NM	NM	NM	ND / ND
05/11/92	1209	QA/QC field duplicate	ND / ND	ND / ND	ND / ND	2 / ND
05/11/92	1219	SBC near Ramsay	1.3 / 1.1	52 / 52	ND / ND	471 / 479
05/11/92	1221	CFR at Beavertail Hill	NM	NM	NM	ND / ND
05/20/92	1452	Yankee Doodle Creek	ND / ND	ND / ND	ND / ND	ND / ND
05/20/92	1462	Ruby R above Ruby Reservoir	ND / ND	ND / ND	ND / ND	ND / ND
05/20/92	1467	Ruby R below Ruby Reservoir	NM	NM	NM	1 / 1

1. Abbreviations: NM (not measured); ND (not detectable)

2. Detection limits: cadmium (0.2 ppb); copper, lead and zinc (1 ppb).

N. Sample reanalyses

Several EPA TR duplicate results did not meet target RPDs. For these samples, the laboratory digested a third aliquot of sample for reanalysis. Table 12 summarizes the results of these reanalyses.

Table 12.
Sample reanalysis - duplicate digested samples.

Sample Number and Analyte	Site	Sample (ug/l)	Duplicate (ug/l)	Redigest (ug/l)
992 - copper	Clark Fork River at Deer Lodge	24.65	38.75	27.65
992 - lead	Clark Fork River at Deer Lodge	2.45	4.6	1.95
1200 - copper	Clark Fork River at Beavertail Hill	7.5	22.0	7.9
1200 - lead	Clark Fork River at Beavertail Hill	0.9	2.05	1.5
1200 - zinc	Clark Fork River at Beavertail Hill	6.5	24.0	9.0
1431 - cadmium	Ruby River above Ruby Reservoir	0.225	1.78	0.115

All reanalyses were closer to the sample concentration than the original duplicate. These redigested samples were averaged with the original sample result to obtain the reported result.

Several samples were reanalyzed due to suspected sample contamination. Table 13 summarizes results of these reanalyses.

Table 13.
Sample reanalyses due to suspected sample contamination.

Sample Number and Analyte	Site	First Analysis (ug/l)	Reanalysis (ug/l)
485 - EPA TR zinc	Clark Fork River at Turah	85	90
493 - EPA TR zinc	Big Hole River at Notch Bottom	12	13
498 - EPA TR zinc	Big Hole River at Kalsta Ranch	14	13
839 - MT TR lead	Rock Creek near Stonehenge	3	< 1
850 - MT TR lead	Ruby River below Ruby Reservoir	2	< 1
1005 - EPA TR lead	Upper Silver Bow Creek	21	23
1009 - EPA TR lead	Yankee Doodle Creek	3	3

Because the results of sample 1005 appeared to be unrealistically high, given the sampling location (Silver Bow Creek above Yankee Doodle Tailings) and lack of apparent impact, a second aliquot of sample 1005 was digested and analyzed. The result was less than the detection limit, indicating that the original sample analysis was probably affected by contamination during laboratory preparation.

IV. CUSTODY AND DOCUMENT CONTROL

A. Field custody

COC includes sample tags, custody seals, field logbook, and COC records. Field logbooks and COC records were reviewed for adherence to the QAPP and for consistency. Because no sample tags were used, this information does not appear on the COC. Field custody of samples adhered to the QAPP. Custody transfer to the analytical laboratory is documented on COC records.

B. Sample delivery

Samples were hand-delivered to the analytical laboratory. This is documented on COC records.

This deviation from the QAPP is noted:

- condition of custody seals upon delivery to the laboratory was noted by the field sampler on the COC records

No samples were lost due to broken seals, damaged or destroyed sample bottles, or loose or unattached sample bottle caps.

C. Laboratory custody

Commencement of custody by the analytical laboratory is documented on COC records. Samples were stored in a locked cabinet. Dates and times of movement of samples out of and into the storage area by laboratory personnel involved in sample preparation and analysis were documented by those individuals on custody records mounted inside the cabinet. Custody of samples outside the storage cabinet was maintained by those persons removing samples.

D. Sample tracking

Sample numbers are traceable from field collection through laboratory analysis. Laboratory numbers were assigned to field samples and were recorded in the laboratory sample log-in book. These numbers were also recorded on COC records. Laboratory numbers are also entered on all analytical output. Therefore, sample numbers are traceable from the field to the final analytical output through the field logbook; sample tracking forms; COC records; sample log-in book; and the analytical output. Inconsistencies between the field logbook, sample tracking forms, and COC records in the recording of field sample numbers have been corrected.

E. Document control

Field notebooks and COC records were stored in the offices of the NRDP. Access to these offices is limited to NRDP, security and maintenance personnel.

F. Document review

Documents which were reviewed for completeness and accuracy include the field logbook, sample tracking forms, COC records and laboratory custody records. No deviations from the QAPP are noted as a result of this review.

Field forms included sample tracking forms and flowsheets for recording flow-gauging information. All samples collected in the field were recorded on the sample tracking forms. Measurements taken during flow-gauging were recorded on flowsheets, along with the following information: site name; date; field team members.

G. Identity of sample collector

Identity of the sample collector was recorded on each sample bottle and on the COC record. The sample collector was also the field team leader, who maintained and signed the field logbook and COC records.

V. RESULTS OF DATA QUALIFICATION

Qualifiers have been applied to data as summarized in Tables 14 through 19.

Table 14.
EPA total recoverable (EPA TR) and Montana total recoverable (MT TR) metals concentrations
in Silver Bow Creek and the Clark Fork River¹

Sampling Location	Date	Sample Number	Cadmium		Copper		Lead		Zinc	
			EPA TR	MT TR	EPA TR	MT TR	EPA TR	MT TR	EPA TR	MT TR
Silver Bow Creek near Ramsay	04/06/92	0492	2.1	1.9	244	233	28	27	559	585
	04/24/92	0841	1.8	1.4	130	141	10	10	449	494
	05/12/92	1195	1.7	1.6	94JK-17	111	5	5	581	648
Clark Fork River at Deer Lodge	04/05/92	0482	0.3	ND	37	35	3	3	52UJB19	41UJB9
	04/15/92	0684	0.2JL122	NM	26	NM	2	NM	30	NM
	04/23/92	0842	ND	ND	15JS64	14	ND	1UJB9	17	16
	05/03/92	0992	ND	ND	26JS128	NM	2	NM	39	NM
	05/11/92	1190	ND	ND	15JS191	14	1	1	14	14
	05/20/92	1442	0.3	NM	11	NM	ND	NM	13UJB4	NM
Clark Fork River at Gold Creek	04/05/92	0481	0.4	0.3	53	48	7	6	74UJB19	54
	04/15/92	0680	0.2JL122	NM	22JS128	NM	3	NM	20	NM
	04/23/92	0845	ND	ND	19JS64	15	2	1UJB9	18	15
	05/03/92	1008	ND	NM	16	NM	3	NM	26	NM
	05/11/92	1194	ND	ND	13JS191	12	2	1	15	13
	05/20/92	1441	ND	NM	7	NM	ND	NM	10UJB4	NM
Clark Fork River at Bearmouth	04/05/92	0489	0.4	ND	33UJB7	29	7	6	65UJB19	41UJB9
	04/15/92	0683	0.2JL122	NM	17	NM	3	NM	24	NM
	04/23/92	0847	ND	ND	22JS64	22	4	4UJB9	30	26
	05/03/92	1001	ND	NM	21	NM	3	NM	29	NM
	05/11/92	1204	ND	ND	8JS191	7	ND	ND	11	10
	05/20/92	1438	ND	NM	4	NM	ND	NM	5UJB4	NM
Clark Fork River at Beavertail Hill	04/05/92	0490	0.2	0.2	33UJB7	28	6	6	69UJB19	42UJB9
	04/15/92	0688	ND	NM	18	NM	3	NM	23	NM
	04/23/92	0843	ND	ND	18JS64	17	3	3UJB9	28	25
	05/03/92	1000	ND	ND	17	NM	3	NM	30	NM
	05/11/92	1200	ND	ND	8JS191	7	1	ND	8JL133	8
	05/20/92	1447	ND	NM	5	NM	ND	NM	4UJB4	NM
Clark Fork River at Turah	04/05/92	0485	ND	ND	45	15	7	3	85UJB19	24UJB9
	04/15/92	0692	ND	NM	11	NM	2	NM	16	NM
	04/23/92	0846	ND	ND	12JS64	11	2	2UJB9	17	12
	05/03/92	1007	ND	NM	9	NM	4	NM	20	NM
	05/11/92	1196	ND	ND	4JS191	3	ND	ND	8	8
	05/20/92	1443	0.2	NM	3	NM	ND	NM	5UJB4	NM

¹ Concentrations in ug/l. ND = concentrations below the detection limit (cadmium = 0.2 ug/l; copper, lead and zinc = 1 ppb). NM = not measured.

Table 15.
EPA total recoverable (EPA TR) and Montana total recoverable (MT TR) metals concentrations
in the Big Hole River, Rock Creek, and Ruby River¹

Sampling Location	Date	Sample Number	Cadmium		Copper		Lead		Zinc	
			EPA TR	MT TR	EPA TR	MT TR	EPA TR	MT TR	EPA TR	MT TR
Big Hole River at Kalata Ranch	04/06/92	0498	ND	ND	2UJB7	ND	1	ND	13UJB19	3UJB9
	04/14/92	0678	ND	NM	4JS128	NM	1	NM	3UJB3	NM
	04/24/92	0838	ND	ND	NDJS64	ND	ND	ND	2UJB3	1
	05/02/92	0993	ND	NM	1	NM	2	NM	7UJB3	NM
	05/12/92	1199	ND	ND	2JS191	1	ND	ND	5	2
	05/21/92	1434	ND	NM	3	NM	ND	NM	4UJB4	NM
Big Hole River at Notch Bottom	04/06/92	0493	ND	ND	1UJB7	2UJB5	1	ND	13UJB19	3UJB9
	04/14/92	0675	ND	NM	3JS128	NM	2	NM	4UJB3	NM
	04/24/92	0836	ND	ND	1JS64	ND	ND	NM	3UJB3	1
	05/02/92	1006	ND	NM	1	NM	2	NM	4UJB3	NM
	05/12/92	1192	ND	ND	3JS191	2	ND	ND	3	1
	05/21/92	1435	ND	NM	ND	NM	ND	NM	3UJB4	NM
Rock Creek near Stonchenge	04/05/92	0486	ND	ND	ND	ND	2	ND	8UJB19	ND
	04/15/92	0686	ND	NM	ND	NM	1	NM	8UJB3	NM
	04/23/92	0839	ND	ND	2JS64	ND	ND	ND	2UJB3	ND
	05/03/92	1010	ND	NM	2	NM	1	NM	4UJB3	NM
	05/11/92	1198	ND	ND	ND	ND	ND	ND	3	ND
	05/20/92	1445	ND	NM	ND	NM	ND	NM	2UJB4	NM
Rock Creek near mouth	04/05/92	0483	ND	ND	ND	ND	ND	ND	4UJB19	1UJB9
	04/15/92	0681	ND	NM	ND	NM	ND	NM	2UJB3	NM
	04/23/92	0837	ND	ND	3JS64	2	1	ND	5UJB3	1
	05/03/92	1011	ND	NM	ND	NM	1	NM	4UJB3	NM
	05/11/92	1193	ND	ND	ND	ND	ND	ND	3	ND
	05/20/92	1448	ND	NM	ND	NM	ND	NM	2UJB4	NM
Ruby River above Ruby Reservoir	04/06/92	0494	ND	ND	1UJB7	ND	3	1	13UJB19	7UJB9
	04/14/92	0676	0.2JL122	NM	8	NM	3	NM	6UJB3	NM
	04/24/92	0848	ND	ND	2JS64	1	2	2UJB9	8UJB3	7
	05/02/92	0998	ND	NM	3	NM	4	NM	15UJB3	NM
	05/12/92	1203	ND	ND	2JS191	ND	2	1	10	5
	05/21/92	1431	ND	NM	3	NM	3	NM	13UJB4	NM
Ruby River below Ruby Reservoir	04/06/92	0495	ND	ND	ND	ND	ND	ND	12UJB19	ND
	04/14/92	0687	ND	NM	ND	ND	1	NM	2UJB3	NM
	04/24/92	0850	ND	ND	NDJS64	ND	ND	ND	3UJB3	1
	05/02/92	0996	ND	NM	ND	ND	ND	NM	3UJB3	NM
	05/12/92	1205	ND	ND	ND	ND	ND	ND	3	ND
	05/21/92	1444	ND	NM	ND	ND	ND	NM	2UJB4	NM

¹ Concentrations in ug/l. ND = concentrations below the detection limit (cadmium = 0.2 ug/l; copper, lead and zinc = 1 ppb). NM = not measured.

