APPENDIX A

FOURTH QUARTER 2006 DATA VERIFICATION REPORT FOR SAMPLES COLLECTED BY PHELPS DODGE SIERRITA, INC.

FOURTH QUARTER 2006
DATA VERIFICATION REPORT FOR
SAMPLES COLLECTED BY PHELPS DODGE SIERRITA, INC.

Prepared for:

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TABLES

1. INTRODUCTION

This report summarizes the data verification review of groundwater samples collected and analyzed for the fourth quarter 2006 (Q4-2006) by Phelps Dodge Sierrita, Inc. (PDSI) pursuant to Mitigation Order on Consent Docket No. P-50-06. PDSI conducted groundwater sampling and analysis, and provided the results to Hydro Geo Chem (HGC) for preparation of the Q4-2006 groundwater monitoring report (HGC, 2006b). This data verification report focuses on laboratory results for samples collected by PDSI between November 8, 2006 and November 21, 2006 and subsequently analyzed by ACZ Laboratories, Inc. (ACZ). Data verification for samples collected and analyzed by other entities and reported by HGC (HGC, 2006b) is not provided in this report.

Quality assurance/quality control (QA/QC) procedures are specified in the *Quality Assurance Project Plan for Aquifer Characterization Plan* (QAPP) (Appendix E in HGC, 2006a) for field sampling, chain-of-custody (COC) documentation, laboratory analysis, and reporting. Because field sampling procedures were reviewed by PSDI following the provisions of *Quality Assurance/Quality Control Plan for Water Monitoring, Phelps Dodge Sierrita, Inc.* (PDSI, 2005), field sampling is not reviewed in this report. This report does review sample handling and evaluates laboratory QA/QC according to the data quality indicators (DQIs) given in the QAPP.

Appendix E of the main text contains laboratory reports for Q4-2006 samples collected by PDSI, including COC forms, laboratory correspondence, QC summaries, data qualifiers, and any case narratives. The Q4-2006 analytical results for PDSI samples pertain to 40 samples contained in 10 reports having the following ACZ project numbers:

ACZ Project ID	Wells Reported
L59908	MH-10
L59935	MH-13A, MH-13B, MH-13C, MH-30
L59977	PZ-8, MH-28, MH-29
L59979	MH-25A, MH-25B, MH-25C, MH-26A, MH-26B, MH-26C
L60014	IW-1, IW-2, IW-3A, IW-6A, IW-9, IW-10
L60019	IW-14, IW-15, IW-16, IW-17, DUP111506A
L60077	PZ-7
L60082	S-1, S-3, S-4, S-5, S-6, DUP111706A
L60131	IW-11, IW-22
L60150	IW-18, IW-19, IW-20, IW-21, IW-23, DUP112106A

Note:
All samples were filtered in the field using one disposable 0.45-micron filter per sample.

2. SAMPLE HANDLING

All samples collected by PDSI were surrendered by Bill Dorris and shipped to ACZ. COC documentation accompanied all samples submitted to ACZ. The COC documentation included the sample names, the date and time that samples were collected, and the date and time the samples were received by ACZ. All sample bottles were intact, properly preserved, and in good condition upon receipt, although the temperatures of two sample shipping containers exceeded 4 degrees Celsius (°C):

- The shipping container housing MH-10, MH-15W, MH-17, MH-18, MH-21, MH-23, and MH-24 was at 5.2 °C.
- The shipping container housing IW-1, IW-2, IW-3A, IW-6A, IW-9, and IW-10 was at 5.5 °C.

The time between sample collection by PDSI and receipt of samples by ACZ ranged from about 48 hours to four days, with the exception of samples collected during the morning of November 21, 2006 were not received until the afternoon of November 28, 2006. The seven day time for these samples (IW-11 and IW-22) is less than the holding time for all analytes except for total dissolved solids (TDS). Section 3.4 discusses laboratory holding times.

3. LABORATORY QUALITY CONTROL

As specified in the QAPP, laboratory quality control was maintained for all analysis through proper licensure, the use of approved analytical methods, quality control measurements, appropriate turn-around-time for analysis (timeliness), method detection limits (MDLs), and practical quantitation limits (PQLs). Each of these controls is discussed in the following subsections.

The review of laboratory QC included a review to identify any qualified data and an assessment to determine their significance. Additionally, the laboratory QC summaries were reviewed to verify that results met QA criteria.

3.1 Licensure

ACZ is licensed with the Arizona Department of Health Services (license number AZ0102) and is accredited in accordance with the National Environmental Laboratory Accreditation Conference.

3.2 Analytical Methods

All analyses were performed using U.S. Environmental Protection Agency (EPA) analytical methods that meet the target MDL requirements of the QAPP (Section 3.5):

- EPA SM4500 SO4-D (Gravimetric): sulfate
- EPA M200.7 (Inductively Coupled Plasma (ICP)): calcium, magnesium, potassium, sodium
- EPA M325.2 (Colorimetric): chloride
- EPA M353.2 (Automated Cadmium Reduction): nitrate/nitrite
- EPA SM2320B (Titration): alkalinity
- EPA SM4500F-C (Ion-Selective Electrode): fluoride
- EPA M160.1 (Gravimetric): TDS

3.3 Quality Control Measurements

The following routine quality control measures were used during sample analyses:

- Preparation blanks, calibration blanks, and calibration standards
- Analytical/matrix spikes and analytical/matrix spike duplicates
- Laboratory control samples
- Laboratory sample duplicates
- Trip blank samples

3.3.1 Preparation Blanks, Calibration Blanks, and Calibration Standards

Preparation blanks were run with each group of samples submitted for sulfate and TDS analyses. All preparation blanks were prepared from analyte-free water and treated as routine samples. Analyses of the preparation blanks showed that none of the analytes were detected at the indicated MDL.

Results from analyses of initial calibration blanks and initial calibration standards conducted by ICP, colorimetric, automated cadmium reduction, and ion-selective electrode methods were reviewed. Calibration standards and blanks for all analytes were within tolerances given the ACZ quality assurance plan, with the exception that sodium was detected in the calibration blank analyzed with the batch of samples from wells IW-1, IW-2, IW-3A, IW-6, IW-9, and IW-10. However, the concentration of sodium detected in the blank was more than a factor of ten lower than concentrations measured in the PDSI samples indicating the sodium analyses of the PDSI samples should not be significantly affected.

A high bias was noted in the continuing calibration blanks for fluoride in the batch containing samples from wells MH-25A, MH-25B, MH-25C, MH-26A, MH-26B, and MH-26C (ACZ project L59979). The case narrative indicates that these samples were run multiple times to reduce bias.

3.3.2 Analytical/Matrix Spikes and Analytical/Matrix Spike Duplicates

Analyses of spikes and spike duplicate samples conducted by ICP, colorimetric, automated cadmium reduction, and ion-selective electrode methods were reviewed. Analytical spike recoveries that were outside the tolerance criteria specified by the ACZ QA plan are listed in Table A.1. In each of these cases, ACZ qualifiers explained that the laboratory control samples showed acceptable recovery, which indicates acceptable accuracy in terms of the method level QC performed. The relative percent differences (RPDs) between spikes and spike duplicates were below the 20 percent tolerance criteria given by the ACZ QA plan, indicating acceptable precision.

3.3.3 Laboratory Control Samples

Analyses of laboratory control samples conducted by wet chemistry methods were reviewed. Wet chemistry methods include gravimetric and titration methods used for analysis of alkalinity, sulfate, and TDS. Recoveries for all laboratory control samples were between 80 and 120 percent, falling within the acceptable range based on ACZ QA criteria.

3.3.4 Laboratory Duplicate Samples

Laboratory duplicate samples were checked for analyses conducted by colorimetric, automated cadmium reduction, ion-specific electrode, and wet chemistry methods.

The RPDs for most laboratory duplicate samples were within 20 percent, which is the tolerance range set by ACZ. The RPD for nine of the samples submitted exceeded the 20 percent tolerance. In each of these instances, the analyte concentrations were less than ten times the MDL, which is too low for accurate quantification of RPD according to ACZ. In summary, there were no significant exceedances of RPD QA criteria for the laboratory duplicate samples.

Field duplicate samples are discussed in Section 4.1.

3.3.5 Trip Blank Samples

A trip blank sample accompanied each shipment of samples sent to and analyzed by ACZ. These samples were submitted along with the field samples in order to evaluate the potential for contaminant introduction under field conditions. As required by the QAPP, one trip blank was collected for every 20 field samples collected. Neither sulfate nor other major element ions were detected in any of the trip blank samples.

3.4 Timeliness

In most cases, hold times for analyses were met. For sulfate, exceptions were that the hold time for sulfate was exceeded in a confirmatory QC analysis of sulfate in the sample from MH-25A and PZ-7. For other analytes, hold times that were exceeded include the following:

- Total alkalinity in samples from IW-14, IW-15, IW-16, and IW-17
- TDS in the sample from IW-23

The exceedances of hold times are considered minor and are not expected to significantly impact data quality.

3.5 Detection Limits

The range of MDLs and PQLs are shown in Table A.2. The MDLs for analyses generally met the target MDLs in the QAPP. Increases in the MDL were probably due to sample dilutions and are not expected to impact data quality.

4. DATA QUALITY INDICATORS

The QAPP provides several DQIs for assessing the overall quality of the data. These DQIs include the following:

- Precision
- Bias
- Accuracy
- Representativeness
- Comparability
- Completeness
- Sensitivity

Each of these DQIs is discussed below in relation to the Q4-2006 groundwater sampling and analysis conducted by PDSI. Also discussed are two auxiliary DQIs: the cation-anion balance and the TDS ratio.

4.1 Precision

Precision indicates how well a measurement can be reproduced. Precision is quantified by calculating the RPD between duplicate samples. For the purposes of quality control and assurance, precision was quantified by calculating the RPD between duplicate samples among the following groups of samples:

- Laboratory duplicate samples
- Field and field duplicate samples

As discussed in Sections 3.3.2 and 3.3.4, there were no significant exceedances of RPD QA criteria for spike duplicates or laboratory duplicates.

The RPDs for three field duplicate samples from IW-10, IW-18, and S-3 were below the 20 percent acceptance criterion for most analytes. Among 36 individual analyses of analytes, two fluorides, one nitrate, and one chloride RPDs were above the 20 percent acceptance criteria. The RPD values shown in Table A.3 ranged from zero to 41.65 percent. Two of the samples with high RPDs were from the interceptor wellfield area and had relatively high TDS concentrations. One sample was from well S-3 which is characterized by low TDS concentrations. Overall, the high RPDs in these four instances is not expected to have a significant impact on the aquifer characterization, and the overall precision of the data is judged to be sufficient for the purpose of aquifer characterization.

4.2 Bias

Bias is a systematic distortion of measurements causing consistent errors in one direction. Bias is controlled in this data set by the consistent application of standardized sample collection and analysis procedures. As noted in Section 3.3.1, bias in fluoride analyses was noted by ACZ and corrected for by running analyses multiple times to reduce bias.

4.3 Accuracy

Accuracy is a measure of the agreement of a measurement to a known value and is measured using the recoveries from laboratory control samples. As discussed in Sections 3.3.1, 3.3.2, and 3.3.3, there were no significant exceedances of the recovery QA criteria for calibration standards, spikes, and laboratory control standards. Therefore, the overall accuracy of the data is judged to be sufficient for the purposes of aquifer characterization.

4.4 Representativeness

All samples were taken from well locations that were specified in the Work Plan (HGC, 2006a) using sampling procedures in the QAPP. Therefore, the samples are judged to provide a good representation of groundwater quality within the study area defined by the Work Plan. The analytical data are judged to be representative of groundwater conditions in the study area because the analyses used standard procedures and methods that met QA/QC guidelines of the QAPP.

4.5 Comparability

All samples were collected using standardized procedures (HGC, 2006a and PDSI, 2005) and were analyzed by ACZ using standardized methods. Insofar as standardized sample collection and analytical methods have been adhered to, the sample results are comparable.

4.6 Completeness

All samples collected by PDSI were subsequently analyzed and reported by ACZ. All samples collected by PDSI and all analyses conducted by ACZ are judged to satisfy the QA/QC criteria for this project and to be usable for aquifer characterization. Thus, the completeness of results is 100 percent.

4.7 Sensitivity

MDLs were as specified in Table E.2 of the QAPP, with the exception of several samples where MDLs were 5 to 10 times higher than given in the QAPP. The ACZ laboratory report did not document the reason for the several elevated MDLs; however, they were likely due to sample dilution. In all cases, concentrations for sulfate, the major parameter of concern, were greater than 10 times the MDL. Therefore, the analytical sensitivity is considered acceptable.

4.8 Auxiliary Data Quality Indicators

Auxiliary DQIs are indicators that, although not mentioned in the QAPP, are useful for assessing the reliability of the laboratory analyses. These auxiliary DQIs include the laboratory measured cation-anion balance and the ratio between measured and calculated TDS. Each of these auxiliary indicators is discussed below.

4.8.1 Cation-Anion Balance

The concentration (in milliequivalents per liter [meq/L]) of cations and of anions in groundwater should theoretically be approximately the same. Therefore, the balance between anions and cations is one measure of the overall reliability of the laboratory measurements. The cation-anion balance can be expressed as the difference between the milliequivalents of cations and the milliequivalents of anions divided by the sum of the milliequivalents of both cations and anions. When computed in this manner, a cation-anion balance of 5 percent is considered good (Scott Habermahl, ACZ project manager, personal communication). The cation-anion balance was within 5 percent for all samples except the following (Table A.4):

- MH-25A - 27.8 percent
- MH-26A - 5.7 percent
- PZ-7 - 9.1 percent
- MH-13C - 5.1 percent
- MH-30 - 14.7 percent

In general, the cation-anion balance indicates no apparent significant analytical errors. In the case of samples with cation-anion balances greater than 5, the laboratory QC summaries for those samples were checked. There were no obvious QC failures that would account for the elevated cation-anion balances.

4.8.2 TDS Ratio

The ratio between the measured and computed concentration of TDS is also an indicator of the overall quality of the sample analyses. A TDS ratio between 0.8 and 1.2 is considered good (Scott Habermahl, ACZ project manager, personal communication). The TDS ratio, for all samples, was within the acceptance criteria specified by ACZ except the following (Table A.5):

- MH-25A had a ratio 1.60
- MH-26A had a ratio 1.26
- PZ-7 had a ratio of 1.26
- S-3 had a ratio of 1.26

The laboratory QC summaries of samples with high TDS ratios were checked. There were no obvious QC failures that would account for the elevated TDS ratios. Overall, the low TDS ratios indicate no apparent analytical errors.

5. LIMITATIONS

The opinions and recommendations presented in this report are based upon the scope of services and information obtained through the performance of the services, as agreed upon by HGC and the party for whom this report was originally prepared. Results of any investigations, tests, or findings presented in this report apply solely to conditions existing at the time HGC's investigative work was performed and are inherently based on and limited to the available data and the extent of the investigation activities. No representation, warranty, or guarantee, express or implied, is intended or given. HGC makes no representation as to the accuracy or completeness of any information provided by other parties not under contract to HGC to the extent that HGC relied upon that information. This report is expressly for the sole and exclusive use of the party for whom this report was originally prepared and for the particular purpose that it was intended. Reuse of this report, or any portion thereof, for other than its intended purpose, or if modified, or if used by third parties, shall be at the sole risk of the user.

6. REFERENCES

Hydro Geo Chem, Inc (HGC). 2006a. Work Plan to Characterize and Mitigate Sulfate with Respect to Drinking Water Supplies in the Vicinity of the Phelps Dodge Sierrita Tailing Impoundment, Pima County, Arizona. August 11, 2006, revised October 31, 2006.

HGC. 2006b. Groundwater Monitoring Report Fourth Quarter 2006, Tasks 2.2 and 2.3 of Aquifer Characterization Plan. December 29, 2006.

Phelps Dodge Sierrita, Inc. 2005. Quality Assurance/Quality Control Plan for Water Monitoring, Phelps Dodge Sierrita, Inc. June 2005.

TABLES

TABLE A.1
Spike Recoveries Outside of Acceptance Criteria

Parameter	Samples Affected	Recovery (%)	Tolerance		Qualifier[1]	ACZ ID	ACZ Project ID
			Minimum (%)	Maximum (%)			
Chloride	MH-10	122.8	90	110	M1	L59908-01AS	L59908
Nitrate/Nitrite	MH-10	111.9	90	110	M1	L59908-04AS	L59908
Nitrate/Nitrite	MH-13A, MH-13B, MH-13C, MH-30	111.9	90	110	M1	L59908-01AS	L59935
Potassium	MH-13A, MH-13B, MH-13C, MH-30	119.3	85	115	M1	L59908-04AS	L59935
Nitrate/Nitrite	PZ-8, MH-28, MH-29	75.6	90	110	M2	L59977-01AS	L59977
Fluoride	MH-25A, MH-25B, MH-25C, MH-26A, MH-26B MH-26C	118	85	115	M1	L59979-01AS	L59979
Nitrate/Nitrite	MH-25A, MH-25B, MH-25C, MH-26A, MH-26B MH-26C	120.6	90	110	M1	L59903-04AS	L59979
Chloride	IW-1, IW-2, IW-3A, IW-6A, IW-9, IW-10	127.6	90	110	M1	L60014-05AS	L60014
Chloride	S-1, S-3, S-4, S-5, S-6, DUP111706A	120	90	110	M1	L60082-01AS	L60082
Chloride	IW-11, IW-22	112.5	90	110	M1	L60131-01AS	L60131
Calcium	IW-18, IW-19, IW-20, IW-21, IW-23, DUP112106A	80.1	85	115	M3	L59979-01AS	L60150

Notes:

[1] *M1 = Matrix spike recovery was high, the method control sample was acceptable.*
M2 = Matrix spike recovery was low, the method control sample was acceptable.
M3 = The accuracy of the spike recovery does not apply because analyte concentration is disproportionate to the spike level.
The recovery of the method control sample was acceptable.

TABLE A.2
Method Detection Limits (MDLs) and Practical Quantitation Limits (PQLs) Used in Q4-2006 Groundwater Sample Analysis

Analyte	MDL range (mg/L)	PQL range (mg/L)	Target MDL[1] (mg/L)
Sulfate	10 to 100	50 to 500	50 to 500
Calcium	0.2 to 1	2 to 5	2 to 5
Magnesium	0.2 to 1	2 to 5	2 to 5
Potassium	0.3 to 2	1 to 5	1 to 5
Sodium	0.3 to 2	1 to 5	1 to 5
Alkalinity	2	20	20
Chloride	2 to 20	10 to 100	10 to 100
Fluoride	0.1 to 1	0.5 to 5	0.5 to 5
Nitrate/Nitrite	0.02 to 0.06	0.1 to 3	0.1 to 3
TDS	10	50	50

Notes

[1] *Target MDL from Table E.2 of the QAPP*

MDL = Method Detection Limit
PQL = Practical Quantitation Limit
mg/L = milligrams per liter

TABLE A.3
Relative Percent Differences (RPDs) of Duplicate Field Samples Collected by PDSI

	IW-10			**IW-18**			**S-3**		
ACZ Project Number:	**L60014**	**L60019**		**L60150**	**L60131**		**L60082**	**L60082**	
Parameter	**Field Sample (mg/L)**	**Field Duplicate (mg/L)**	**RPD (%)**	**Field Sample (mg/L)**	**Field Duplicate (mg/L)**	**RPD (%)**	**Field Sample (mg/L)**	**Field Duplicate (mg/L)**	**RPD (%)**
Calcium	515	540	4.74	530	524	1.14	46	45.5	1.09
Magnesium	95.4	98	2.69	112	112	0.00	4.8	4.7	2.11
Potassium	10.6	11.6	9.01	7.5	7.3	2.70	2.8	2.8	0.00
Sodium	155	168	8.05	107	108	0.93	51.9	51.6	0.58
Total alkalinity	158	158	0.00	129	127	1.56	151	151	0.00
Chloride	154	151	1.97	132	95	32.60	12	15	22.22
Fluoride	0.3	0.2	40.00	0.3	0.3	0.00	0.6	0.6	0.00
Nitrate/nitrite	0.9	0.94	0.00	1.92	2.93	41.65	1.31	1.39	5.93
TDS	2960	2920	4.35	2800	2790	0.36	340	320	6.06
Sulfate	1650	1650	1.36	1610	1620	0.62	60	60	0.00
TDS calculated	2680	2710	1.11	2580	2540	1.56	269	271	0.74
TDS (ratio measured/calculated)	1.1	1.08	1.83	1.09	1.1	0.91	1.26	1.18	6.56