Table 17.
Dissolved hazardous substance concentrations in Silver Bow Creek and the
Clark Fork River¹

Sampling Location	Date	Sample Number	Cadmium	Copper	Lead	Zinc
Silver Bow Creek near Ramsay	04/06/92	0513	1.0	75	ND	304JC116K-5
	04/24/92	0855	0.7	53	1	219
	05/12/92	1219	1.2	52	ND	475
Clark Fork River at Deer Lodge	04/05/92	0503	ND	10	ND	11JC116K-5
	04/15/92	0710	ND	7	ND	11UJB3
	04/23/92	0853	ND	7	ND	6
	05/03/92	0988	ND	9	ND	11
	05/11/92	1217	ND	8	ND	4
	05/20/92	1464	ND	6JL79	ND	13
Clark Fork River at Gold Creek	04/05/92	0507	ND	5	ND	7JC116K-5
	04/15/92	0702	ND	4	ND	3UJB3
	04/23/92	0862	ND	5	1	4
	05/03/92	0978	ND	4	ND	2JL136
	05/11/92	1220	ND	6	ND	2
	05/20/92	1459	ND	3JL79	ND	3
Clark Fork River at Bearmouth	04/05/92	0508	ND	3	ND	6JC116K-5
	04/15/92	0706	ND	4	ND	3UJB3
	04/23/92	0867	ND	4	ND	5
	05/03/92	0977	ND	4	ND	3
	05/11/92	1211	ND	5	ND	3
	05/20/92	1465	ND	3	ND	4
Clark Fork River at Beavertail Hill	04/05/92	0501	ND	3	ND	4JK-5
	04/15/92	0699	ND	4	ND	3UJB3
	04/23/92	0857	ND	3	ND	2
	05/03/92	0986	ND	4	ND	2
	05/11/92	1221	ND	5	ND	2
	05/20/92	1453	ND	3JL79	ND	2
Clark Fork River at Turah	04/05/92	0509	ND	2	ND	6
	04/15/92	0703	ND	2	ND	2
	04/23/92	0858	ND	2	ND	2
	05/03/92	0990	ND	2	ND	2
	05/11/92	1223	ND	1	ND	2
	05/20/92	1458	ND	NDJL79	ND	ND

1. Concentrations in ug/l. ND = concentrations below the detection limit (cadmium = 0.2 ug/l; copper, lead and zinc = 1 ppb).

Table 18.
Dissolved metals concentrations in the Big Hole River, Rock Creek and the Ruby River¹

Sampling Location	Date	Sample Number	Cadmium	Copper	Lead	Zinc
Big Hole River at Kalsta Ranch	04/06/92	0517	ND	ND	ND	2JC116K-5
	04/14/92	0693	ND	ND	ND	3UJB3
	04/24/92	0863	ND	ND	ND	ND
	05/02/92	0987	ND	ND	ND	1
	05/12/92	1222	ND	2	ND	ND
	05/21/92	1463	ND	NDJL79	ND	ND
Big Hole River at Notch Bottom	04/06/92	0515	ND	ND	ND	27
	04/14/92	0709	ND	ND	ND	4UJB3
	04/24/92	0865	ND	ND	ND	ND
	05/02/92	0983	ND	ND	ND	1
	05/12/92	1218	ND	2	ND	ND
	05/21/92	1469	ND	ND	ND	ND
Rock Creek near Stonehenge	04/05/92	0502	ND	ND	ND	5JC116K-5
	04/15/92	0708	ND	ND	ND	3UJB3
	04/23/92	0868	ND	ND	ND	2
	05/03/92	0974	ND	ND	ND	ND
	05/11/92	1214	ND	ND	ND	7
	05/20/92	1455	ND	NDJL79	ND	ND
Rock Creek near mouth	04/05/92	0504	ND	ND	ND	4JK-5
	04/15/92	0698	ND	ND	ND	4UJB3
	04/23/92	0856	ND	2	ND	ND
	05/03/92	0973	ND	ND	ND	ND
	05/11/92	1224	ND	ND	ND	ND
	05/20/92	1457	ND	NDJL79	ND	ND
Ruby River above Ruby Reservoir	04/06/92	0516	ND	ND	ND	5JK-5
	04/14/92	0694	ND	3	ND	2UJB3
	04/24/92	0866	ND	ND	ND	ND
	05/02/92	0982	ND	ND	ND	2
	05/12/92	1213	ND	ND	ND	ND
	05/21/92	1462	ND	NDJL79	ND	ND
Ruby River below Ruby Reservoir	04/06/92	0514	ND	ND	ND	4JK-5
	04/14/92	0695	ND	ND	ND	4UJB3
	04/24/92	0864	ND	ND	ND	ND
	05/02/92	0989	ND	ND	ND	ND
	05/12/92	1215	ND	ND	ND	ND
	05/21/92	1467	ND	ND	ND	ND

1. Concentrations in ug/l. ND = concentrations below the detection limit (cadmium = 0.2 ug/l; copper, lead and zinc = 1 ppb).

Table 19.
Dissolved metals concentrations in Silver Bow Creek, Yankee Doodle Creek,
Blacktail Creek, Bison Creek and Flint Creek¹

Sampling Location	Date	Sample Number	Cadmium	Copper	Lead	Zinc
Silver Bow Creek above Yankee Doodle Tailings	04/15/92	0705	ND	ND	ND	3UJB3
	05/02/92	0991	ND	ND	ND	ND
	05/21/92	1470	ND	1	ND	ND
Yankee Doodle Creek above Yankee Doodle Tailings	04/14/92	0697	ND	ND	ND	2UJB3
	05/02/92	0984	ND	ND	ND	ND
	05/21/92	1452	ND	NDJL79	ND	1
Blacktail Creek at Thompson Park	04/14/92	0696	ND	2	ND	3UJB3
	05/02/92	0981	ND	2	ND	ND
	05/21/92	1468	ND	3	ND	1
Bison Creek at Elk Park	04/06/92	0511	ND	5	ND	16JC116K-5
	05/24/92	0859	ND	2	ND	6
	05/12/92	1216	ND	8	ND	3
Flint Creek	04/05/92	0506	ND	ND	ND	7JC116K-5
	04/15/92	0700	ND	ND	ND	4UJB3
	04/23/92	0860	ND	ND	ND	ND
	05/03/92	0985	ND	ND	ND	ND
	05/11/92	1225	ND	1	ND	ND
	05/20/92	1466	ND	ND	ND	2

1. Concentrations in ug/l. ND = concentrations below the detection limit (cadmium = 0.2 ug/l; copper, lead and zinc = 1 ppb).

VI. PRECISION, ACCURACY, REPRESENTATIVENESS, COMPLETENESS AND COMPARABILITY

A. Precision

Precision is evaluated by examining replicate samples (field and laboratory replicates). The relative percent difference of replicate samples should be ≤ 35 percent. Replicates that fall within this window would demonstrate good sampling and laboratory measurement technique. Replication has been incorporated into both the sampling and analytical ends of this effort. Replication has included 1) the collection of field duplicates (surface water) or triplicates (periphyton); 2) the analysis of laboratory replicates (two subsamples collected from the same sample); and 3) duplicate (GFAA) or triplicate (ICP) injections of the same sample.

As demonstrated by a review of laboratory data, and as demonstrated by a review of replicate samples (see Tables 5 through 8, 12 and 13) data are of acceptable precision.

B. Accuracy

Accuracy is assessed by evaluating blanks, spikes, and laboratory control samples. Target limits for accuracy is ± 25 percent. Only a small percentage of samples were qualified for not meeting target limits for accuracy. As demonstrated by a review of laboratory data, data are of acceptable precision.

C. Representativeness

Representativeness is determined by a number of factors, including site selection criteria, sample collection procedures, sample collection equipment, sample containers, sample contamination, sample preservation and storage, and holding times for analysis.

The surface water data have been deemed to be representative for the following reasons:

- sample collection sites were selected based on sound, well-reasoned objectives, as described in the Assessment Plan (NRDP, 1992; NRDLP, 1994; and Lipton, et. al., 1995);
- sample collection cross-sections or grab-sampling locations at each site were identified by criteria presented in NRDP SOP 2.0 and NRDP SOP 3.0;
- sample collection procedures were designed to accomplish specific objectives, and resulted in the collection of samples that were representative of the media being sampled, given those objectives;

- sample containers conformed to EPA recommendations for the analytes of interest;
- samples were preserved and stored following EPA recommendations; and
- no recommended sample holding times were exceeded prior to analysis.

D. Completeness

Completeness is defined as the percentage of measurement data that remain valid after discarding any invalid data due to field or laboratory QC. Data fully meet the >95% completeness criteria for field and laboratory QC. One flow measurement (Flint Creek below Douglas Creek, May 21) was discarded because of a lost field datasheet. One analysis (sample number 1005, upper Silver Bow Creek, EPA TR lead) was rejected due to suspected contamination. Reanalysis of this sample, as noted in Section IV-N, resulted in an undetected value which was used in the assessment.

E. Comparability

Comparability involves the evaluation of data characteristics which may limit use of data in conjunction with other datasets. No data characteristics were identified which limit the use of these data. Samples were collected and analyzed by methods commonly used by other agencies involved in the collection and analysis of surface water samples in the Clark Fork Basin. In fact, one of the objectives of the surface water sampling effort was to evaluate the comparability of two methods commonly used to collect surface water samples (grab and composite sampling) and three methods commonly used to analyze surface water samples (EPA TR, MT TR, and dissolved). For the purposes of the surface water injury assessment, it was deemed appropriate, because of the comparability of the two sample collection methods, to use data collected by either method. A comparison of the three analytical methods established that each method results in different datasets (that is, EPA TR concentrations are greater than either MT TR concentrations or dissolved concentrations). These differences have been accounted for and specifically considered in the analysis and interpretation of surface water data.

VII. REFERENCES

Lipton, J., D. Beltman, H. Bergman, D. Chapman, T. Hillman, M. Kerr, J. Moore and D. Woodward. 1995. Prepared by RCG/Hagler, Bailly, Inc. for the Montana Natural Resource Damage Litigation Program. Helena, MT 59620.

NRDP. 1992. Assessment Plan: Part II. Clark Fork River Basin NPL Sites, Montana. State of Montana, Natural Resource Damage Program. April, 1992.

NRDP. 1994. Assessment Plan: Part III. Clark Fork River Basin NPL Sites, Montana. State of Montana, Natural Resource Damage Program. April, 1992.

U.S. EPA. 1985. Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses.

Viar & Co. 1988. Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses.