Notes:

mg/L= milligrams per liter
RPD= Relative Percent Difference

TABLE A.4
Cation - Anion Balance

Sample	Cation-Anion Balance (%)	Anions (meq/L)	Cations (meq/L)
IW-1	1	14.7	15
IW-10	-1.7	42.1	40.7
IW-11	3	39.3	41.7
IW-14	-1.6	44.5	43.1
IW-15	-1.3	42.8	41.7
IW-16	-1.5	43.7	42.4
IW-17	0.6	39.2	39.7
IW-18	0.6	40.1	40.6
IW-19	-0.1	39.1	39
IW-2	4.3	5.6	6.1
IW-20	1.4	38.4	39.5
IW-21	1.3	39.4	40.4
IW-22	-1.1	42.3	41.4
IW-23	3.3	39.5	42.2
IW-3A	-0.1	39.5	39.4
IW-4	-3.6	38.6	35.9
IW-5	-2.6	42	39.9
IW-6a	-1.1	42.7	41.8
IW-9	-2.1	43	41.2
MH-10	0.7	33.6	34.1
MH-11	-1.7	38.9	37.6
MH-12	2	28.9	30.1
MH-13A	1.2	42.4	43.4
MH-13B	1.2	29.1	29.8
MH-13C	5.1	4.7	5.2
MH-25A	-27.8	6.9	3.9
MH-25B	-0.6	40.3	39.8
MH-25C	-0.5	32.4	32.1
MH-26A	5.7	3.3	3.7
MH-26B	-0.1	38.2	38.1
MH-26C	0.8	19.3	19.6
MH-28	0.1	44.7	44.8
MH-29	-0.4	41.3	41
MH-30	-14.7	41.7	31
PZ-7	9.1	10	12
PZ-8	-2.1	14.6	14
S-1	2.9	5.1	5.4
S-3	4.2	4.6	5
S-4	3	4.8	5.1
S-5	4.5	5.3	5.8
S-6	4.5	6.4	7

Note:

meq/L = milliequivalents/liter

TABLE A.5
TOTAL DISOLVED SOLIDS (TDS) RATIO

Sample	TDS Measured (mg/L)	TDS Calculated (mg/L)	TDS Ratio
IW-1	1010	919	1.10
IW-10	2960	2680	1.10
IW-2	380	330	1.15
IW-3A	2770	2530	1.09
IW-4	2770	2430	1.14
IW-5	2980	2640	1.13
IW-6a	3050	2770	1.10
IW-9	2960	2750	1.08
MH-10	2350	2160	1.09
MH-11	2720	2480	1.10
MH-12	1970	1870	1.05
MH-13A	2970	2750	1.08
MH-13B	2030	1880	1.08
MH-13C	310	300	1.03
MH-25A	560	350	1.60
MH-25B	2770	2580	1.07
MH-25C	1300	1290	1.07
MH-26A	230	182	1.26
MH-26B	2620	2450	1.07
MH-26C	1300	1240	1.05
PZ-7	800	633	1.26
IW-14	3010	2840	1.06
IW-15	2920	2730	1.07
IW-16	2970	2760	1.08
IW-17	2770	2520	1.10
IW-11	2890	2590	1.12
IW-22	2950	2720	1.08
IW-18	2800	2580	1.09
IW-19	2700	2490	1.08
IW-20	2730	2480	1.10
IW-21	2760	2540	1.09
IW-23	2880	2580	1.12
PZ-8	920	890	1.03
MH-28	3220	2910	1.11
MH-29	2880	2650	1.09
S-1	350	299	1.17
S-3	340	269	1.26
S-4	320	280	1.14
S-5	360	312	1.15
S-6	440	374	1.18

Note

mg/L = miligrams/liter
TDS = Total Dissoved Solids

APPENDIX B

FIRST QUARTER 2007 DATA VERIFICATION REPORT FOR SAMPLES COLLECTED BY HYDRO GEO CHEM, INC.

FIRST QUARTER 2007
DATA VERIFICATION REPORT FOR SAMPLES COLLECTED BY HYDRO GEO CHEM, INC.

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March 30, 2007

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TABLES

1. INTRODUCTION

This report summarizes the data verification review of groundwater samples collected and analyzed for the first quarter 2007 (Q1-2007) by Hydro Geo Chem, Inc. (HGC) pursuant to Mitigation Order on Consent Docket No. P-50-06. This data verification report focuses on samples collected by HGC between January 2, 2007 and February 27, 2007 and subsequently analyzed by ACZ Laboratories, Inc. (ACZ). The samples collected by HGC were obtained from private wells outside the control of PDSI as described in the project Work Plan (HGC, 2006).

Quality assurance (QA) and quality control (QC) procedures are specified in the *Quality Assurance Project Plan for Aquifer Characterization Plan* (QAPP) (Appendix E of HGC, 2006) for field sampling, chain-of-custody (COC) documentation, laboratory analysis, and reporting. This report reviews field sampling, and sample handling, and evaluates laboratory QA/QC according to the data quality indicators (DQIs) given in the QAPP.

Appendix E of the main text of this report contains laboratory reports for the Q1-2007 samples collected by HGC, including COC forms, laboratory correspondence, QC summaries, qualifier reports, and any case narratives. The Q1-2007 analytical results for HGC samples pertain to 49 (filtered and unfiltered) samples contained in 18 reports having the following ACZ project numbers:

ACZ Project ID	Sample Treatment	Wells Reported
L60567	F	GW-640358
L60584	U	GW-640358
L60568	F	ESP-1, ESP-2, ESP-3, CW-7, CW-9, CW-6, GW-DUP-010307
L60585	U	ESP-1, ESP-2, ESP-3, CW-7, CW-9, CW-6, GW-DUP-010307
L60625	F, U	GW-639055, GW-634037, GW-206214,
L60647	F	GV-1- 603428, GV-2-603429, SIWELL-208825, CANOARANCH-586729
L60648	U	GV-1- 603428, GV-2-603429, SIWELL-208825, CANOARANCH-586729
L60671	F, U	ST-5-608531, ST-6-608530, ST-7-566940
L60693	F, U	GW-627429, GW-529142, GW-599357
L60731	F, U	GW-501760
L60766	F, U	GW-634036
L60780	F, U	GW-509604
L60852	F, U	CW-8, CW-10, GW-577707
L60869	F, U	GW-550533
L60876	F, U	GW-540451
L60994	F, U	GW-515867, GW-532595
L61121	F, U	GW-635386
L61280	F, U	GW-608521, GW-608597, DUP022707A, DUP022707B, EQ022707A, EQ022707B

Note:
F =field filtered sample (0.45 micron filter)
U = unfiltered sample

2. FIELD OPERATIONS

Most of the samples collected by HGC were collected and surrendered by Kimberly Garcia, HGC QA Manager, or Mark Arneson, HGC Environmental Field Technician. Field operations for this project included:

- Field investigations to determine well locations, possible alternates, and to discuss the groundwater monitoring project with private well owners and water companies in order to get their approval for well access on either a quarterly or semi-annual basis;
- Measuring static water levels at all private wells and water companies not under the control of PDSI or TBPI, which included drilling water-level access ports and installing plugs at three private wells;
- Collection of groundwater samples for water quality analysis, which included well purging, field-filtering samples for dissolved constituent analysis, and collecting an unfiltered sample for sulfate.

All documentation relating to the groundwater samples and water level measurements collected for this monitoring program was maintained for each day of field activities in a dedicated field notebook; specific information regarding purge volume calculations and water level measurements were maintained daily using HGC groundwater sampling forms (Appendix E).

2.1 Field Investigations

Initial field investigations were conducted to evaluate the well's potential for inclusion in the groundwater monitoring program and the potential for obtaining water level measurements from the well. All field investigations were performed under the direction of HGC's QA Manager. Alternate wells for inclusion in the groundwater monitoring program were also evaluated for accessibility and the potential for obtaining water level measurements from the well. All wells that were evaluated for inclusion in this groundwater monitoring program are shown in Table 1. All documentation of field activities was reviewed for quality assurance and meets the documentation requirements stated in the QAPP.

2.2 Water Level Monitoring

Static water level measurements were attempted at each well that was sampled for water quality and at all wells where only water level monitoring was specified in the Work Plan. In all cases, water levels were measured while the well pump was off, although it was not always possible to ascertain from the well owner how long the pump had been off.

In three of the private wells, there was no water level access port present for collecting water level measurements. In each of these cases, an access port and plug was installed using a ½” drill with the well owner’s permission.

2.3 Groundwater Sampling

Groundwater samples were collected from wells designated for sampling in the quarterly and semi-annual monitoring schedule of the Work Plan. More detailed information regarding the wells sampled for water quality and water level measurements is listed in Table 1.

2.3.1 Pre-Sampling Field Activities

Pre-sampling activities relating to QA/QC requirements of this project are:

- Electrical conductivity and pH meter calibration and calibration verification;
- Stock supplies of decontamination equipment and proper sample storage and transport supplies;
- Water level indicator accuracy and battery check;
- Water level measurement under static conditions.

Field documentation and verbal correspondence with staff indicate good calibration and decontamination practices. Field instruments were calibrated at the beginning of each day of sampling, and each day that sampling extended for more than half of the day, a mid-day calibration check was performed to ensure that the instrument was reading accurately. The field instruments were also decontaminated with de-ionized water after each sample was collected along with the decontamination of other field filtering equipment. Laboratory grade de-ionized water was purchased for the purposes of decontamination on an as-needed basis, and ice was purchased each day of sampling for the purposes of packing and shipping the samples for analysis.

Prior to measuring the water level at each well, the battery on the water level indicator was checked and the sensitivity of the indicator was adjusted if necessary. Water level measurements were verified by measuring the depths to water multiple times in order to obtain an accurate reading.

2.3.2 Well Purging, Field Measurements, and Sample Collection

Ideally, three wetted casing volumes were purged from each well prior to sampling. However, it was not always possible to do so in some cases due to well owners' objections regarding discharge to the surface. When three casing volumes could not be purged, this condition was noted in the field notebook and on groundwater sampling forms (Appendix E).

Field measurements were collected at varying intervals during well purging at each well where a water quality sample was collected. Field parameters were monitored until a consistent measurement was obtained every time a water quality sample was collected. In every case where the purge volume was less than three casing volumes, the field parameters (pH, Electrical conductivity, and temperature in degrees Celsius (°C) had become stable prior to collecting groundwater samples.

Groundwater sampling consisted of the collection of a filtered sample for the analysis of the major element ions (calcium, magnesium, sodium, potassium, sulfate, chloride, nitrate, nitrite, and fluoride) and for alkalinity and total dissolved solids (TDS). An unfiltered sample for the analysis of sulfate was also collected. All bottles were provided by ACZ. Bottles were checked for the correct preservative and maintained in a clean, and secure work area, until used in the field.

2.3.3 Post-Sampling Field Activities

Post-sampling field activities consisted of equipment decontamination, sample storage, and sample shipping. Each piece of equipment that comes into contact with the sample was decontaminated using a small amount of Alconox detergent and de-ionized water. A thorough rinse of the equipment with de-ionized water protected against inadvertent contamination. Field documentation included in the field notebook indicated consistent adherence to this requirement.

Samples were shipped using a secure double bag method. Samples were shipped three to a bag and tied shut to prevent any contamination from melted ice. Samples and the ice were then bagged within the cooler to prevent the coolers from leaking any melted ice water during shipping.

2.4 Well Survey

A ground surface and measuring-point elevation survey was conducted for wells from which depth-to-water measurements were made. An independent surveyor surveyed wells that did not have any elevation survey data associated with them. The data generated from this elevation survey are used to provide accurate regional groundwater elevations for the Green Valley area. These data are shown in Table 3 and Figure 2 of the main text. Section 3.2 of the main text discusses this in more detail.

3. SAMPLE HANDLING

Most of the samples collected by HGC were sampled and surrendured by Kimberly Garcia, HGC QA Manager, and shipped to ACZ Laboratories for analysis. Mark Arneson, HGC Environmental Field Technician, surrendered samples collected on January 25 and February 15 of 2007. COC documentation accompanied all samples submitted to ACZ, and included the sample names, the date and time that samples were collected, and the date and time the samples were received by ACZ. All sample bottles were intact, properly preserved, and in good condition upon receipt, although the temperatures of six sample shipping containers exceeded 4 ° C:

- Sample shipping container housing GW-640358 was at 5.5 ° C
- Sample shipping container housing ESP-1, ESP-2, ESP-3, CW-7, CW-9, CW-6, and GW-DUP was at 5.2 ° C
- Sample shipping container housing for samples received on 1/4/2007 was at 5.3 ° C
- Sample shipping container housing for samples received on 1/9/2007 was at 5 ° C
- Sample shipping container housing for samples received on 1/10/2007 was at 5.1 ° C
- Sample shipping container housing for samples received on 1/25/2007 was at 5.5 ° C

The time between sample collection by HGC and receipt of samples by ACZ was about 24 hours, with the exception of samples collected on January 2, and January 23, 2007. These samples were received by ACZ approximately 42 and 43 hours, respectively, after samples were collected. This delay was due in part to collecting a sample from a private well owner late in the day to accommodate their work schedule. These samples were received by the lab with less than half of the holding time remaining for the analysis of nitrate and nitrite; thus, the analysis performed for these analytes exceeded the holding time and was flagged as such in the analytical reports submitted by ACZ. Section 4.4 discusses this and the laboratory holding times in more detail.

4. LABORATORY QUALITY CONTROL

As specified in the QAPP, laboratory quality control was maintained for all analysis through proper licensure; the use of approved analytical methods, quality control measurements, appropriate turn-around-time for analysis (timeliness), method detection limits (MDLs), and practical quantitation limits (PQLs). Each of these controls is discussed in the following subsections.

The review of laboratory QC included a review to identify any qualified data and an assessment to determine their significance. Additionally, the laboratory QC summaries were reviewed to verify that results met QA criteria.

4.1 Licensure

ACZ is licensed with the Arizona Department of Health Services (license number AZ0102) and is accredited in accordance with the National Environmental Laboratory Accreditation Conference.

4.2 Analytical Methods

All analyses were performed using US Environmental Protection Agency (EPA) analytical methods that meet the target MDL requirements of the QAPP (Section 4.5):

- EPA 300.0 [Ion-Chromatography]: sulfate, chloride, fluoride
- EPA M200.7 [Inductively Coupled Plasma (ICP)]: calcium, magnesium, potassium, sodium
- EPA M353.2 [Automated Cadmium Reduction]: nitrate/nitrite
- EPA SM2320B [Titration]: alkalinity
- EPA M160.1 [Gravimetric]: TDS

Two of these methods, ion chromatography and ICP, involve direct injection of the sample into the analytical instrument. The other methods listed are classical wet chemistry techniques that require the use of preparation blanks under the ACZ quality assurance plan and the QAPP.

4.3 Quality Control Measurements

The following routine quality control measures were used during sample analyses:

- Preparation blanks, calibration blanks, and calibration standards
- Analytical/matrix spikes and analytical/matrix spike duplicates
- Laboratory control samples
- Laboratory sample duplicates
- Trip blank samples

4.3.1 Preparation Blanks, Calibration Blanks, and Calibration Standards

Preparation blanks were run with each group of samples submitted for for sulfate and TDS analyses. All preparation blanks were prepared from analyte-free water and treated as routine samples. Results of the analyses of the blanks showed that the target analytes were not detected at the indicated MDL.

Results from the analyses of the initial calibration blanks and initial calibration standards conducted by ICP and ion chromatography methods were reviewed. For all the analytes, calibration standards and blanks fall within the acceptance criteria specified in the ACZ quality assurance plan and the QAPP.

4.3.2 Analytical/Matrix Spikes and Analytical/Matrix Spike Duplicates

Analyses of spikes and spike duplicate samples conducted by ICP, ion chromatography, and automated cadmium reduction methods were reviewed. Instances in which analytical spikes had recoveries outside the acceptance criteria specified by the ACZ QA plan are listed in Table B.1. In each of these cases the laboratory control samples showed acceptable recovery, which indicates acceptable accuracy in terms of the method level QC performed. The relative percent differences (RPDs) between analytical spikes and analytical spike duplicates were below the 20 percent tolerance criteria set by the ACZ QA plan for all the spike duplicates analyzed. This indicates acceptable precision for the purpose of aquifer characterization.

4.3.3 Laboratory Control Samples

Analysis of laboratory control samples conducted by wet chemistry methods were reviewed. Wet chemistry methods include titration and gravimetric methods used for analysis of alkalinity, and TDS. Recoveries for all laboratory control samples were between 80 and 120 percent, falling within the acceptable range specified by ACZ QA criteria.

4.3.4 Laboratory Duplicate Samples

Analyses of laboratory duplicate samples conducted by ion chromatography, automated cadmium reduction, and wet chemistry (e.g., alkalinity and TDS) methods were reviewed. The RPDs for all laboratory duplicate samples were less than or equal to 20 percent, within the acceptance criteria set by ACZ. In some cases the RPD values calculated by ACZ were not used for data validation when the analyte concentration was too low for accurate evaluation. In these cases when the RPD was not used for laboratory data validation, the analytical data are qualified with an “RA”, which indicates that the concentration of the duplicate sample was less than ten times the MDL. Field duplicate samples are discussed in Section 5.1.

4.3.5 Trip Blank Samples

Two trip blanks accompanied the samples shipped to ACZ for the analytes of interest. These samples were collected in the field using de-ionized water. These samples were submitted along with other samples to evaluate the potential for contaminant introduction under field conditions. As required in Section 4.2.1.5 of the QAPP, one trip blank sample was collected for every 20 samples collected. Neither of the two trip blank samples submitted showed any detections.

4.4 Timeliness

The majority of samples submitted to the lab for analyses were analyzed within their appropriate holding time. Exceptions to this occurred for the following analyses: nitrate/nitrite, TDS, and alkalinity. Nitrate/nitrite as N and nitrite holding times were exceeded for samples collected on January 2, 2007 (GW-640358-010207), January 24 (CW-8, CW-10 and 577707), and January 25, 2007 (GW-550533 and GW-540451). ACZ explained that the analysis for nitrate/nitrite as N and nitrite were performed past the holding time because the samples collected on January 2 were received with less than half of the holding time remaining. Samples for analysis of alkalinity and TDS sampled on January 24 and 25 were received on January 26 with more than half of the holding time remaining, but required re-analysis that was performed beyond the holding time. This delay was due to a QC failure during the initial analysis. The TDS analysis for samples GW-550533 and GW-540451 met the initial holding times for the samples, but exceeded the holding time for the re-analysis needed due to a QC failure. Similarly, the holding time exceedance for alkalinity on sample GW-540451, collected on January 25, 2007, was also due to a QC re-analysis that was performed beyond holding time. Since these exceedances do not significantly effect the quality of data reported, all data with a holding time exceedance were accepted as useable for the purpose of aquifer characterization.

4.5 Detection Limits

The MDLs and PQLs of the analytical methods used by ACZ are shown in the Table B.2. The MDLs for analyses of samples collected by HGC for Q1-2007 were equal to or less than the target MDLs identified in the QAPP.

5. DATA QUALITY INDICATORS

The QAPP provides several DQIs for assessing the overall quality of the data. These DQIs include the following:

- Precision
- Bias
- Accuracy
- Representativeness
- Comparability
- Completeness
- Sensitivity

Each of the DQIs are discussed below in relation to the Q1-2007 groundwater sampling and analysis conducted by HGC. Also discussed are two auxiliary DQIs: the cation-anion balance and the TDS ratio.

5.1 Precision

Precision indicates how well a measurement can be reproduced. Precision is quantified by calculating the RPD between duplicate samples. For the purposes of quality control and quality assurance, precision was quantified by calculating the RPD between duplicate samples among the following groups of samples:

- Laboratory duplicate samples
- Field and field duplicates samples

As discussed in Section 4.3.2 and 4.3.4, no significant exceedances of RPD QA criteria occurred for spike duplicates or laboratory duplicates.

Field and laboratory COC documentation show results for three field duplicate samples (GW-DUP010307A, DUP022707A, and DUP022707B) and two equipment blank samples (EQ022707A and EQ022707B). The RPDs between the field duplicates showed that all the RPDs met the DQI of 20% or less (Table B.3). The fluoride, nitrite, and magnesium concentrations of one of the field duplicate samples were too low for accurate evaluation. Thus, these RPDs were not used for data verification. Overall, DQI for precision is deemed to be met for all analytes. Additionally, the 5 percent goal of collecting one duplicate sample for every 20 samples, as stated in Section 4.2.1.5 of the QAPP, was exceeded by one percent with the collection of three duplicate samples.

5.2 Bias

Bias is a systematic distortion of measurement causing consistent errors in one direction. Bias was managed in this data set by the consistent application of standardized sample collection and analysis procedures.

5.3 Accuracy

Accuracy is a measure of the agreement of a measurement to a known value and is measured using the recoveries from laboratory control standards. As discussed in Sections 4.3.1, 4.3.2, and 4.3.3, no significant exceedances of the recovery QA criteria occurred for calibration standards, spikes, and laboratory control samples. Based on this information, the overall analytical accuracy is judged to be sufficient for the purposes of aquifer characterization.