**QUALITY ASSURANCE/QUALITY CONTROL REPORT
GROUND WATER SAMPLING**

TABLE OF CONTENTS

TABLE OF CONTENTS	i
LIST OF ACRONYMS	.iii
LIST OF TABLES	iv
I INTRODUCTION	1
II SAMPLE COLLECTION AND FIELD QA/QC	1
A. Sampling Bottle Preparation	1
B. Sampling Date and Time	2
C. Sampling Team	2
D. Sampling Locations	2
E. Physical Description of Sampling Location	2
F. Sample Collection Methods	2
G. Field Preparation Methods	2
H. Sample Numbers	2
I. Sample Preservation	2
J. Sample Shipping Information	3
K. Field Instrument Calibrations and Field Measurements	3
L. QC Samples	3
L1. Bottle Blanks	3
L2. Trip Blanks	3
L3. Filter Blanks	4
L4. Decontamination Blanks	4
L5. Field Replicates	6
L6. Standard Reference Material	6
III LABORATORY QA/QC	9
A. Data Qualifiers	9
B. Sample Holding Times	9
C. Sample Preparation Methods	9
D. Analytical Methods and Detection Limits	10
E. Instrument Calibration	10
F. Calibration Blanks	10
G. Preparation (Method) Blanks	10
H. Laboratory Fortified Blank	12
I. ICP Interference Check Samples	12
J. Interement Correction Factors	12

K.	Spikes	12
L.	Laboratory Control Sample	13
M.	Internal Standards	13
N.	Duplicates	13
IV	CUSTODY AND DOCUMENT CONTROL	14
A.	Field Custody	14
B.	Sample Delivery	14
C.	Laboratory Custody	14
D.	Sample Tracking	14
E.	Document Control	14
F.	Document Review	15
G.	Identity of Sample Collector	15
V	RESULTS - DATA QUALIFICATION	15
VI	PRECISION, ACCURACY, REPRESENTATIVENESS, COMPLETENESS AND COMPARABILITY	17
A.	Precision	17
B.	Accuracy	17
C.	Representativeness	17
D.	Completeness	18
E.	Comparability	18
VII	REFERENCES	18

LIST OF ACRONYMS

CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification
CLP	Contract Laboratory Program
COC	Chain-of-Custody
CRDL	Contract Laboratory Detection Limit
EPA	Environmental Protection Agency
GFAA	Graphite Furnace Atomic Absorption
ICB	Initial Calibration Blank
ICPMS	Inductively-Coupled Plasma Mass Spectroscopy System
ICS	Interference Check Sample
IDL	Instrument Detection Limit
LCS	Laboratory Control Sample
LFB	Laboratory Fortified Blank
LRB	Laboratory Reagent Blank
MBMG	Montana Bureau of Mines and Geology
MDL	Method Detection Limit
NA	Not Analyzed
NRDA	Natural Resource Damage Assessment
NRDP	Natural Resource Damage Program
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
SAP	Sampling and Analysis Plan
SC	Specific Conductance
SOP	Standard Operating Procedure

LIST OF TABLES

1.	Results of Field Blank Analyses	5
2.	Results of Field Duplicate Analyses	7
3.	Relative Percent Difference of Field Duplicate Samples	8
4.	Laboratory Methodologies for Analysis of Groundwater	11
5.	Detection Limits for Groundwater Analyses	11
6.	Metals Concentrations in Groundwater	17

QUALITY ASSURANCE/QUALITY CONTROL REPORT GROUNDWATER SAMPLING

I. INTRODUCTION

The purpose of this report is to evaluate and summarize the quality assurance (QA) and quality control (QC) associated with the collection and analysis of groundwater samples for the Clark Fork Basin Natural Resource Damage Assessment (NRDA). QA/QC guidance was provided by the Natural Resource Damage Program (NRDP) Quality Assurance Project Plan (QAPP). Results of groundwater assessment activities are summarized in Butte Groundwater Injury Assessment Report (Maest et. al., 1995). QA/QC guidance was provided by the Natural Resource Damage Program (NRDP) Quality Assurance Project Plan (QAPP) (NRDP, 1992).

The organization of this report generally follows the data validation outline presented in Section 11.0 of the QAPP. Section II describes Sample Collection and Field QA/QC, including deviations from sampling protocols and standard operating procedures (SOPs) referenced in the Assessment Plan, Part II (NRDP, 1992) or described in the Butte Groundwater Injury Assessment Report (Maest et. al., 1995). (Modifications to the Assessment Plan and research protocols contained therein are summarized in NRDL, 1995). Section III describes and evaluates Laboratory QA/QC. Section IV summarizes Custody and Document Control. Section V presents results of data qualification. Section VI discusses Precision, Accuracy, Representativeness, Completeness and Comparability.

II. SAMPLE COLLECTION AND FIELD QA/QC

There are no Environmental Protection Agency (EPA) control limits nor corrective actions for field QC samples, with the exception of field blanks. EPA (1985) and Viar & Co. (1988) consider field QC as useful in assessing a laboratory's performance independent of sample or method problems, and as supporting evidence in the overall assessment of a data set or sampling event. Field QC is not the basis for accepting or rejecting data, but rather acts as additional evidence in support of these conclusions arrived at by a review of the complete data set. Therefore, except in the case of gross errors, poor performance on field QC samples does not invalidate data.

The following items were reviewed for field sample collection and preparation QA/QC:

A. Sample bottle preparation

Sample bottles were precleaned following CFRSSISOP HG-3.1. No deviations from this SOP were noted.

B. Sampling date and time

Sampling dates and times were recorded in the field logbook and on chain-of-custody (COC) records. Discrepancies between the field logbook and COC records have been corrected.

C. Sampling team

The sample collector is identified in field logbooks and on COC records. The signature of the sample collector appears on the bottom of each page of field logbooks.

D. Sampling locations

Sampling locations were identified by a unique well name or number. Sampled wells are identified in field logbooks and on COC records.

E. Physical description of sampling location

Sampling locations were not physically described in field logbooks. Locations of sampled wells can be identified by reference to maps contained in Maest et. al. (1995).

F. Sample collection methods

Sample collection adhered to referenced protocols and SOPs. The only deviation from sampling protocols noted was not flushing the inside of the submersible pump with distilled water following sampling equipment decontamination, as described by CFRSSISOP G-8.

G. Field preparation methods

Field sample preparation involved the filtering of samples for analysis of dissolved constituents.

H. Sample numbers

Groundwater samples and QC samples were numbered as Well 1, Well 2, etc. Sample descriptions (well name/number or QC sample type) are provided in field logbooks and on COC records.

I. Sample preservation

Samples were preserved following EPA recommendations. Samples collected included 1) 1 500-ml filtered sample preserved with 5 ml of nitric acid (pH <2); 2) 1 500-ml unfiltered sample, unpreserved; and 3) 1 250-ml filtered sample, unpreserved. No deviations from preservation techniques are noted in field logbooks.

J. Sample shipping information

No samples were shipped via commercial carrier. All samples were hand-delivered from the field to the laboratory by the sample collector.

K. Field instrument calibrations and field measurements

Field instruments included pH meter, Eh meter, and specific conductivity meter. Calibrations adhered to CFRSSISOP HG-8 (pH and Eh), and CFRSSISOP HG-7 (specific conductivity). Several deviations from these SOPs are noted. pH meter calibration adhered to the SOP, but for three alluvial wells and two bedrock wells (Hebgen Park and Well D-2), pH meter calibration was not recorded in the field logbook. For Eh and conductivity, meters were not calibrated as frequently as specified in the SOPs, but did meet the frequency specified in the Sampling and Analysis Plan (SAP).

L. QC samples

Field blanks (bottle, trip, filter and decontamination) are used to evaluate sample contamination. They are assessed and qualified the same as preparation blanks (see section IV-G). For any blanks greater than two times the instrument detection limit (IDL), results less than five times the amount in any associated samples are qualified UJB#, where "#" is the value of the highest blank associated with the sample. These data have been qualified as possibly biased high when the reported sample result is less than $5 \times$ blank amount. Referencing the data reports, only two samples are qualified for zinc field blank contamination. These data are fully usable as undetected values at the elevated value.'

Field QC samples are identified in field logbooks and on COC records. Inconsistencies between the field logbook and COC records in recording QC sample information have been corrected.

Results of field blank analyses are presented in Table 1.

L1. Bottle blanks

One bottle blank was analyzed at the frequency specified in the QAPP (one per bottle lot). Analytical results for the bottle blank were less than the IDL.

L2. Trip blanks

A trip blank consisted of a sample bottle containing distilled/deionized water that was transported to and preserved in the field, and returned to the laboratory with other samples for analysis. Trip blanks were collected for three of the five sampling events (less than the frequency specified in the QAPP). Analytical results were not greater than two times the IDL.

L3. Filter blanks

A filter blank was collected by filtering distilled/deionized water from a bottle that was transported into the field. Analytical results were less than the IDL.

L4. Decontamination blanks

Decontamination (rinseate) blanks measure the effectiveness of sampling equipment decontamination. Decontamination blanks consisted of a distilled/deionized water rinse of decontaminated sampling equipment. With one exception (zinc on 4/7/92), analytical results were not more than two times the IDL.

Table 1.
Results of field blank analyses^{1,2}
(concentrations in mg/l)

Date	Blank Type ³	Sample Number	pH	Sulfate	Arsenic	Cadmium	Copper	Iron	Lead	Manganese	Molybdenum	Zinc
03/30/92	Trip	92Q0041	NA	0.0	<.001	<.001	<.002	<.002	<.0004	<.001	<.001	<.003
03/31/92	Rinseate	92Q0042	5.27	<0.1	<.001	<.001	.002	<.002	<.0004	<.001	<.001	.005
04/02/92	Trip	92Q0043	NA	NA	<.001	<.001	<.002	<.002	<.0004	<.001	<.001	<.003
04/07/92	Trip	92Q0143	NA	NA	<.001	<.001	<.002	<.002	<.0004	.002	<.001	.006
05/28/92	Rinseate	92Q0144	7.38	5.5	<.001	<.001	.003	<.002	<.0004	.001	<.001	.007
06/10/92	Bottle	92Q0182	NA	0.0	<.001	<.001	<.002	<.002	<.0004	.002	<.001	.003
06/10/92	Filter	92Q0183	NA	0.0	<.001	<.001	<.002	<.002	<.0004	<.001	<.001	<.003
10/06/92												
10/06/92												
10/06/92												

1. Abbreviations: NA (not analyzed)

L5. Field replicates

Field replicates are used to assess field and laboratory precision, and variability associated with sampling methodologies. The relative percent difference (RPD) can be used to assess field replicate data. Control limits for field replicates is $RPD \leq 25\%$ or $< 2 \times CRDL$ (contract laboratory detection limit) if both results are less than $5 \times CRDL$. If either of the values is less than the IDL, the value is not calculable.

Three field duplicates were collected. This met the frequency specified in the QAPP. Results of field duplicate analyses are summarized in Table 2. Duplicate RPDs are summarized in Table 3. Duplicate analyses met target RPD limits with the exception of the duplicate collected on 10/6/92. For this sample, iron, manganese and zinc did not meet the QAPP RPD limits. Aluminum, Chromium and copper data were less than $5 \times MDL$ and the difference between the duplicate values was less than $2 \times MDL$. These data are therefore within the required control range. There is no defined qualification for field duplicate precision but the possible inhomogeneity of samples 91Q1433 - 1441 is noted. Sample 91Q1433 was selected by the laboratory as a QC duplicate and spike sample. Both of these duplicate samples were well within the control limits indicating that the inhomogeneity of sample 92Q1435 may be sample specific.

L6. Standard Reference Material

No standard reference materials were submitted from the field to the laboratory.

Table 2.
Results of field duplicate analyses

Date	Sample Type	Sample Number	pH	Sulfate (mg/l)	Arsenic (ug/l)	Cadmium (ug/l)	Copper (ug/l)	Iron (ug/l)	Lead (ug/l)	Manganese (ug/l)	Molybdenum (ug/l)	Zinc (ug/l)
04/02/92	Sample ¹	0043	7.35	246.7	<1	<1	<2	97	<0.4	1780	<1	<3
04/02/92	Duplicate	0044	7.38	249.7	<1	<1	<2	102	<0.4	1870	<1	<3
05/28/92	Sample ²	0145	6.82	356.5	32	<1	2	1940	1.8	1430	1	23
05/28/92	Duplicate	0146	6.85	353.0	32	<1	<2	1910	1.8	1410	1	19
10/06/92	Sample ³	1435		43.5	<2	<2	4.6	157	<1.2	98	2	98
10/06/92	Duplicate	1437		43.9	<2	<2	2.9	116	<1.2	20	2	58
1. Sample location: Margaret Ann well (bedrock) 2. Sample location: Well E (bedrock) 3. Sample location: A W-2 well (alluvial). Other sample/duplicate results: specific conductance, umhos/cm (320/320); calcium, mg/l (34.2/38.3); magnesium, mg/l (9.2/9.9); sodium, mg/l (9.8/9.9); potassium, mg/l (2.4/2.6); chloride, mg/l (4.4/4.4); carbonate, mg/l (132.5/132.7); aluminum, ug/l (11.2/7.6); beryllium, ug/l (<1/<1); chromium, ug/l (1.3/1.9); nickel, ug/l (1.7/1.4); silver, ug/l (<1/<1); vanadium, ug/l (<1/<1).												