5.4 Representativeness

All samples were taken from well locations that were specified in the Work Plan (HGC, 2006) using sampling procedures that were specified in the QAPP. Therefore, the samples are judged to provide a good representation of groundwater quality within the study area defined by the Work Plan. The analytical data are judged to be representative of groundwater conditions in the study area because all analyses were performed using standard procedures and methods that met QA/QC guidelines of the QAPP.

5.5 Comparability

All samples were collected using standardized procedures (HGC, 2006) and analyzed by ACZ using standardized methods. Insofar as standardized sample collection and analysis methods have been adhered to, the sample results are comparable.

5.6 Completeness

All samples collected by HGC were subsequently analyzed and reported by ACZ. All samples collected by HGC and analyses conducted by ACZ are judged to satisfy the QA/QC criteria for this project and to be usable for aquifer characterization. Thus, the completeness of analytical results is 100%.

5.7 Sensitivity

The analytical methods used to analyze samples included in this report met the target MDLs specified in Table E.2 of the QAPP. Therefore, the analytical sensitivity is considered acceptable.

5.8 Auxiliary Data Quality Indicators

Auxiliary DQIs are indicators that, although not mentioned in the QAPP, are useful for assessing the reliability of the laboratory analyses. These auxiliary DQIs include the laboratory measured cation-anion balance and the ratio between measured and calculated TDS. Each of these auxiliary indicators is discussed below.

5.8.1 Cation-Anion Balance

The concentration (in milliequivalents per liter [meq/L]) of cations and of anions in groundwater should theoretically be approximately the same. Therefore, the balance between anions and cations is one measure of the overall quality of the laboratory measurements. The cation-anion balance can be expressed as the difference between the milliequivalents of cations and the milliequivalents of anions divided by the sum of the milliequivalents of both cations and anions. When computed in this manner, a cation-anion balance of 5 percent is considered good (Scott Habermahl, ACZ project manager, personal communication). The cation-anion balance was below 5 percent for all samples (Table B.4). Overall, the cation-anion balance for all samples does not indicate any analytical errors.

5.8.2 TDS Ratio

The ratio between the measured and computed concentration of TDS is also an indicator of the overall quality of the sample analyses. A TDS ratio between 0.8 and 1.2 is considered good (Scott Habermahl, ACZ project manager, personal communication). The ratios for all samples fall inside the acceptance criteria specified by ACZ except the sample collected from ESP-2 on January 3, 2007 (Table B.5), which is just outside of the acceptance criteria at 0.78. Overall, the low TDS ratios for all samples indicate no apparent analytical errors.

6. LIMITATIONS

The opinions and recommendations presented in this report are based upon the scope of services and information obtained through the performance of the services, as agreed upon by HGC and the party for whom this report was originally prepared. Results of any investigations, tests, or findings presented in this report apply solely to conditions existing at the time HGC's investigative work was performed and are inherently based on and limited to the available data and the extent of the investigation activities. No representation, warranty, or guarantee, express or implied, is intended or given. HGC makes no representation as to the accuracy or completeness of any information provided by other parties not under contract to HGC to the extent that HGC relied upon that information. This report is expressly for the sole and exclusive use of the party for whom this report was originally prepared and for the particular purpose that it was intended. Reuse of this report, or any portion thereof, for other than its intended purpose, or if modified, or if used by third parties, shall be at the sole risk of the user.

7. REFERENCES

Hydro Geo Chem, Inc (HGC). 2006. Work Plan to Characterize and Mitigate Sulfate with Respect to Drinking Water Supplies in the Vicinity of the Phelps Dodge Sierrita Tailing Impoundment, Pima County, Arizona. August 11, 2006, revised October 31, 2006.

Phelps Dodge Sierrita, Inc. 2005. Quality Assurance/Quality Control Plan for Water Monitoring, Phelps Dodge Sierrita, Inc. June, 2005.

TABLES

TABLE B.1
Analytical Spike Recoveries Outside of Acceptance Criteria

Parameter	Samples affected	Recovery (%)	Tolerance		ACZ Qualifier[1]	ACZ ID	ACZ Project ID
			Minimum (%)	Maximum (%)			
Potassium	GW-639055, GW-634037, GW-206214	128.6	85	115	M1	L60624-01AS	L60625
Potassium	GW-639055, GW-634037, GW-206214	123.7	85	115	M1	L60624-01ASD	L60625
Sodium	GW-639055, GW-634037, GW-206214	121.1	85	115	M1	L60624-01 AS	L60625
Sodium	GW-639055, GW-634037, GW-206214	116.1	85	115	M1	L60624-01 ASD	L60625
Nitrate/nitrite	GV-1- 603428, GV-2-603429, SIWELL-208825, CANOARANCH-586729	77.6	90	110	M2	L60636-01AS	L60647
Nitrite	GV-1- 603428, GV-2-603429, SIWELL-208825, CANOARANCH-586729	88.3	90	110	M2	L60636-01AS	L60647
Potassium	GV-1- 603428, GV-2-603429, SIWELL-208825, CANOARANCH-586729	124.1	85	115	M1	L60629-02 AS	L60647
Potassium	GV-1- 603428, GV-2-603429, SIWELL-208825, CANOARANCH-586729	123.3	85	115	M1	L60629-02 ASD	L60647
Sodium	GV-1- 603428, GV-2-603429, SIWELL-208825, CANOARANCH-586729	146.7	85	115	M3	L60629-02 AS	L60647
Calcium	GW-627429, GW-529142, GW-599357	70	85	115	M3	L60685-04AS	L60693
Calcium	GW-627429, GW-529142, GW-599357	74.7	85	115	M3	L60685-04ASD	L60693
Potassium	GW-627429, GW-529142, GW-599357	119.8	85	115	M1	L60685-04AS	L60693
Potassium	GW-627429, GW-529142, GW-599357	121.2	85	115	M2	L60685-04ASD	L60693
Sodium	GW-627429, GW-529142, GW-599357	82.4	85	115	M3	L60685-04AS	L60693
Potassium	GW-634036	118.1	85	115	M1	L60749-01AS	L60766
Potassium	GW-634036	121.4	85	115	M1	L60749-01ASD	L60766
Sodium	GW-634036	120.9	85	115	MA	L60749-01ASD	L60766
Calcium	GW-509604	61.9	85	115	M3	L60776-03AS	L60780
Calcium	GW-509604	62.7	85	115	M3	L60776-03ASD	L60780
Calcium	CW-8, CW-10, GW-577707	58.9	85	115	M3	L60846-05AS	L60852
Calcium	CW-8, CW-10, GW-577707	54.5	85	115	M3	L60846-05ASD	L60852
Sulfate	CW-8, CW-10, GW-577707	83.7	90	110	M2	L6083301AS	L60852
Calcium	GW-515867, GW-532595,	79	85	115	M3	L60992-10AS	L60994
Calcium	GW-515867, GW-532595,	71.6	85	115	M3	L60992-10ASD	L60994
Magnesium	GW-515867, GW-532595,	82.9	85	115	M3	L60992-10ASD	L60994
Sulfate	GW-515867, GW-532595,	84.5	90	110	M2	L60992-07AS	L60994
Potassium	GW-608521, GW-608597, DUP022707A, DUP022707B, EQ022707A, EQ022707B	116.7	85	115	M1	L61274-03AS	L61280
Potassium	GW-608521, GW-608597, DUP022707A, DUP022707B, EQ022707A, EQ022707B	118.6	85	115	M1	L61274-03ASD	L61280

Notes: *M1 = Matrix spike recovery was high, the method control sample was acceptable*
M2 = Matrix spike recovery was low, the method control sample was acceptable
M3 = The accuracy of the spike recovery does not apply because analyte concentration is disproportionate to the spike level. The recovery of the method control sample was acceptable
MA = Recovery for either the spike or the spike duplicate was outside acceptable limits; The RPD was within acceptable limits

TABLE B.2
Method Detection Limits (MDL) and Practical Quantitation Limits (PQL)

Parameter	MDL (mg/L)	PQL (mg/L)	TARGET MDL[1] (mg/L)
Sulfate	0.5	3	10
Calcium	0.2	1	0.2
Magnesium	0.2	1	0.2
Potassium	0.3	2	0.3
Sodium	0.3	2	0.3
Alkalinity	2	20	2
Chloride	0.5	3	1
Fluoride	0.1	0.5	0.1
Nitrate/Nitrite	0.02	0.1	0.02
TDS	10	20	10

Notes:

[1] *Target MDL from Table E.2 of QAPP*
mg/L = milligrams per liter
TDS = Total Dissolved Solids

TABLE B.3
Relative Percent Difference (RPD) of Duplicate Field Samples

	CW-6			GW-608521			GW-608597		
ACZ Project Number:	**L60568 (F) L60585 (U)**	**L60568 (F) L60585 (U)**		**L61280**	**L61280**		**L61280**	**L61280**	
Parameter	**Field sample (mg/L)**	**Duplicate (mg/L)**	**RPD (%)**	**Field sample (mg/L)**	**Duplicate (mg/L)**	**RPD (%)**	**Field sample (mg/L)**	**Duplicate (mg/L)**	**RPD (%)**
Calcium	42.9	43	0.233	20	20.1	0.499	48.2	48.3	0.207
Magnesium	4.8	4.9	2.062	0.5	0.4	*	6.4	6.5	1.550
Potassium	2.8	2.8	0	2.2	2.2	0	2.2	1.9	14.634
Sodium	37.3	37.3	0	n/a	n/a		n/a	n/a	
Total alkalinity	134	135	0.743	90	88	2.247	132	131	0.760
Cation - Anion balance	0	0	0	n/a	n/a		n/a	n/a	
Sum of anions	4.2	4.2	0	n/a	n/a		n/a	n/a	
Sum of cations	4.2	4.2	0	n/a	n/a		n/a	n/a	
Chloride	11.8	11.9	0.844	12.4	12.2	1.626	8.9	8.9	0
Fluoride	0.6	0.6	*	n/a	n/a		n/a	n/a	
Nitrate	1.8	1.87	3.815	n/a	n/a		n/a	n/a	
Nitrate/nitrite	1.82	1.88	3.243	n/a	n/a		n/a	n/a	
Nitrite	0.02	0.01	*	n/a	n/a		n/a	n/a	
TDS	260	250	3.922	390	380	2.597	270	260	3.774
Sulfate (filtered sample)	49.2	49.5	0.608	173	174	0.576	56.9	56.9	0
Sulfate (unfiltered sample)	49.2	49.8	1.212	173	174	0.576	56.7	56.9	0.35211
TDS calculated	238	239	0.419	n/a	n/a		n/a	n/a	
TDS (ratio measured/calculated)	1.09	1.05	3.738	n/a	n/a		n/a	n/a	

Notes: **RPD was not used for data validation because the sample concentration is too low for accurate evaluation (<10x MDL)*

n/a the owner of this property did not permit this analyte to be tested

F= Filtered Sample

U=Unfiltered Sample

TABLE B.4
Cation-Anion Balance

Sample ID	Anions (meq/L)	Cations (meq/L)	Percent Balance
GW-640358	3.8	3.9	1.3
ESP-3	3.7	3.9	2.6
ESP-2	3.7	3.8	1.3
ESP-1	8.7	9.2	2.8
CW-7	21	21.4	0.9
CW-9	4	3.9	-1.3
CW-6	4.2	4.2	0
GW-DUP010307	4.2	4.2	0
GW-639055	4.1	4.1	0
GW-634037	2.8	2.8	0
GW-206214	4.1	4.2	1.2
GV-603428	4.4	4.3	-1.1
GV-2-603429	6.8	6.5	-2.3
SIWELL-208825	3.9	3.7	-2.6
CANOARANCH-586729	6.6	6.1	-3.9
ST-5-608531	4.1	4.1	0
ST-6-608530	4	4.1	1.2
ST-7-566940	3.9	3.9	0
GW-627429	10.1	10.3	1
GW-529142	4.4	4.4	0
GW-599357	7.6	7.9	1.9
GW-501760	7.9	7.9	0
GW-634036	4.8	5.2	4
GW-509604	14.6	15.8	3.9
GW-577707	3.6	3.5	-1.4
GW-550533	8	8.1	0.6
GW-540451	4.5	4.4	-1.1
GW-515867	7	7.3	2.1
GW-532595	5.2	5.6	3.7
GW-635386	3.1	3.2	1.6

Notes: meg/L = milliequivalents per liter

TABLE B.5
Total Dissolved Solids (TDS) Ratio

Sample ID	Measured	Calculated	Ratio
CANOARANCH-586729	400	369	1.08
CW-10	240	213	1.13
CW-6	260	238	1.09
CW-7	1420	1360	1.04
CW-8	880	827	1.06
CW-9	240	223	1.08
ESP-1	590	546	1.08
ESP-2	160	206	0.78
ESP-3	230	214	1.07
GV-2-603429	410	382	1.07
GV-603428	270	241	1.12
GW-206214	250	214	1.17
GW-501760	480	461	1.04
GW-509604	920	846	1.09
GW-515867	410	409	1.00
GW-529142	250	230	1.09
GW-532595	310	309	1.00
GW-540451	290	257	1.13
GW-550533	550	488	1.13
GW-577707	200	186	1.08
GW-599357	520	467	1.11
GW-627429	630	610	1.03
GW-634036	310	276	1.12
GW-634037	160	148	1.08
GW-635386	200	176	1.14
GW-639055	250	211	1.18
GW-640358	230	199	1.16
GW-DUP010307	250	239	1.05
SIWELL-208825	220	200	1.10
ST-5-608531	250	218	1.15
ST-6-608530	250	227	1.10
ST-7-566940	240	215	1.12

Notes: meg/L = milliequivalents per liter

APPENDIX C

FIRST QUARTER 2007 PDSI DATA VERIFICATION REPORT FOR SAMPLES COLLECTED BY PHELPS DODGE SIERRITA, INC.

FIRST QUARTER 2007
DATA VERIFICATION REPORT FOR SAMPLES COLLECTED BY PHELPS DODGE SIERRITA, INC.

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March 30, 2007

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TABLES

1. INTRODUCTION

This report summarizes the data verification review of groundwater samples collected and analyzed for the first quarter 2007 (Q1-2007) by Phelps Dodge Sierrita, Inc. (PDSI) pursuant to Mitigation Order on Consent Docket No. P-50-06. PDSI conducted groundwater sampling and analysis at wells under its control. The results of sampling and analysis were provided to Hydro Geo Chem, Inc. (HGC) for preparation of the Q1-2007 groundwater monitoring report. This data verification report focuses on laboratory results for the major element ions, as well as total dissolved solids (TDS) and alkalinity in samples collected by PDSI between January 8, 2007 and January 24, 2007 and subsequently analyzed by ACZ Laboratories, Inc. (ACZ).

Quality assurance (QA) and quality control (QC) procedures are specified in the *Quality Assurance Project Plan for Aquifer Characterization Plan* (QAPP) (Appendix E of HGC, 2006) for field sampling, chain-of-custody (COC) documentation, laboratory analysis, and reporting. Because field sampling procedures were reviewed by PDSI following the provisions of *Quality Assurance / Quality Control Plan for Water Monitoring, Phelps Dodge Sierrita, Inc.* (PDSI, 2005), field sampling is not reviewed in this report. This report does review sample handling and evaluates laboratory QA/QC according to the data quality indicators (DQIs) given in the QAPP.

Appendix E of the main text of this report contains laboratory reports for Q1-2007 samples collected by PDSI, including COC forms, laboratory correspondence, QC summaries, data qualifiers, and any case narratives. The Q1-2007 analytical results for PDSI samples pertain to 53 samples contained in 10 reports having the following ACZ Project numbers:

ACZ Project ID	Wells Reported
L60663	IW-1, IW-2, DUP010907A
L60668	PZ-2, MH-10, MH-28, MH-29, MH-30, PZ-8, MW-3
L60685	IW-19, IW-21, IW-20
L60694	MH-25A, MH-25B, MH-25C, PZ-5
L60729	PZ-6, PZ-7, BW-4, PZ-4, TB011506A, EQB011506A
L60758	IW-13, IW-14, IW-15, IW-16, IW-17, DUP011607A
L60762	MH-26A, MH-26B, MH-26C, IW-5, IW-6A, IW-10, IW-11, IW-12
L60773	IW-4, IW-9, IW-18, DUP011807A
L60805	S-1, S-4, S-5, S-6
L60872	IW-22, MH-13B, MH-13A, S-2, S-3, IW-23, PZ-3, MH-13C

Note:
All samples were filtered in the field using one disposable 0.45 micron filter per sample.

2. SAMPLE HANDLING

All samples collected by PDSI were surrendered by Bill Dorris and shipped to ACZ. COC documentation accompanied all samples submitted to ACZ. The COC documentation included the sample name, the date and time that samples were collected, and the date and time the samples were received by ACZ. All of the sample bottles were intact, properly preserved, and in good condition upon receipt with the exception of one of the eight trip blank sample bottles broken during shipment to ACZ on January 16, 2007.

The temperatures of the following five sample shipping containers exceeded 4 degrees Celsius (° C):

- Sample shipping container housing IW-1, IW-2, and DUP010907 was at 5.1 ° C.
- Sample shipping container housing PZ-2, MH-10, MH-28, MH-29, MH-30, PZ-8, and BW-3 was at 5.3 ° C.
- Sample shipping container housing MH-25A, MH-25B, MH-25C, and PZ-5 was at 5.3 ° C.
- Sample shipping container housing PZ-6, PZ-7, BW-4, PZ-4,TB011506A, and EQB011506 was at 4.9 ° C.
- Sample shipping container housing IW-22, MH-13B, MH-13A, S-2, S-3, IW-23, PZ-3, MH-13C was at 4.4 ° C.

The time between sample collection by PDSI and receipt of samples by ACZ ranged from about one to four days. Section 3.4 discusses laboratory holding times.

3. LABORATORY QUALITY CONTROL

As specified in the QAPP, laboratory QC was maintained for all analysis through proper licensure, the use of approved analytical methods, QC measurements, appropriate turn-around-time for analysis (timeliness), method detection limits (MDLs), and practical quantitation limits (PQLs). Each of these controls is discussed in the following subsections.

The review of laboratory QC included a review to identify any qualified data and an assessment to determine their significance. Additionally, the laboratory QC summaries were reviewed to verify that results met QA criteria.

3.1 Licensure

ACZ is licensed with the Arizona Department of Health Services (license number AZ0102) and is accredited in accordance with the National Environmental Laboratory Accreditation Conference.

3.2 Analytical Methods

All analyses performed used U.S. Environmental Protection Agency (EPA) analytical methods comparable to target methods identified in the QAPP and meet the target MDL requirements of the QAPP (Section 3.5):

- EPA SM4500 SO4-D (Gravimetric): sulfate
- EPA M200.7 (Inductively Coupled Plasma (ICP)): calcium, magnesium, potassium, sodium
- EPA M325.2 (Colorimetric): chloride
- EPA M353.2 (Automated Cadmium Reduction): nitrate/nitrite
- EPA SM2320B (Titration): alkalinity
- EPA SM4500F-C (Ion-Selective Electrode): fluoride
- EPA M160.1(Gravimetric): Total Dissolved Solids (TDS)

3.3 Quality Control Measurements

The following routine QC measures were used during sample analyses:

- Preparation blanks, calibration blanks, and calibration standards
- Analytical/matrix spikes and analytical/matrix spike duplicates
- Laboratory control samples
- Laboratory duplicate samples
- Trip blank samples

3.3.1 Preparation Blanks, Calibration Blanks, and Calibration Standards

Preparation blanks were run with each group of samples submitted for sulfate and TDS analyses. All preparation blanks were prepared from analyte-free water and treated as routine samples. Analytical results of all of the preparation blanks showed that no target analytes were detected at the indicated MDL.

Initial calibration blanks and initial calibration standards were checked for analyses conducted by ICP, colorimetric, automated cadmium reduction, and ion-selective electrode methods. The recovery percentage of these calibration blanks and standards were within the acceptance criteria specified by the ACZ QA plan and the QAPP.

3.3.2 Analytical/Matrix Spikes and Analytical/Matrix Spike Duplicates

Analyses of spike and spike duplicate samples conducted by ICP, colorimetric, automated cadmium reduction, and ion-selective electrode methods were reviewed. Instances in which analytical spikes and the analytical spike duplicate recoveries were outside the acceptance criteria specified by the ACZ QA plan are listed in Table C.1. In each of these cases, however, ACZ qualifiers explained that laboratory control samples showed acceptable recovery, which indicates acceptable accuracy in terms of the method level QC performed. Additionally, the relative percent differences (RPDs) between analytical spikes and analytical spike duplicates were below the 20 percent tolerance criteria set by the ACZ QA plan. This indicates acceptable precision for the purpose of aquifer characterization.