Table 3.
Relative percent difference of field duplicate samples¹

Date	pH	Sulfate (mg/l)	Arsenic (ug/l)	Cadmium (ug/l)	Copper (ug/l)	Iron (ug/l)	Lead (ug/l)	Manganese (ug/l)	Molybdenum (ug/l)	Zinc (ug/l)
4/2/92	NC	1	A	A	A	5	A	5	A	A
5/28/92	NC	1	0	A	NC	2	0	1	0	19
10/6/92	NC	1	A	A	A	30	0	132	0	51

1. Abbreviations: NC (not calculable; one value is below the method detection limit)

A (acceptable; duplicate results are both less than the MDL, or both results were $< 5 \times \text{MDL}$ and the duplicate difference was $< 2 \times \text{MDL}$)

2. Sample location: Margaret Ann well (bedrock)

3. Sample location: Well E (bedrock)

4. Sample location: AW-2 well (alluvial). Other duplicate RPDs: specific conductance (0); calcium (11); magnesium (7); sodium (1); potassium (8); chloride (0); carbonate (0); aluminum (A); beryllium (A); chromium (A); nickel (19); silver (A); vanadium (A).

III. Laboratory QA/QC

A. Data qualifiers

The following qualifiers are applied, as appropriate, to data as a result of the data validation process. More detailed descriptions of the validation process is provided in subsections IV-D through IV-M.

- "JCX" - qualified due to lack of calibration blank frequency of 1 per 20.
- "JD#" - # is the value of the relative percent difference (RPD) when RPD is outside target QC limits of 25% RPD.
- "J*#" - # is one-half the difference between the two duplicate values when values are less than 5X the IDL. For these low values, the duplicate data difference must be $< 2 \times \text{IDL or MDL}$.
- "JS#" - # is the value of the percent recovery of the spike when the matrix spike recovery is outside of target QC limits ($100\% \pm 25\%$).
- "JK#" - calibration blank is outside of target QC limits (K denotes a negative blank whose absolute value "#" is greater than $2 \times \text{IDL}$).
- "JL#" - # is the value of the percent recovery of the laboratory control sample (LCS) from the true value when the percent recovery is outside target QC limits ($100\% \pm 20\%$), or the range defined by the supplier.
- "JC#" - # is the percent recovery of the continuing calibration verification (CCV) standard from the true value when the percent recovery is outside target QC limits ($100\% \pm 10\%$).
- "JF#" - # is the percent recovery of the laboratory fortified blank when the percent recovery is outside target QC limits ($100\% \pm 15\%$).
- "JI#" - # is the value of the percent recovery of the internal standard when the percent recovery is outside target QC limits (60 to 125%).
- "UJB#" - # is the value of the highest blank affecting data. The reported value is due to contamination from field collection or laboratory preparation of the sample.

B. Sample holding times

All samples were analyzed within the recommended holding times.

C. Sample preparation methods

Sample preparation followed the required methods.

D. Analytical methods and detection limits

Analyses were made at the Montana Bureau of Mines and Geology (MBMG) Analytical Division. Analyses followed methods identified in Table 4. Metals were analyzed at the Montana Bureau of Mines and Geology (MBMG) Analytical Division by Inductively-Coupled Plasma Mass Spectroscopy (ICPMS). ICPMS methods follow EPA Method 200.8 Determination of Trace Elements in Waters and Waste by ICP/MS, Revision 4.4, April 1991 and EPA proposed Method 6020 CLP-M Version 8.

Detection limits are specified in Table 5.

E. Instrument calibration

All instrument initial and continuing calibrations adhered to the relevant analytical methods. Any out of control calibrations were recalibrated and samples re-analyzed. All instrument calibrations adhered to the relevant analytical method. CRDL detection limits were met for all analytes.

F. Calibration blanks

Calibration blanks include initial calibration blanks (ICB) and continuing calibration blanks (CCB). ICBs and CCBs were analyzed at the frequency required in the QAPP. All calibration blanks were free of carryover or other contamination.

G. Preparation (method) blanks

Preparation blanks, analogous to a laboratory reagent blank (LRB) are made up of the laboratory grade water and reagents used in the sample preparation or analytical method. These reagents are carried through all method preparation and analysis procedures. Results in the preparation blank which are more than two times the IDL may indicate contamination in the samples associated with that preparation blank. At least one LRB was analyzed with each set of samples. No data were qualified for laboratory contamination.

Table 4
Laboratory methodologies for analysis of groundwater

Sample Type and Parameters	Method
Raw, unpreserved	
Specific conductance	EPA 120.1
pH	EPA 150.1
alkalinity	EPA 310.1
Filtered, unpreserved	
Fluoride	EPA 340.2
Chloride	EPA 300.0A
Bromide	EPA 300.0A
Nitrate-nitrogen	EPA 300.0A
Ortho-phosphorous	EPA 300.0A
Sulfate	EPA 300.0A
Filtered, preserved	
Dissolved Ca, Mg, Na, K, Fe, Ag, Al, B, Cr, Ni, P, Sr, Ti, V, Zn	EPA 200.7
Dissolved As, Cd, Cu, Mn, Mo, Pb, Zn	EPA 200.8

Table 5.
Detection limits for groundwater analyses.

Analyte	Contract Required Detection Limit (CRDL) (ug/l)	Method Detection Limit (MDL) (ug/l)
Arsenic	10	0.7
Cadmium	5	0.6
Copper	25	1.4
Iron	15	1.4
Lead	3	1.4
Manganese	15	1.4
Molybdenum	No Limit	0.7
Zinc	20	2.7

H. Laboratory fortified blank

The laboratory fortified blank (LFB) is used as an accuracy check in the same manner as the Laboratory Check Sample (LCS). The LCS is an EPA certified standard. The LFB is made from laboratory reagent water and spiked with laboratory standards. The LFB is a check on laboratory solutions. The EPA methods list internal guidance limits for the LFB. For the purposes of data validation, the EPA LCS QC limits of 75 - 125% recovery have been applied. No laboratory fortified blanks were out of control and no data have been qualified.

I. ICP interference check samples

The ICP interference check sample (ICS) consists of two solutions (solution A and solution B) combined and analyzed to verify interelement correction factors. The SOW requires analysis of ICSA and ICSAB solutions at the beginning and end of each sample run, or twice every 8 hours, whichever is more frequent, to monitor interferences due to high concentrations of other analytes. The laboratory analyzed one ICS sample per sample run, as specified in the QAPP. The ICS contained the required analytes of an ICSAB solution, but at diluted levels appropriate to analyte levels in the samples. Target control limits of 100 ± 25 percent were used for validating and qualifying data. No data were qualified due to ICS recoveries outside the target control limits.

Interferences for ICP-MS are monitored by control of isobaric elemental interferences and polyatomic ion interferences. All data met acceptance criteria.

J. Interelement correction factors

Interelement correction factors do not apply to the ICPMS method, given the rigor of correction in the tuning and calibration of the analytical instrument. Iron data were analyzed by ICP. Iron data are not affected by the Interference Control Factors but the ICF data were acceptably reported.

K. Spikes

Matrix spikes are used to assess the effect of the sample matrix on measurement methodology. A pre-digest spike was added to a minimum of 10% of samples. Target control limits of 100 ± 25 percent were used for data validation. No data were qualified for out of control spike recoveries.

L. Laboratory Control Sample

Laboratory method accuracy is further verified by analysis of laboratory control samples (LCS) prepared from EPA or approved reference solutions. This sample is also termed a Quality Control Sample (QCS) in the ICP-MS method. Several U.S. Geological Survey samples were used for the ICP-MS studies. LCS's were analyzed at the frequency required in the QAPP. Seven samples in one set were qualified "JL#" (where # is the value of the percent recovery) for being outside of the QC limits. These samples could possibly be biased high, but the other 4 samples in the set were undetected indicating the probable lack of high bias to the entire data set. Re-analysis were performed on three of these samples. The re-analyses were fully acceptable and the results verify the accuracy of the original results. The high bias appears to be a function of the LCS and not of the method performance.

M. Internal Standards

Internal standards are analyzed to monitor for drift in instrument calibration. The internal standard is added to all samples and the blank. The recovery in the blank is used to assess the recoveries in other samples. EPA Method 200.8 requires the absolute response of any one internal standard must be within 60-125% of the original response in the calibration blank. EPA Method 6020 requires that when the intensity of an internal standard is less than 30 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed for the affected samples after performing a fivefold dilution. The target limits used were 60 -125%. No data are qualified for internal standard recovery limits.

N. Duplicates

Duplicate samples are a measure of precision. Laboratory duplicates were analyzed to assess the replicability of laboratory subsampling and analytical techniques. This involved taking two separate aliquots of sample through sample digestion and analysis. Target control limits of RPD <25% percent were used for validating data.

Duplicate samples were analyzed at the target frequency of 10% in all analytical batches.

IV. CUSTODY AND DOCUMENT CONTROL

A. Field custody

COC records were reviewed for completeness and adherence to the QAPP, and for consistency with information recorded in field logbooks. Inconsistencies between field logbooks and COC records have been corrected. Custody transfer from the sample collector to the analytical laboratory is documented on COC records.

B. Sample delivery

Samples were delivered by the sample collector to the analytical laboratory. No samples were lost due to broken seals, damaged or destroyed sample bottles, or loose or unattached sample bottle caps.

C. Laboratory custody

Commencement of custody by the analytical laboratory is documented on COC records. Samples were logged into the laboratory and given a laboratory identification number. The sample storage area of the MBMG Analytical Division is a locked, restricted access area within the main office. A custody logbook is maintained to document movement of samples into and out of the storage area.

D. Sample tracking

Sample numbers are traceable from field collection through laboratory analysis. Inconsistencies between the field logbook and COC records in the recording of field sample numbers have been corrected.

Laboratory numbers were assigned to field samples and were recorded in the sample log-in book. A laboratory batch number identification form ties field numbers to laboratory numbers. Laboratory numbers are entered on all analytical output. Therefore, sample numbers are traceable from the field to the final analytical output through the field logbook; COC records; sample log-in book; the batch number identification form; and the analytical output.

E. Document control

Field notebooks and COC records were stored in the offices of MBMG. Access to these offices is restricted to project, security and maintenance personnel.

F. Document review

Documents which were reviewed for completeness and accuracy include the field logbook, COC records and laboratory forms and records. No deviations from the QAPP are noted as a result of this review.

G. Identity of sample collector

Identity of the sample collector was recorded in the field logbook and on COC records.

V. RESULTS - DATA QUALIFICATION

The following data qualifiers have been applied to surface water data as a result of data validation:

- "JL" - laboratory control sample recovery is outside target QC limits (100% $\pm$ 20%)
- "UJB#" - estimated due to contamination of an associated field or laboratory blank. The "#" is the value of the highest blank associated with that sample.

Data and data qualifiers are summarized in Table 6.

Table 6
Metals Concentrations in Groundwater (concentrations in ug/l)

Well	Sample Number	Arsenic	Cadmium	Copper	Iron	Lead	Manganese	Molybdenum	Zinc
Hebgen Park	92Q00040	1.7	1.3	1.8	<21	2.2	32	<1.0	99
Margaret Ann	92Q00044	0.7	<0.6	<1.4	94	<0.4	1776	<1.0	<3
Well B	92Q00046	13.4	<0.6	<1.4	151	0.4	1406	3.3	64
Well D1	92Q00070	10.0	<0.6	<1.4	4030	<0.4	1440	<1.0	1983
Well E	92Q00145	32.2	<0.6	1.8	1894	1.8	1425	1.2	23UJB6
Well D2	92Q00147	<0.7	<0.6	<1.42	25140	1.2	3540	<1.0	1691
AW-1	92Q01433	<1.9	6.2	3.4	152JL212	0.8	15	<2.0	85
AW-2	92Q01435	<1.9	1.6	4.6	157JL212	0.7	97	<2.0	98
AW-3	92A1441	<1.9	1.4	3.0	72JL212	<0.4	74	<2.0	188

VI. PRECISION, ACCURACY, REPRESENTATIVENESS, COMPLETENESS AND COMPARABILITY

A. Precision

Precision is evaluated by examining replicate samples for scatter in terms of the difference between laboratory and field duplicate values. No data have been qualified for unacceptable precision.

B. Accuracy

Accuracy is evaluated by verifying the recovery calculations for spiked samples. Verification occurred during the data tabulation and data validation process. No data have been qualified for laboratory spike accuracy. Several iron data were qualified for a LCS out of control. The possible high bias of this LCS recovery was not substantiated by the remaining data in the set which were undetected. Re-analysis of part of these data verified that the original values were accurate and not affected by a high bias.