3.3.3 Laboratory Control Samples

Laboratory control samples were run for each group of samples submitted for analysis by wet chemistry methods. Wet chemistry methods consisted of gravimetric and titration methods used to determine alkalinity, sulfate, and TDS. Recoveries for all laboratory control samples were between 80 and 120 percent, which is within the acceptance criteria specified by ACZ.

3.3.4 Laboratory Duplicate Samples

Analyses of laboratory duplicate samples conducted by colorimetric, automated cadmium reduction, ion-specific electrode, and wet chemistry methods were reviewed. Field duplicate samples are discussed in Section 4.1.

The RPDs for the laboratory duplicate samples were below 20 percent in most cases, falling within the acceptance criteria set by ACZ. Instances in which RPDs exceeded acceptance criteria are listed in Table C.2. In all these cases, the data were flagged with an "RA" qualifier, which means that the RPD was not used for data validation because the sample concentration was too low for accurate evaluation. In cases where valid RPDs could be calculated, all results met QA criteria, and the results demonstrate an appropriate level of precision in laboratory analysis of these samples.

3.3.5 Trip Blank Samples

Two trip blanks (TB011506A and EQB011506A) accompanied the samples shipped to ACZ on January 15, 2007. Detections in the trip blank samples included calcium, magnesium, nitrate/nitrite as N, and sodium. The concentrations of sodium in both trip blanks were between the MDL and the PQL. Calcium was detected above the PQL in the TB011506A blank and between the MDL and the PQL in the EQB011506A blank. The concentrations of magnesium and nitrate/nitrite were between the MDL and the PQL in the TB011506A blank. The low level detections of calcium, sodium, magnesium, and nitrate/nitrite as N are not considered significant given the concentrations of these constituents in the samples.

3.4 Timeliness

Holding times for the analysis of sulfate and the other analytes were met for all samples.

3.5 Detection Limits

The MDLs and PQLs of the analytical methods used by ACZ are shown in the Table C.3. The MDLs for analyses of samples were equal to or less than the target MDLs identified in the QAPP except for chloride. The MDL for chloride was 5 milligrams per liter (mg/L) rather than the 1 mg/L stated in the QAPP. The higher MDL is acceptable given the magnitude of chloride concentrations in the samples.

4. DATA QUALITY INDICATORS

The QAPP provides several DQIs for assessing the overall quality of the data. These DQIs include the following:

- Precision
- Bias
- Accuracy
- Representativeness
- Comparability
- Completeness
- Sensitivity

Each of these DQIs is discussed below in relation to the Q1-2007 groundwater sampling and analysis conducted by PDSI. Also discussed are two auxiliary DQIs: the cation-anion balance and the TDS ratio.

4.1 Precision

Precision indicates how well a measurement can be reproduced. Precision is quantified by calculating the RPD between duplicate samples. For the purposes of QC and QA, precision was quantified by calculating the RPDs between duplicates among the following groups of duplicate samples:

- Laboratory duplicate samples
- Field samples and field duplicate samples

As discussed in sections 3.3.2 and 3.3.4, there were no significant exceedances of RPD QA criteria for spike duplicates or laboratory duplicates.

The RPDs for three pairs of field duplicate samples submitted were all below the 20 percent acceptance criterion (Table C.4) except for fluorine in MH-29. The RPD for this analysis was not used for data validation because the sample concentration is too low for accurate evaluation. The overall precision of the data is judged to be sufficient for the purpose of aquifer characterization.

4.2 Bias

Bias is a systematic distortion of measurements causing consistent errors in one direction. Bias is managed in this data set by the consistent application of standardized sample collection and analysis procedures.

4.3 Accuracy

Accuracy is a measure of the agreement of a measurement to a known value and is measured using the recoveries from laboratory control samples. As discussed in Sections 3.3.1, 3.3.2, and 3.3.3, no significant exceedances of the recovery QA criteria occurred for calibration standards, spikes, and laboratory control standards. Based on this information, the overall accuracy of the data is judged to be sufficient for the purpose of aquifer characterization.

4.4 Representativeness

All samples were taken from locations specified in the Work Plan (HGC, 2006) using sampling procedures specified in the QAPP. Therefore, the samples are judged to provide a good representation of groundwater quality at the locations. The analytical data are judged to be representative of groundwater conditions because the analyses used standard procedures and methods that met QA/QC guidelines of the QAPP.

4.5 Comparability

All samples were collected using standardized procedures (HGC, 2006 and PDSI, 2005) and were analyzed by ACZ using standardized methods. Insofar as standardized sample collection and analytical methods are adhered to, the sample results should be comparable.

4.6 Completeness

All samples collected by PDSI were subsequently analyzed and reported by ACZ. All samples collected by PDSI and analyzed by ACZ are judged to satisfy the QA/QC criteria for this project and to be usable for aquifer characterization. Thus, the completeness of analytical results is 100 percent.

4.7 Sensitivity

The analytical methods used to analyze the PDSI samples meet the MDL requirements specified in Table E.2 of the QAPP. Therefore, the analytical sensitivity is considered acceptable for use in aquifer characterization.

4.8 Auxiliary Data Quality Indicators

Auxiliary DQIs are indicators that, although not mentioned in the QAPP, are useful for assessing the reliability of the laboratory analyses. These auxiliary DQIs include the laboratory measured cation-anion balance and the ratio between measured and calculated TDS. Each of these auxiliary indicators is discussed below.

4.8.1 Cation-Anion Balance

The concentration (milliequivalents per liter [meq/L]) of cations and of anions in groundwater should theoretically be approximately the same. Therefore, the balance between anions and cations is one measure of the overall reliability of the laboratory measurements. The cation-anion balance can be expressed as the milliequivalent of cations minus the milliequivalents of anions divided by the milliequivalent sum of cations and anions. When computed in this manner, a cation-anion balance of 5 percent is indicative of good overall analytical results (Scott Habermahl, ACZ project manager, personal communication). The percent difference for the cation-anion balance was below 5 percent for all samples except for

MH-26A (8.1 percent), PZ-8 (15.2 percent), and S-1 (-18.6 percent) (Table C.5). Overall, the cation-anion balance indicates no apparent significant analytical errors.

4.8.2 TDS Ratio

The ratio between the measured and computed concentration of TDS is also an indicator of the overall quality of the sample analyses. A TDS ratio between 0.8 and 1.2 is indicative of good agreement between measured and completed values (Scott Habermahl, ACZ project manager, personal communication). The ratios for all samples are between 0.8 and 1.2 except for one sample collected from MH-26A (Table C.6). This sample also showed a poor cation-anion balance of 8.1 (Table C.5). Overall, the low TDS ratios for the majority of the PDSI samples indicate a good level of agreement in the sample results and no apparent analytical errors.

5. LIMITATIONS

The opinions and recommendations presented in this report are based upon the scope of services and information obtained through the performance of the services, as agreed upon by HGC and the party for whom this report was originally prepared. Results of any investigations, tests, or findings presented in this report apply solely to conditions existing at the time HGC's investigative work was performed and are inherently based on and limited to the available data and the extent of the investigation activities. No representation, warranty, or guarantee, express or implied, is intended or given. HGC makes no representation as to the accuracy or completeness of any information provided by other parties not under contract to HGC to the extent that HGC relied upon that information. This report is expressly for the sole and exclusive use of the party for whom this report was originally prepared and for the particular purpose that it was intended. Reuse of this report, or any portion thereof, for other than its intended purpose, or if modified, or if used by third parties, shall be at the sole risk of the user.

6. REFERENCES

Hydro Geo Chem, Inc (HGC). 2006. Work Plan to Characterize and Mitigate Sulfate with Respect to Drinking Water Supplies in the Vicinity of the Phelps Dodge Sierrita Tailing Impoundment, Pima County, Arizona. August 11, 2006, revised October 31, 2006.

Phelps Dodge Sierrita, Inc. 2005. Quality Assurance/Quality Control Plan for Water Monitoring, Phelps Dodge Sierrita, Inc. June, 2005.