C. Representativeness

Representativeness is determined by a number of factors, including site selection criteria, sample collection procedures, sample collection equipment, sample containers, sample contamination, sample preservation and storage and holding times for analysis.

Groundwater data have been deemed to be representative for the following reasons:

- sample collection site identification and selection were based on sound, well-reasoned objectives, as described in the Assessment Plan;
- sample collection procedures addressed the objectives of the groundwater sampling identified in the Assessment Plan, and were most representative of the environment being sampled, given those objectives;
- sample containers conformed to EPA recommendations for the analytes of interest;
- samples were preserved and stored following EPA recommendations;
- no sample holding times were exceeded prior to analysis;

D. Completeness

Completeness is defined as the percentage of measurement data that remain valid after discarding any invalid data due to field or laboratory QC. Data fully meet the >95% completeness criteria for field and laboratory QC. No samples were rejected due to unacceptable field or laboratory QA/QC.

E. Comparability

Comparability involves the evaluation of data characteristics which may limit comparability to other datasets. No data characteristics were identified which limited the comparability of this data to other datasets for the objectives of the groundwater assessment. Samples were collected and analyzed by standard and commonly used methods.

VII. REFERENCES

Maest, A., J. Metesh and R. Brand. 1995. Butte Groundwater Injury Assessment Report, Clark Fork River Basin NPL Sites. Prepared Natural Resource Damage Litigation Program. January.

NRDP. 1992. Assessment Plan: Part II. Clark Fork River Basin NPL Sites, Montana. State of Montana, Natural Resource Damage Program. April, 1992.

NRDP. 1994. Assessment Plan: Part III. Clark Fork River Basin NPL Sites, Montana. State of Montana, Natural Resource Damage Program. April, 1992.

NRDLP. 1995. Modifications to Assessment Plan, Clark Fork Basin NPL Sites, Montana, Natural Resource Damage Litigation Program. January.

U.S. EPA. 1985. Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses.

Viar & Co. 1988. Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses. Revised.

**QUALITY ASSURANCE/QUALITY CONTROL REPORT
SOILS SAMPLING**

TABLE OF CONTENTS

TABLE OF CONTENTS	.i
LIST OF ACRONYMS	.iii
LIST OF TABLES	iv
 I	
INTRODUCTION	1
 II	
SAMPLE COLLECTION AND FIELD QA/QC	1
A. Sampling Date and Time	2
B. Sampling Team	2
C. Sampling Locations	2
D. Physical Description of Sampling Location	2
E. Sample Collection Methods	2
F. Field Preparation Methods	3
G. Sample Numbers	3
H. Sample Preservation	3
I. Sample Shipping Information	3
J. Field Instrument Calibrations and Field Measurements	3
K. QC Samples	3
K1. Trip Blanks	4
K2. Decontamination Blanks	4
K3. Field Replicates	5
K4. Standard Reference Material	5
 III	
LABORATORY QA/QC	9
A. Data Qualifiers	9
B. Sample Holding Times	9
C. Sample Preparation Methods	10
D. Analytical Methods and Detection Limits	10
E. Instrument Calibration	12
F. Calibration Blanks	12
G. Preparation Blanks (Laboratory Reagent Blank)	12
H. Laboratory Fortified Blank	13
I. ICP Interference Check Samples	13
J. Interelement Correction Factors	13
K. Spikes	14
L. Internal Standards	14
M. Duplicates	14
N. ICPMS Quality Control	16

IV	CUSTODY AND DOCUMENT CONTROL	16
A.	Field Custody	16
B.	Sample Delivery	16
C.	Laboratory Custody	17
D.	Sample Tracking	17
E.	Document Control	17
F.	Document Review	17
G.	Identity of Sample Collector	17
V	RESULTS - DATA QUALIFICATION	17
VI	PRECISION, ACCURACY, REPRESENTATIVENESS, COMPLETENESS AND COMPARABILITY	24
A.	Precision	24
B.	Accuracy	24
C.	Representativeness	24
D.	Completeness	24
E.	Comparability	25
VII	REFERENCES	25

LIST OF ACRONYMS

CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification
CEC	Cation Exchange Capacity
CLP	Contract Laboratory Program
COC	Chain-of-Custody
CRDL	Contract Laboratory Detection Limit
EPA	Environmental Protection Agency
ICB	Initial Calibration Blank
ICPMS	Inductively-Coupled Plasma Mass Spectroscopy System
ICS	Interference Check Sample
ICSA	Interference Check Sample - A
ICSB	Interference Check Sample - B
IDL	Instrument Detection Limit
LCS	Laboratory Control Sample
LFB	Laboratory Fortified Blank
LRB	Laboratory Reagent Blank
MBMG	Montana Bureau of Mines and Geology
MDL	Method Detection Limit
MSU	Montana State University
NRDA	Natural Resource Damage Assessment
NRDP	Natural Resource Damage Program
OM	Organic Matter
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
SOP	Standard Operating Procedure

LIST OF TABLES

1.	Results of Trip Blanks Analyses	6
2.	Results of Decontamination Blanks Analyses (Field Samples)	7
3.	Results of Decontamination Blanks Analyses (Laboratory Samples)	7
4a.	Results of Field Replicate Analyses	8
4b.	Results of Field Replicate Analyses	8
5.	Laboratory Methodologies for Analysis of Soils	11
6.	Detection limits for Soils Analyses	12
7a.	Results of Laboratory Split Sample Analyses	15
7b.	Relative Percent Difference of Laboratory Split Sample Analyses	16
8a.	Hazardous Substance Concentrations in Riparian Impact Soils (0-2") Silver Bow Creek, Clark Fork River and Opportunity Ponds	18
8b.	Hazardous Substance Concentrations in Riparian Control Soils (0-2") Divide Creek, Little Blackfoot River and Flint Creek	19
8c.	Hazardous Substance Concentrations in Uplands Impact Soils (0-2") Stucky Ridge and Smelter Hill	20
8d.	Hazardous Substance Concentrations in Uplands Impact Soils (0-2") Mount Haggin	21
8e.	Hazardous Substance Concentrations in Uplands Controls Soils (0-2") Stucky Ridge, Smelter Hill and Mount Haggin	22
8f.	Hazardous Substance Concentrations in Uplands Impact and Control Soils (0-6") Stucky Ridge, Smelter Hill and Mount Haggin	23

QUALITY ASSURANCE/QUALITY CONTROL REPORT SOILS SAMPLING

I. INTRODUCTION

The purpose of this report is to evaluate and summarize the quality assurance (QA) and quality control (QC) associated with the collection and analysis of soil samples for the Clark Fork Basin Natural Resource Damage Assessment (NRDA). QA/QC guidance was provided by the Natural Resource Damage Litigation Program (NRDLP) Quality Assurance Project Plan (QAPP). Results of groundwater assessment activities are summarized in Terrestrial Resources Injury Assessment Report (Lipton et. al., 1995). QA/QC guidance was provided by the Natural Resource Damage Program (NRDP) Quality Assurance Project Plan (QAPP) (NRDP, 1992a).

The organization of this report generally follows the data validation outline presented in Section 11.0 of the QAPP. Section II describes Sample Collection and Field QA/QC, including deviations from sampling protocols and standard operating procedures (SOPs) referenced in the Assessment Plan, Part II (NRDP, 1992b) or described in the Lipton et. al. (1995). (Modifications to the Assessment Plan and research protocols contained therein are summarized in NRDLP, 1995). Section III describes and evaluates Laboratory QA/QC. Section IV summarizes Custody and Document Control. Section V presents results of data qualification. Section VI discusses Precision, Accuracy, Representativeness, Completeness and Comparability.

II. SAMPLE COLLECTION AND FIELD QA/QC

QC samples were collected to evaluate sample contamination and the replicability of sample collection methods. QC samples for evaluating sample contamination included trip blanks decontamination swipes of sampling equipment. Replicate samples were collected to validate sample collection and processing methods.

There are no Environmental Protection Agency (EPA) control limits nor corrective actions for field QC samples, with the exception of field blanks. EPA (1985) and Viar & Co. (1988) consider field QC as supporting evidence in the overall assessment of a data set or sampling event. Field QC is not the basis for accepting or rejecting data, but rather acts as additional evidence in support of these conclusions arrived at by a review of the complete data set. Therefore, except in the case of gross errors, poor performance on field QC-samples does not invalidate data.

The following items were reviewed for sample collection and preparation, and field QA/QC:

A. Sampling date and time

Sampling dates and times were recorded in the field logbook and on chain-of-custody (COC) records. These documents were reviewed for completeness and accuracy. Inconsistencies between these documents have been corrected.

B. Sampling team

Names of the sample collector and observation recorder are recorded in field logbooks.

C. Sampling locations

Sampling locations were identified by transect number. Transect numbers were recorded in field logbooks and on chain-of-custody records.

D. Physical description of sampling location

Sampling locations were not physically described in the field logbooks. Sampling locations were described by a unique transect number. Transects are located on topographic maps contained in the Administrative Record.

E. Sample collection methods

Sample collection adhered to the soil sampling protocols described in Lipton, et al. (1995). When circumstances required field decisions to ensure that samples collected were representative of the media being sampled, such decisions were noted in field logbooks. Deviations from soil sampling protocols are noted below:

- Transect AA8, site 4: sample inadvertently collected south of the transect instead of north.
- Transect RR14: transect was shorter than intended due to an incorrect calculation.
- Transect RR6: transect was in a flooded hay meadow; it was moved slightly to a dry area of the field.
- Transect CC3, site 5: flag was missing; sample was dug at last flagging north.

J. Sample shipping information

No samples were shipped via commercial carrier. All samples were hand-delivered from the field to the laboratory by the sample collector.

K. Field instrument calibrations and field measurements

Field instruments included pH meter, Eh meter, and specific conductivity meter. Calibrations adhered to CFRSSISOP HG-8 (pH and Eh), and CFRSSISOP HG-7 (specific conductivity). Several deviations from these SOPs are noted. pH meter calibration adhered to the SOP, but for three alluvial wells and two bedrock wells (Hebgen Park and Well D-2), pH meter calibration was not recorded in the field logbook. For Eh and conductivity, meters were not calibrated as frequently as specified in the SOPs, but did meet the frequency specified in the Sampling and Analysis Plan (SAP).

L. QC samples

Field blanks (bottle, trip, filter and decontamination) are used to evaluate sample contamination. They are assessed and qualified the same as preparation blanks (see section IV-G). For any blanks greater than two times the instrument detection limit (IDL), results less than five times the amount in any associated samples are qualified UJB#, where "#" is the value of the highest blank associated with the sample. These data have been qualified as possibly biased high when the reported sample result is less than 5 x blank amount. Referencing the data reports, only two samples are qualified for zinc field blank contamination. These data are fully usable as undetected values at the elevated value.'

Field QC samples are identified in field logbooks and on COC records. Inconsistencies between the field logbook and COC records in recording QC sample information have been corrected.

Results of field blank analyses are presented in Table 1.

L1. Bottle blanks

One bottle blank was analyzed at the frequency specified in the QAPP (one per bottle lot). Analytical results for the bottle blank were less than the IDL.

L2. Trip blanks

A trip blank consisted of a sample bottle containing distilled/deionized water that was transported to and preserved in the field, and returned to the laboratory with other samples for analysis. Trip blanks were collected for three of the five sampling events (less than the frequency specified in the QAPP). Analytical results were not greater than two times the IDL.

L3. Filter blanks

A filter blank was collected by filtering distilled/deionized water from a bottle that was transported into the field. Analytical results were less than the IDL.

L4. Decontamination blanks

Decontamination (rinseate) blanks measure the effectiveness of sampling equipment decontamination. Decontamination blanks consisted of a distilled/deionized water rinse of decontaminated sampling equipment. The rinseate blank collected on October 8, 1992 contained substantial amounts of copper, iron, lead, manganese and zinc. The source of contamination was not precisely identified, however the field sampler raised the possibility that the nitric acid decontamination solution may have contacted some metal fittings on the sampling line. Although there is potential carryover from the decontamination sample to the next collected field sample, purging three casing volumes from the well before sampling would alleviate any carryover. Nonetheless, samples collected on October 8th and 9th are qualified "UJB#", where "#" is the value of analyte in the decontamination blank.

Table 1.
Results of field blank analyses^{1,2}
(concentrations in mg/l)

Date	Blank Type ¹	Sample Number	pH	Sulfate	Arsenic	Cadmium	Copper	Iron	Lead	Manganese	Molybdenum	Zinc
03/30/92	Trip	92Q0041	NA	0.0	<.001	<.001	<.002	<.002	<.0004	<.001	<.001	<.003
03/31/92	Rinseate	92Q0042	5.27	<0.1	<.001	<.001	.002	<.002	<.0004	<.001	<.001	.005
04/02/92	Trip	92Q0043	NA	NA	<.001	<.001	<.002	<.002	<.0004	<.001	<.001	<.003
04/07/92	Trip	92Q0143	NA	NA	<.001	<.001	<.002	<.002	<.0004	.002	<.001	.006
05/28/92	Rinseate	92Q0144	7.38	5.5	<.001	<.001	.003	<.002	<.0004	.001	<.001	.007
06/10/92	Bottle	92Q0182	NA	0.0	<.001	<.001	<.002	<.002	<.0004	.002	<.001	.003
06/10/92	Filter	92Q0183	NA	0.0	<.001	<.001	<.002	<.002	<.0004	<.001	<.001	<.003
10/08/92	Trip	92Q1434	NA	NA	<.002	<.001	.005	<.013	<.0004	<.003	<.002	.003
10/08/92	Rinseate	92Q1436	NA	NA	<.002	<.001	.026	.613	.0069	.035	<.002	1601
10/09/92	Filter	92Q1438	NA	NA	<.002	<.001	<.003	<.013	.0006	<.003	<.002	<.002
10/09/92	Bottle	92Q1439	NA	NA	<.002	<.001	<.003	<.013	<.0004	<.003	<.002	.004
10/09/92	Trip	92Q1440	NA	NA	<.002	<.001	<.003	<.013	<.0004	<.003	<.002	<.002

1. Abbreviations: NA (not analyzed)

L5. Field replicates

Field replicates are used to assess field and laboratory precision, and variability associated with sampling methodologies. The relative percent difference (RPD) can be used to assess field replicate data. Control limits for field replicates is $RPD \leq 25\%$ or $< 2 \times CRDL$ (contract laboratory detection limit) if both results are less than $5 \times CRDL$. If either of the values is less than the IDL, the value is not calculable.

Three field duplicates were collected. This met the frequency specified in the QAPP. Results of field duplicate analyses are summarized in Table 2. Duplicate RPDs are summarized in Table 3. Duplicate analyses met target RPD limits with the exception of the duplicate collected on 10/6/92. For this sample, iron, manganese and zinc did not meet the QAPP RPD limits. Aluminum, Chromium and copper data were less than $5 \times MDL$ and the difference between the duplicate values was less than $2 \times MDL$. These data are therefore within the required control range. There is no defined qualification for field duplicate precision but the possible inhomogeneity of samples 91Q1433 - 1441 is noted. Sample 91Q1433 was selected by the laboratory as a QC duplicate and spike sample. Both of these duplicate samples were well within the control limits indicating that the inhomogeneity of sample 92Q1435 may be sample specific.

L6. Standard Reference Material

No standard reference materials were submitted from the field to the laboratory.

Table 2.
Results of field duplicate analyses¹

Date	Sample Type	Sample Number	pH	Sulfate (mg/l)	Arsenic (ug/l)	Cadmium (ug/l)	Copper (ug/l)	Iron (ug/l)	Lead (ug/l)	Manganese (ug/l)	Molybdenum (ug/l)	Zinc (ug/l)
04/02/92	Sample ²	0043	7.35	246.7	<1	<1	<2	97	<0.4	1780	<1	<3
04/02/92	Duplicate	0044	7.38	249.7	<1	<1	<2	102	<0.4	1870	<1	<3
05/28/92	Sample ³	0145	6.82	356.5	32	<1	2	1940	1.8	1430	1	23
05/28/92	Duplicate	0146	6.85	353.0	32	<1	<2	1910	1.8	1410	1	19
10/08/92	Sample ⁴	1435	NA	43.5	<2	<2	4.6	157	<1.2	98	2	98
10/08/92	Duplicate	1437	NA	43.9	<2	<2	2.9	116	<1.2	20	2	58

1. NA (not analyzed)
2. Sample location: Margaret Ann well (bedrock)
3. Sample location: Well E (bedrock)
4. Sample location: AW-2 well (alluvial). Other sample/duplicate results: specific conductance, umhos/cm (320/320); calcium, mg/l (34.2/38.3); magnesium, mg/l (9.2/9.9); sodium, mg/l (9.8/9.9); potassium, mg/l (2.4/2.6); chloride, mg/l (4.4/4.4); carbonate, mg/l (132.5/132.7); aluminum, ug/l (11.2/7.6); beryllium, ug/l (<1/<1); chromium, ug/l (1.3/1.9); nickel, ug/l (1.7/1.4); silver, ug/l (<1/<1); vanadium, ug/l (<1/<1).

Table 3.
Relative percent difference of field duplicate samples¹

Date	pH	Sulfate (mg/l)	Arsenic (ug/l)	Cadmium (ug/l)	Copper (ug/l)	Iron (ug/l)	Lead (ug/l)	Manganese (ug/l)	Molybdenum (ug/l)	Zinc (ug/l)
04/02/92	NC	1	A	A	A	5	A	5	A	A
05/28/92	NC	1	0	A	NC	2	0	1	0	19
10/08/92	NC	1	A	A	A	30	0	132	0	51

1. Abbreviations: NC (not calculable; one value is below the method detection limit)
A (acceptable; duplicate results are both less than the MDL, or both results were $< 5 \times \text{MDL}$ and the duplicate difference was $< 2 \times \text{MDL}$)
2. Sample location: Margaret Ann well (bedrock)
3. Sample location: Well E (bedrock)
4. Sample location: AW-2 well (alluvial). Other duplicate RPDs: specific conductance (0); calcium (11); magnesium (7); sodium (1); potassium (8); chloride (0); carbonate (0); aluminum (A); beryllium (A); chromium (A); nickel (19); silver (A); vanadium (A).

III. Laboratory QA/QC

A. Data qualifiers

The following qualifiers are applied, as appropriate, to data as a result of the data validation process. More detailed descriptions of the validation process is provided in the subsections IV-D through IV-M.

- "JCX" - qualified due to lack of calibration blank frequency of 1 per 20;
- "JD#" - # is the value of the RPD when RPD is outside target QC limits of 20 % RPD;
- "J*#" - # is one-half the difference between the two duplicate values when values are less than 5X the IDL. For these low values, the duplicate data difference must be $< 2 \times \text{IDL or MDL}$;
- "JS#" - # is the value of the percent recovery of the spike when the matrix spike recovery is outside of target QC limits ($100\% \pm 25\%$);
- "JK" - calibration blank is outside of target QC limits (K denotes a negative blank whose absolute value is greater than $2 \times \text{IDL}$);
- "JL#" - # is the value of the percent recovery of the laboratory control sample (LCS) from the true value when the percent recovery is outside target QC limits ($100\% \pm 20\%$), or the range defined by the supplier;
- "JC#" - # is the percent recovery of the continuing calibration verification (CCV) standard from the true value when the percent recovery is outside target QC limits ($100\% \pm 10\%$);
- "JF#" - # is the percent recovery of the laboratory fortified blank when the percent recovery is outside target QC limits ($100\% \pm 15\%$);
- "JI#" - # is the value of the percent recovery of the internal standard when the percent recovery is outside target QC limits (60 to 125%);
- "UJB#" - # is the value of the highest blank affecting data. The reported value is due to contamination from field collection or laboratory preparation of the sample.

B. Sample holding times

All samples were analyzed within EPA's suggested holding time limit of six months.

C. Sample preparation methods

Three types of soils samples were collected. These samples were:

- "Chemistry" samples collected from the 0-2 inch soil depth at all sampling sites. These samples were analyzed for metals only.
- "Phytotoxicity screening samples" were collected from the 0-2 inch depth at all sites designated for vegetation and wildlife evaluation. Soils were analyzed for metals and other soil chemistry parameters.
- "Extended samples" that were used for chemical analyses and phytotoxicity tests (screening and extended tests). Samples were collected from the 0-2 inch and 0-6 inch depth. Samples were analyzed for metals and other soil chemistry parameters.

Soil sub-samples were dried, sieved, composited and split for analyses.

D. Analytical methods and detection limits

All 2-inch and 6-inch samples of all three types were analyzed for total metals (arsenic, cadmium, copper, lead, and zinc). The 2-inch extended samples were also analyzed for plant available metals. The 2-inch screening and extended phytotoxicity tested samples were analyzed for the following: pH, texture (particle size), soil nutrients, organic matter (OM), and cation exchange capacity (CEC). Soil nutrient analyses included nitrate ($\text{Ca}(\text{OH})_2$), phosphorous (NaHCO_3 extractable, and potassium (NH_4OAc extractable).

General soil parameters and soil nutrients were analyzed at the Montana State University (MSU) Soil Analytical Laboratory. Metals were analyzed at the Montana Bureau of Mines and Geology (MBMG) Analytical Division by Inductively-Coupled Plasma Mass Spectroscopy (ICP/MS).

Analytical methodologies are identified in Table 5. Detection limits for ICPMS analyses are provided in Table 6.

Table 5
Laboratory methodologies for analysis of soils

Parameter	Method
Soil organic matter	Page et al., 1982 Sims and Haby, 1970
pH	Clesceri et al., 1989 Page et al., 1982 USDA Handbook No. 60
Cation exchange capacity	Bower et al., 1952
Particle size	Bouyoucos, 1936 Day, 1965 Gee and Bauder, 1979
Nitrate	Extraction: Page et al., 1982 Sims and Jackson, 1971 Color development: Clesceri et al., 1989 Technicon Method N. 100-70W Willis, 1980
Phosphorous	Olsen et al., 1954 Page et al., 1982 Wantanabe and Olsen, 1965
Potassium	Page et al., 1982
Total metals	EMSL Method 200.8 (Long and Martin, 1991) EPA proposed Method 6020 CLP-M Version 8.0

Table 6.
Detection limits for soils analyses.

Analyte	Contract Required Detection Limit (CRDL) (ug/l)	Method Detection Limit (MDL) (mg/kg)	Lowest Lab Standard (ug/l)
Arsenic	3	0.86	5
Cadmium	5	0.16	2.5
Copper	25	0.16	10.0
Lead	3	0.32	10.0
Zinc	20	3.53	1.0

E. Instrument calibration

All instrument calibrations adhered to the relevant analytical method. CRDL detection limits were met for all analytes.

Calibration standards and instrument calibration are verified by analysis of laboratory control samples (LCS) prepared from EPA reference solutions. LCS were analyzed at the frequency required in the QAPP. Three samples were qualified "JL#" for not meeting LCS target recovery limits. All other data meet the LCS accuracy criteria.

F. Calibration blanks

Calibration blanks include initial calibration blanks (ICB) and continuing calibration blanks (CCB). ICBs and CCBs were analyzed at the frequency required in the QAPP. All blanks met target QC limits.

G. Preparation blanks (laboratory reagent blank)

Preparation blanks are made up of the laboratory grade water and reagents used in the sample preparation or analytical method. These reagents are carried through all method preparation and analysis procedures. Results in the preparation blank that are more than two times the IDL may indicate contamination in the samples associated with that preparation blank.

At least one a laboratory reagent blank (LRB) was analyzed with each set of samples. For five samples, the analytical value in the reagent blank exceeded the MDL. Six samples

(92:802, 803, 804, 807, 764, 765) were affected by zinc which was found in the reagent blank at 24 ug/l (4.8 mg/kg). Data for zinc which are reported at less than 24 mg/kg would be qualified UJB4.8. These data are fully usable as undetected values and the results obtained from these samples are considered to be derived predominantly from laboratory contamination.

One preparation blank affected sample 92-522, which would be qualified as follows: As (UJB3); Cd (UJB78); Cu (UJB22); Pb (UJB5); Zn (UJB127). All results from this sample which are reported at less than 5 x the blank value are considered to be from laboratory contamination.