TABLES

TABLE C.1
Spike Recoveries Outside of Acceptance Criteria

Parameter	Samples Affected	Recovery	Tolerance		ACZ Qualifier[1]	Work Group	ACZ ID	ACZ Project ID
		(%)	Minimum (%)	Maximum (%)				
Potassium	IW-1, IW-2, DUP 010907A	116.6	85	115	M1	WG219145	L60663-02AS	L60663
Potassium	IW-1, IW-2, DUP 010907A	115.5	85	115	M1	WG219145	L60663-07AS	L60663
Chloride	PZ-2,MH-10, MH-28, MH-29, MH-30, PZ-8, BW-3	35	90	110	M2	WG219238	L60589-01AS	L60668
Potassium	PZ-2,MH-10, MH-28, MH-29, MH-30, PZ-8, BW-3	117	85	115	M1	WG219145	L60663-07AS	L60668
Potassium	PZ-2,MH-10, MH-28, MH-29, MH-30, PZ-8, BW-3	115.5	85	115	M1	WG219145	L60663-07ASD	L60668
Calcium	IW-19, IW-21, IW-20	70	85	115	M3	WG219198	L60685-04AS	L60685
Calcium	IW-19, IW-21, IW-20	74.7	85	115	M3	WG219198	L60685-04ASD	L60685
Potassium	IW-19, IW-21, IW-20	119.8	85	115	M1	WG219198	L60685-04AS	L60685
Potassium	IW-19, IW-21, IW-20	121.2	85	115	M1	WG219198	L60685-04ASD	L60685
Sodium	IW-19, IW-21, IW-20	82.4	85	115	M3	GW219891	L60685-04AS	L60685
Sodium	IW-19, IW-21, IW-20	89.4	85	115	M3	GW219891	L60685-04ASD	L60685
Calcium	MH-25A, MH-25B, MH-25C, PZ-5	53.9	85	115	M3	WG219259	L60694-02AS	L60694
Calcium	MH-25A, MH-25B, MH-25C, PZ-5	57.3	85	115	M3	WG219259	L60694-02ASD	L60694
Sodium	MH-25A, MH-25B, MH-25C, PZ-5	-112.7	85	115	M3	WG219196	L60673-04AS	L60694
Sodium	MH-25A, MH-25B, MH-25C, PZ-5	-153.9	85	115	M3	WG219196	L60673-04ASD	L60694
Calcium	PZ-6, PZ-7, BW-4, PZ-4,TB011506A, EQB011506A	76.4	85	115	M3	WG219356	L60726-03AS	L60729
Calcium	PZ-6, PZ-7, BW-4, PZ-4,TB011506A, EQB011506A	69.9	85	115	M3	WG219356	L60726-03ASD	L60729
Chloride	PZ-6, PZ-7, BW-4, PZ-4,TB011506A, EQB011506A	115.9	90	110	M1	WG219490	L60727-01AS	L60729
Potassium	PZ-6, PZ-7, BW-4, PZ-4,TB011506A, EQB011506A	123	85	115	M1	WG219353	L60726-03AS	L60729
Potassium	PZ-6, PZ-7, BW-4, PZ-4,TB011506A, EQB011506A	121	85	115	M1	WG219353	L60726-03ASD	L60729
Calcium	IW-13, 1W-14, IW-15, IW-16, IW-17, DUP 011607A	66.3	85	115	M3	WG219466	L60758-02AS	L60758
Calcium	IW-13, 1W-14, IW-15, IW-16, IW-17, DUP 011607A	-8.1	85	115	M3	WG219466	L60758-02ASD	L60758
Magnesium	IW-13, 1W-14, IW-15, IW-16, IW-17, DUP 011607A	69.9	85	115	MA	WG219466	L60758-02ASD	L60758
Sodium	IW-13, 1W-14, IW-15, IW-16, IW-17, DUP 011607A	68.1	85	115	MA	WG219466	L60758-02ASD	L60758
Calcium	MH-26A, MH-26B, MH-26C, IW-5, IW-6A, IW-10, IW-11, IW-12	61.5	85	115	M3	WG219495	L60760-01AS	L60762
Calcium	MH-26A, MH-26B, MH-26C, IW-5, IW-6A, IW-10, IW-11, IW-12	84.3	85	115	M3	WG219495	L60760-01ASD	L60762
Calcium	MH-26A, MH-26B, MH-26C, IW-5, IW-6A, IW-10, IW-11, IW-12	81.6	85	115	M3	WG219495	L60762-04AS	L60762
Calcium	MH-26A, MH-26B, MH-26C, IW-5,IW-6A, IW-10, IW-11, IW-12	82.2	85	115	M3	WG219495	L60762-04ASD	L60762
Potassium	MH-26A, MH-26B, MH-26C, IW-5, IW-6A, IW-10, IW-11, IW-12	117.2	85	115	MA	WG219667	L60761-06ASD	L60762
Calcium	IW-4, IW-9, IW-18 DUP 011807A	82.5	85	115	M3	WG219469	L60773-02AS	L60773
Calcium	IW-4, IW-9, IW-18 DUP 011807A	56.5	85	115	M3	WG219469	L60773-02ASD	L60773
Potassium	IW-4, IW-9, IW-18 DUP 011807A	118.2	85	115	MA	WG219469	L60773-02AS	L60773
Fluoride	S-1, S-4, S-5, S-6	117.8	95	105	M1	WG219852	L60811-02AS	L60805
Nitrate/Nitrite	S-1, S-4, S-5, S-6	88.9	90	110	M2	WG219735	L60788-05AS	L60805
Fluoride	IW-22, MH-13B, MH-13A, S-2, S-3, IW-23, PZ-3, MH-13C	72	95	105	M2	WG220368	L60912-01AS	L60872

Notes:

[1] *M1 = Matrix spike recovery was high, the method control sample was acceptable*
M2 = Matrix spike recovery was low, the method control sample was acceptable
M3 = The accuracy of the spike recovery does not apply because analyte concentration is disproportionate to the spike level. The recovery of the method control sample was acceptable.
MA = Recovery for either the spike or the spike duplicate was outside acceptable limits; the RPD was within acceptable limits.

TABLE C.2
Laboratory Duplicate Samples Outside of Acceptance Criteria

Parameter	Samples Affected	RPD	ACZ Qualifier[1]	ACZ ID	ACZ Project ID
Fluoride	IW-1, IW-2, DUP	23.5	RA	L60663-06DUP	L60663
Fluoride	IW-1, IW-2, DUP	40	RA	L60668-03DUP	L60663
Nitrite/Nitrate	IW-1, IW-2, DUP	36.7	RA	L60659-01DUP	L60663
Fluoride	PZ-2,MH-10, MH-28, MH-29, MH-30, PZ-8, BW-3	40	RA	L60668DUP	L60668
Nitrite/Nitrate	PZ-6, PZ-7, BW-4, PZ-4,TB011506A, EQB011506A	200	RA	L60729-06DUP	L60729
Fluoride	IW-22, MH-13B, MH-13A, S-2, S-3, IW-23, PZ-3, MH-13C	33.3	RA	L60872-03DUP	L60872

Notes:

[1] *RA = Relative Percent Difference (RPD) was not used for data validation because the sample concentration is too low for accurate evaluation (<10 x MDL).*

TABLE C.3
Method Detections Limits (MDL) and Practical Quantitation Limits (PQL)

Parameter	MDL (mg/L)	PQL (mg/L)	Target MDL[1] (mg/L)
Sulfate	10	50	10
Calcium	0.2	1	0.2
Magnesium	0.2	1	0.2
Potassium	0.3	2	0.3
Sodium	0.3	2	0.3
Alkalinity	2	20	2
Chloride	5	30	1
Fluoride	0.1	0.5	0.1
Nitrate/Nitrite	0.02	0.1	0.02
TDS	10	20	10

Notes:

[1] *Target MDL from Table E.2 of the QAPP*

mg/L = milligrams per liter

TABLE C.4
Relative Percent Difference (RPD) of Duplicate Field Samples

	IW-4			IW-14			MH-29		
ACZ Project Number:	**L60773-61**	**L60773-04**		**L60758-02**	**L60758-08**		**L60663-08**	**L60668-04**	
Parameter	**Field sample (mg/L)**	**Duplicate (mg/L)**	**RPD (%)**	**Field sample (mg/L)**	**Duplicate (mg/L)**	**RPD (%)**	**Field sample (mg/L)**	**Duplicate (mg/L)**	**RPD (%)**
Calcium	530	495	6.83	524	513	2.12	566	555	1.96
Magnesium	93	88.2	5.30	118	116	1.71	101	97.8	3.22
Potassium	9.9	10.2	2.99	8.1	7.8	3.77	11.4	11.3	0.88
Sodium	164	165	0.61	161	157	2.52	172	164	4.76
Total alkalinity	148	148	0.00	125	125	0.00	158	160	1.26
Chloride	142	141	0.71	122	124	1.63	136	133	2.23
Fluoride	0.2	0.2	0.00	0.3	0.3	0.00	0.3	0.2	40.00 *
Nitrate/nitrite	0.74	0.76	2.67	1.39	1.4	0.72	0.67	0.66	1.50
TDS	2800	2780	0.72	3050	3070	0.65	2860	2720	5.02
Sulfate	1610	1590	1.25	1790	1810	1.11	1650	1660	0.60
TDS calculated	2640	2580	2.30	2800	2800	0.00	2730	2720	0.37
TDS ratio (measured/calculated)	1.06	1.08	1.87	1.09	1.1	0.91	1.05	1.08	2.82

Notes:

** RPD was not used for data validation because the sample concentration is too low for accurate evaluation (<10x MDL).*

mg/L = milligram per liter

TABLE C.5
Cation-Anion Balance

Sample ID	Cations (meq/L)	Anions (meq/L)	Percent Balance
IW-10	39.4	42.2	-3.4
IW-11	41.4	41.8	-0.5
IW-12	39.8	39.5	0.4
IW-14	43.2	43.5	-0.3
IW-15	40.6	41.3	-0.9
IW-16	41.1	42.8	-2.0
IW-17	38.9	39.8	-1.1
IW-18	40.2	41.0	-1.0
IW-19	39.5	40.9	-1.7
IW-2	6.0	5.7	2.6
IW-1	15.8	15.2	1.9
IW-20	39.2	40.7	-1.9
IW-21	40.2	40.6	-0.5
IW-22	42.5	41.6	1.1
IW-23	43.1	41.9	1.4
IW-4	41.6	40.8	1.0
IW-5	42.4	43.9	-1.7
IW-6A	42.8	43.5	-0.8
IW-9	41.9	41.1	1.0
MH-10	34.3	34.0	0.4
MH-13A	42.6	42.8	-0.2
MH-13B	29.5	29.7	-0.3
MH-13C	5.1	5	1.0
MH-25A	3.9	3.6	4.0
MH-25B	41.0	40.6	0.5
MH-25C	33.2	31.4	2.8
MH-26A	4	3.4	8.1
MH-26B	38.4	38.9	-0.6
MH-26C	19.9	19.6	0.8
MH-28	48	46.7	1.4
MH-29	44.4	41.6	3.3
MH-30	43.0	43.1	-0.1
PZ-7	11.4	11.3	0.4
PZ-8	20.1	14.8	15.2
S-1	5.7	8.3	-18.6
S-2	5.6	5.1	4.7
S-3	5.4	5.2	1.9
S-4	5.1	5	1.0
S-5	5.9	5.9	0.0
S-6	7.3	7.0	2.1

Notes:

meq/L = milliequivalents per liter

TABLE C.6
Total Dissolved Solids (TDS) Ratio

Sample ID	Measured (mg/L)	Calculated (mg/L)	Ratio
IW-10	2920	2670	1.09
IW-11	2920	2700	1.08
IW-12	2720	2560	1.06
IW-14	3050	2800	1.09
IW-15	2940	2660	1.11
IW-16	2970	2700	1.10
IW-17	2820	2530	1.11
IW-18	2830	2610	1.08
IW-19	2700	2580	1.05
IW-2	380	336	1.13
IW-1	1000	959	1.04
IW-20	2370	2570	0.92
IW-21	2760	2590	1.07
IW-22	2860	2710	1.06
IW-23	2830	2710	1.04
IW-4	2800	2640	1.06
IW-5	3010	2790	1.08
IW-6A	3030	2820	1.07
IW-9	2970	2680	1.11
MH-10	2310	2170	1.06
MH-13A	2900	2750	1.05
MH-13B	2020	1900	1.06
MH-13C	300	310	0.97
MH-25A	230	197	1.17
MH-25B	2790	2620	1.06
MH-25C	2210	2040	1.08
MH-26A	240	186	1.29
MH-26B	2710	2490	1.09
MH-26C	1350	1260	1.07
MH-29	2860	2730	1.05
MH-30	3000	2780	1.08
PZ-7	780	686	1.14
PZ-8	990	1010	0.98
S-1	530	442	1.20
S-2	320	303	1.06
S-3	310	302	1.03
S-4	330	292	1.13
S-5	370	345	1.07
S-6	450	409	1.10

Notes:

mg/L = milligrams per Liter