H. Laboratory fortified blank

The laboratory fortified blank (LFB) is used as an accuracy check in the same manner as the Laboratory Check Sample (LCS). The LCS is an EPA certified standard. The LFB is made from laboratory reagent water and spiked with laboratory standards. The LFB is a check on laboratory solutions. The EPA methods list internal guidance limits for the LFB. For the purposes of data validation, the EPA LCS QC limits of 75 - 125% recovery have been applied. Using these limits, four samples were qualified JF74 for arsenic for a 74% recovery and four were qualified JF71 for a 71% recovery. These recoveries are very near the 25% limit and data are not considered to be affected by these results. A small low bias may be present in the arsenic standard. The LCS recoveries for these samples were well within limits and indicated integrity to the accuracy of results.

I. ICP interference check samples

The ICP interference check sample (ICS) consists of two solutions (solution A and solution B) combined and analyzed to verify interelement correction factors. The SOW requires analysis of ICSA and ICSAB solutions at the beginning and end of each sample run, or twice every 8 hours, whichever is more frequent, to monitor interferences due to high concentrations of other analytes. The laboratory analyzed one ICS sample per sample run, as specified in the QAPP. The ICS contained the required analytes of an ICSAB solution, but at diluted levels appropriate to analyte levels in the samples. Target control limits of 100 ± 25 percent were used for validating and qualifying data.

No data were qualified due to ICS recoveries outside the target control limits.

J. Interelement correction factors

Interelement correction factors do not apply to the ICPMS method, given the rigor of correction in the tuning and calibration of the analytical instrument.

K. Spikes

Matrix spikes are used to assess the effect of the sample matrix on digestion and measurement methodology. A pre-digest spike was added to a minimum of 10% of samples. Target control limits of 100 + 25 percent were used for validating.

Nine different soil samples were qualified for spike recoveries which were out of limits. Twenty data points were affected.

L. Internal Standards

Internal standards are analyzed to monitor for drift in instrument calibration. The internal standard is added to all samples and the blank. The recovery in the blank is used to assess the recoveries in other samples. EPA Method 200.8 requires the absolute response of any one internal standard must be within 60-125% of the original response in the calibration blank. EPA Method 6020 requires that when the intensity of an internal standard is less than 30 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed for the affected samples after performing a fivefold dilution. Samples outside of target limits of 60-125% are qualified "JI#".

Six samples were qualified "JI#" for internal standards outside of target limits.

M. Duplicates

Duplicate samples are a measure of precision. Laboratory duplicates were analyzed to assess the replicability of laboratory subsampling and analytical techniques. This involved taking two separate aliquots of sample through sample digestion and analysis. Target control limits of RPD <35% percent for samples and <50% for field duplicates was used for validating data.

Duplicate samples were analyzed at the target frequency of 10% in all analytical batches except Batch #2. For this batch, one duplicate was analyzed for 42 samples. No qualification has resulted for this situation. In total, one sample (92-537) was qualified "JD56" for cadmium RPD outside of control limits.

Laboratory split samples were also analyzed. These were collected from samples processed (dried, sieved, and composited) at the MSU Soil Analytical Laboratory. These splits document the homogeneity of samples following compositing, and the representativeness of subsampling. Results of split sample analyses are provided in Tables 7a and 7b. All RPDs met target limits. Results indicate that sample processing was acceptable.

F. Document review

Documents which were reviewed for completeness and accuracy include the field logbook, COC records and laboratory forms and records. No deviations from the QAPP are noted as a result of this review.

G. Identity of sample collector

Identity of the sample collector was recorded in the field logbook and on COC records.

V. RESULTS - DATA QUALIFICATION

The following data qualifiers have been applied to surface water data as a result of data validation:

- "JL" - laboratory control sample recovery is outside target QC limits (100% $\pm$ 20%)
- "UJB#" - estimated due to contamination of an associated field or laboratory blank. The "#" is the value of the highest blank associated with that sample.

Data and data qualifiers are summarized in Table 6.

Table 6
Metals Concentrations in Groundwater (concentrations in ug/l)

Well	Sample Number	Arsenic	Cadmium	Copper	Iron	Lead	Manganese	Molybdenum	Zinc
Hebgen Park	92Q0040	1.7	1.3	1.8	<21	2.2	32	<1.0	99
Margaret Ann	92Q0044	0.7	<0.6	<1.4	94	<0.4	1776	<1.0	<3
Well B	92Q0046	13.4	<0.6	<1.4	151	0.4	1406	3.3	64
Well D1	92Q0070	10.0	<0.6	<1.4	4030	<0.4	1440	<1.0	1983
Well E	92Q0145	32.2	<0.6	1.8	1894	1.8	1425	1.2	23UJB7
Well D2	92Q0147	<0.7	<0.6	<1.42	25140	1.2	3540	<1.0	1691
AW-1	92Q1433	<1.9	<2.0	3.4UJB26	152UJB613	0.8UJB7	15UJB35	6.2	85UJB1601
AW-2	92Q1435	<1.9	<2.0	4.6UJB26	157UJB613	0.7UJB7	97UJB35	1.6	98UJB1601
AW-3	92A1441	<1.9	<2.0	3.0UJB26	72UJB613	<0.4	74UJB35	1.4	188UJB1601

C. Laboratory custody

Commencement of custody by the analytical laboratory is documented on COC records. Samples were stored in a locked cabinet. Custody of samples outside the storage cabinet was maintained by those persons removing samples.

D. Sample tracking

Sample numbers are traceable from field collection through laboratory analysis. Inconsistencies between the field logbook and COC record in the recording of field sample numbers have been corrected.

Laboratory numbers were assigned to field samples and were recorded in the sample log-in book. A separate form for holding times ties field numbers to laboratory numbers. Laboratory numbers appear on analytical output. Therefore, sample numbers are traceable from the field to the final analytical output through the field logbook; COC records; sample log-in book; holding time records and the analytical output.

E. Document control

Field notebooks were stored in secured offices at RCG/Hagler Bailly Inc. COC records were stored in the offices of NRDLP. Access to these offices is limited to project, security and maintenance personnel.

F. Document review

Documents which were reviewed for completeness and accuracy include field logbooks, COC records and laboratory forms and records. No deviations from the QAPP are noted as a result of this review.

G. Identity of sample collector

Members of each sampling team (observation recorder and sample collector) are identified in field notebooks for each sampling date.

V. RESULTS - DATA QUALIFICATION

Qualifiers have been applied to data as summarized in Tables 8a through 8e.

Table 8a
Hazardous Substance Concentrations in Riparian Impact Soils (0-2")
Silver Bow Creek, Clark Fork River and Opportunity Ponds
(concentrations in mg/kg)

Sample	As (ppm)	Cd (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
Reach 1					
R1	414.1	4.3	485.5	631.5	1500.9
R2	186.7JS177	12.2JS155	615.2	392.0JS194	3702.0
R3	509.0	17.8	4014.0	780.2	5108.0
R4	295.0JF74	4.7JD56	927.8	468.0	5108.0
R4	382.6JF74	5.8JD56	478.0	528.3	5108.0
R5	418.9JS177	10.3JS155	1645.7	885.8JS194	3568.0
R6	336.4JS74	3.7	478.0	528.3	1460.9
Reach 2					
R9	186.7JS177	2.4JS155	407.5	337.6JS194	906.4
R8	163.6JS69	1.7	407.6	314.2	720.5
R4	172.1	1.6	485.5	285.4	754.4
R9	409.0	3.7	1414.5	631.5	2152.0
R10	425.6JS132	6.3JS148	1269.6	836.6JS202	2076.0
R11	169.6JS74	1.1	478.0	307.3	1160.8
R12	230.1	3.7	1928.9	437.8	2010.0
Reach 1					
R13	334.7JF83	8.5	3644.0	236.8	1607.2
R14	268.1	5.8	1887.4	200.8	1267.6
R14	327.9	3.7	1723.4	780.2	1312.6
R14	230.1	3.5	1183.2	240.8	1033.5
R15	476.4JS74	8.5	1928.9	360.0	1267.6
R16	291.8JS177	1.1	566.5	780.2	549.5
R17	525.5JS177	5.3	2200.0	339.1	1414.7
Opportunity Ponds					
OP1	1398.1	68.1	9980.0	722.6JI220	2676.0JF117
OP2	204.2	1.1	728.2	460.0	475.7
OP3	18.5	0.7	301.6	54.2	68.0
OP4	237.7JS65	0.8	420.0JS73	213.4	204.2
OP5	123.5JS65	1.9	337.0JS73	58.4	267.7

Table 8b
Hazardous Substance Concentrations in Riparian Control Soils (0-2")
Divide Creek, Little Blackfoot River and Flint Creek
(concentrations in mg/kg)

Sample	As (ppm)	Cd (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
Control Reach 1 Divide Creek					
RR1	10.0JS132	0.7JS148	16.8	19.6JS202	37.1
RR2	17.5JS132	0.8JS148	56.4	22.0JS202	75.9
RR3	19.3JS132	1.0JS148	16.0	23.7JS202	87.1
RR17	19.3JS132	0.5JS148	17.0	17.3JS202	87.1
RR5	23.1JS132	5.8JS148	16.0	40.0JS202	136.0
RR9	76.4JS132	1.1JS148	56.4	34.5JS202	117.6
Control Reach 2 Little Blackfoot					
RR7,13	22.9	0.4	16.8	19.1	100.6
RR7	25.9	0.5	16.8	19.1	135.0
RR8	44.1	0.6	25.1	43.2	117.4
RR9	33.9JS177	0.5	13.8	19.1	169.7
RR10	92.6	1.0	32.4	19.1	151.4JF117
RR11	12.5	0.6	17.0	28.2	87.1
RR18	12.9	0.3	13.8	19.1	62.4JF117
Control Reach 3 Flint Creek					
RR13	9.4	1.2	17.0	20.3	55.2JF117
RR17	92.6	1.4	17.0	139.3	361.0
RR11	112.0	1.7	72.8	176.1	468.0
RR16	36.6	0.6	33.2	19.1	194.4
RR17	51.4	0.6	13.8	66.5	201.3
RR18	145.4JS65	1.4	64.6JS73	139.3	523.8

Table 8c
Hazardous Substance Concentrations in Uplands Impact Soils (0-2")
Stucky Ridge and Smelter Hill
(concentrations in mg/kg)

Sample	As (ppm)	Cd (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
Stucky Ridge					
A1	240.0JS65	7.3	825.6JS73	124.7	217.1
A2	222.7	3.2	662.8	108.3	177.1
A3	381.4	7.3	2856.0	136.6	580.5
A4	386.8JS65	7.3	1024.0JS73	136.6	194.9
A5	624.3	5.0	2136.0JS73	136.6	580.5
A6	285.5	2.9	1179.2	109.6	271.0
A7	142.7	2.6	513.4	68.7	167.4
A8	143.5	4.1	1062.5	82.4	327.7
A9	178.5JS65	2.3	1515.7JS73	71.9	226.7
A10	429.6	4.2	1467.1	152.8	394.4
Smelter Hill					
B1	310.5	7.8	1010.2	156.8	281.5
B2	278.5	7.6	691.5	174.0	205.1
B3	243.8	10.5	1049.9	207.8	497.5
B4	335.1	7.4	404.9	168.8	206.4
B5	183.3	13.5	963.0	235.2	456.5
B6	386.1JS65	16.9	1658.2JS73	303.4	603.8
B7	778.4	19.5	2574.0	336.7	758.9
B9	708.7	12.2	622.0	189.2	264.5
B10	615.5	15.6	845.3	339.6	439.6
B11	658.0	16.1	1162.6	239.9	414.3
B12	496.0	9.3	1408.9	209.6	468.7
B13	660.6	20.4	749.7	309.6	553.0
B14	1846.7	51.2	2436.0	548.8 JI160	1207.0
B16	972.9	39.0	1636.5	438.8	1515.0

Table 8d
Hazardous Substance Concentrations in Upland Impact Soils (0-2")
Mount Haggin
(concentrations in mg/kg)

Sample	As (ppm)	Cd (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
Mount Haggin					
C4	133.6	8.6	196.6	96.3	122.9
C7	317.9	6.3	395.8	142.5JS62	185.4JS29
C3	224.2	8.6	374.8	179.0	379.3
C4	238.5	2.3	678.7	88.2	76.6
C5	178.2JS69	3.4	185.4	94.1	87.8
C6	299.6	3.4	549.0	185.4	236.7
C7	107.6JS69	3.6	185.3	88.2	123.1
C4	237.1	6.7	224.9	180.0JS62	168.8JS29
C4	630.0JS69	10.6	678.7	229.2	318.7
C10	181.6	4.5	261.6	125.7JS62	126.4JS29
C12	215.6	8.6	224.9	90.4	158.6
C12	336.9	12.2	371.5	176.7	304.6
C13	336.9	12.7	519.2	204.4	255.4
C14	247.4	10.8	395.8	179.4	263.1
C15	576.3	13.1	588.6	223.1JS62	340.4JS29

Table 8e
Hazardous Substance Concentrations in Uplands Control Soils (0-2")
Stucky Ridge, Smelter Hill and Mount Haggin
(concentrations in mg/kg)

Sample	As (ppm)	Cd (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
Stucky Ridge Controls					
AA2	59.2	4.3	189.0	112.7JS62	147.5JS29
AA3	82.7JL43	4.0JL49	172.2JL43	81.8JL49	182.6JL43
AA6	82.1	4.3	215.4	101.8	138.7
AA8	59.2	1.9	172.3	52.1	164.6
AA10	119.6	1.9	135.5	60.8	121.0
Smelter Hill Controls					
BB2	88.3	1.9	126.2	52.1	110.8
BB3,15	88.3	4.0	236.5	77.5	176.1
BB5	103.6JF83	1.9	96.4	41.0JS62	80.2JS29
BB7	132.3	3.6	146.8	57.3	162.7
BB9	59.2	1.9	189.0	51.5	176.1
BB11	86.3	4.3	189.0	49.0	160.2
BB13	65.7	1.9	107.9	49.8	104.2
BB16	74.4	2.8	117.8	60.8	125.6
Mount Haggin Controls					
CC3	107.6	4.3	88.0	36.5	96.9
CC3	106.6JF74	5.1JD56	186.6	94.1	165.4
CC5	53.0	2.3	104.7	49.8	110.8
CC7	65.7	4.1	201.5	119.7	176.1
CC9	110.8JS74	1.3	58.6	31.1	78.4
CC12	115.5JS177	1.7JS155	85.1	32.0JS194	93.4
CC14	136.4	2.2	106.6	32.6	124.4

Table 8f
Hazardous Substance Concentrations in Uplands Impact and Control Soils (0-6")
Stucky Ridge, Smelter Hill and Mount Haggin
(concentrations in mg/kg)

Sample	As (ppm)	Cd (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
Stucky Ridge					
A3	188.9	3.2	1029.6	64.7	253.7
A6	184.9	2.2	935.1	70.0	191.4
A10	385.6JL43	4.0JL49	1272.4JL43	130.3JL49	351.2JL43
Smelter Hill					
B3	114.0JS69	3.2	395.4	76.6	240.5
B5	134.2JS69	7.1	542.3	139.4	191.4
B11	578.2JS69	10.0	395.4	190.3	429.8
B13	539.0JL43	16.4JL49	576.4JL43	248.0JL49	477.2JL43
B11	642.5	10.0	972.9	306.3	792.6
Mount Haggin					
C1	93.5	1.4	395.4	51.0	119.9
C7	133.1JF74	2.8JD56	198.5	75.3	103.3
C7	395.4	10.0	395.4	169.7	283.0
C14	188.9	5.5	194.5	70.0	212.9
Smelter Hill Controls					
BB3,15	84.3	2.5	125.5	76.6	128.4
BB13	45.2	1.4	72.0	84.3	83.8
Mount Haggin Controls					
CC3	70.2JS69	1.4	89.4	76.6	792.6
CC5	40.7	0.7	41.6	21.7	68.8

VI. PRECISION, ACCURACY, REPRESENTATIVENESS, COMPLETENESS AND COMPARABILITY

A. Precision

Precision is evaluated by examining replicate samples (field and laboratory replicates). The relative percent difference of replicate samples should be within ± 35 percent. Replicates that fall within this window would demonstrate good sampling and laboratory measurement technique. Replication has been incorporated into both the sampling and analytical ends of this effort. Replication has included 1) the collection of field replicates; and 2) the analysis of laboratory duplicates and splits (two subsamples collected from the same sample). injections of the same sample.

As demonstrated by a review of laboratory data, and as demonstrated by a review of replicate samples (Tables 4 and 7) data are of acceptable precision.

B. Accuracy

Accuracy is assessed by evaluating blanks, spikes, and laboratory control samples. Target limits for accuracy is ± 35 percent. Only a small percentage of samples were qualified for not meeting target limits for accuracy. As demonstrated by a review of laboratory data (Table 8), data are of acceptable accuracy.

C. Representativeness

Representativeness is determined by a number of factors, including site selection criteria, sample collection procedures, sample containers, sample contamination, sample preservation and storage, and holding times for analysis.

Soils data have been deemed to be representative for the following reasons:

- sampling transects were located based on sound, well-reasoned objectives that are described in the Assessment Plan (NRDP, 1992) and the Injury Assessment Report (Lipton, et. al, 1995);
- sample collection procedures (Lipton, et. al., 1995) were designed to accomplish the described objectives, and provided samples representative of the media being sampled;
- samples were preserved and stored following EPA recommendations; and
- no recommended sample holding times were exceeded prior to analysis.

D. Completeness

Completeness is defines as the percentage of measurement data that remain valid after discarding any invalid data due to field or laboratory QC. Data fully meet the $>95\%$ completeness criteria for field and laboratory QC. No samples were rejected due to unacceptable field or laboratory QA/QC.

E. Comparability

Comparability involves the evaluation of data characteristics which may limit use of these data in conjunction with other datasets. For the terrestrial resources injury assessment (Lipton et. al., 1995), the only soils data used were the data collected by the sampling effort reviewed in this QA/QC report. Therefore, it is unnecessary to identify data characteristics of this dataset that limit its use, or data characteristics of other datasets that may limit their use, for this injury assessment.

VII. REFERENCES

Lipton, J., H. Galbraith, and K. LeJeune. 1995. Terrestrial Resources Injury Assessment Report, Clark Fork River Basin NPL Sites. Prepared Natural Resource Damage Litigation Program. January.

NRDP. 1992a. Assessment Plan: Part I. Clark Fork River Basin NPL Sites, Montana. State of Montana, Natural Resource Damage Program. April, 1992.

NRDP. 1992ba. Assessment Plan: Part II. Clark Fork River Basin NPL Sites, Montana. State of Montana, Natural Resource Damage Program. April, 1992.

NRDLP. 1995. Modifications to Assessment Plan, Clark Fork Basin NPL Sites, Montana, Natural Resource Damage Litigation Program. January.

U.S. EPA. 1985. Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses.

Viar & Co. 1988. Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses. Revised.

**QUALITY ASSURANCE/QUALITY CONTROL REPORT
UNIVERSITY OF WYOMING
FISH TOXICOLOGY STUDIES**

QUALITY ASSURANCE/QUALITY CONTROL REPORT

UNIVERSITY OF WYOMING

FISH TOXICOLOGY STUDIES

This report summarizes the evaluation of quality assurance and quality control associated with fish toxicology studies performed by the University of Wyoming for the Clark Fork Basin Natural Resource Damage Assessment. Results of these studies can be found in Aquatic Resources Injury Assessment Report (Lipton et. al., 1995) and accompanying appendices.

Below are summarized the protocols used to review the fish toxicology studies. These studies include pulse studies; behavioral avoidance studies; food chain studies; and adaptation and acclimation studies. The analytes of concern are cadmium, copper, lead and zinc. Data validation followed the QC referenced in the methods and standard operating procedures submitted with the analytical data, and the U.S. EPA Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses (Viar & Co. 1988) as applicable to the methods. These data have been evaluated as Level III data. Quality control and data validation criteria for Level III data are less rigorous than the Contract Laboratory Program (CLP) criteria. The Level III review for these data are appropriate because the matrix being analyzed did not require application of a higher level, or more rigorous, quality control. Data were derived from samples of laboratory prepared water into which standard solutions of known analyte concentrations were spiked in order to achieve target exposure conditions for fish. Consequently, the matrix is not a complex matrix such as an ambient surface water sample, or a soil sample, for which a higher level of quality control might be desirable. Some data were qualified during the data validation process and the potential biases associated with these data have been considered.

As noted above, metals analyzed for these studies were spiked into laboratory prepared water, and as such, were controlled spike samples. Laboratory methods were atomic absorption (AA) analyses per the EPA Methods of Chemical Analysis of Water and Wastes (MCAWW) with modifications as contained in the University of Wyoming Standard Operating Procedures (SOPs). SOPs have been submitted with the analyses and are included in the Administrative Record.

Discussed below are the specific components of the data validation and assessment process as applied to these samples.

INITIAL AND CONTINUING CALIBRATIONS

Raw data and instrument calibration calculation methods were reviewed. Initial calibration for the Perkin-Elmer AA is performed by the instrument in absorbance units which are not reported in the initial raw data print-out. It was verified that all curves are linear per the log books kept by the analyst. The initial calibration consists of a blank, and a three point

curve. Documentation has been provided by the laboratory analyst to clarify the instrument procedures for the time period of the analyses. Instrument manuals and calibration calculations have also been submitted to the reviewer to verify the accuracy of any calibration that is not fully documented in the original raw data. All initial calibrations were determined to be acceptable for most analyses. Several data sets were re-analyzed as required when initial or continuing calibrations were out of control limits. A few data points have been qualified due to continuing calibrations, but the majority of these data were re-analyzed in other sets. The net result is that final reported data are of acceptable quality.

SPIKES

No matrix spikes are reported for some of the studies. Ordinarily the absence of matrix spikes could preclude an evaluation of the accuracy of the analytical method for complex matrices such as ambient streamwater. The matrix for these studies, however, is laboratory water spiked with known concentrations of analytes. Each sample is, therefore, a spike sample, and the sample values are well within the expected range of standard spike preparations. Accuracy can be determined from the laboratory control sample recoveries. This would be analogous to the Quality Control Check sample defined in the MCAWW methods. No qualification is added for lack of the spike samples and accuracy is determined, in these cases, from the laboratory control samples.

CALIBRATION BLANKS

The order of sample sequence defined for the CLP Statement of Work is not applicable to the these samples analyzed by MCAWW methods, and is not applicable to the software sequence programmed into the curve and drift program for the Perkin Elmer AA used for these analyses. The reviewer has considered, in the data evaluation, the intent of calibration blanks, which is to determine whether there is sample-to-sample carryover or contamination, or baseline drift. The reviewer found no evidence of carryover for which re-analysis was not performed, or for which data qualification has not been applied. Two sets contained negative blanks at $> 2 \times \text{IDL}$ (absolute value). For pulse studies 622 and 714, the impact of the qualification for this circumstance is that the negative values reported are possibly falsely depressed. Even with consideration of the impact of the negative blank value, all reported negative values would still be corrected and elevated to a value at or near the undetected limit. One reported positive value could be biased low. Consequently, all negative values are considered to actually be undetected at the instrument detection limit.

DUPLICATE INJECTION RELATIVE STANDARD DEVIATION

Per the CLP criteria for atomic absorption analyses, if the relative standard deviation (RSD) of the duplicate injections is $> 20\%$, the sample is to be rerun. The MCAWW method and the relevant SOPs do not define quality control for duplicate injections. The vast majority of the samples whose RSD was $> 20\%$ are below the method instrument detection limit (IDL) and would be undetected values to which the limits do not apply. In these undetected cases,

the high RSD is merely a reflection of the expected variability around the IDL and the RSD would not be calculable due to undetected values. The NRDP Quality Assurance Project Plan (QAPP) allows for a 25% RSD for duplicate injections. Additionally, all but a few data points are less than the CLP CRDLs (Contract Required Detection Limits) and qualification may technically not be required. The CLP Statement of Work requires reported values to be > CRDL, not the IDL, for the 20% RSD qualification to apply. Consequently, the reviewer has qualified only those samples with values greater than the CRDL.

ANALYTICAL SPIKES

Since analyses were performed by direct aspiration, analytical spikes were not performed. It is not expected that spiked water samples would have matrix interferences. The MCAWW methods do not require analytical spikes, nor analysis by Method of Standard Additions when spike recoveries are out of control limits.

