



Groundwater Chemistry Monitoring, Sampling, and Analysis
Annual Report for Fiscal Year 2002

NWRPO-2003-04

Prepared for
Nye County Department of Natural Resources and Federal Facilities,
Nuclear Waste Repository Project Office, Grant No. DE-FC28-02RW12163

Prepared by
Drew Hall and John Walton, University of Texas, El Paso

December 2003

This report was prepared by the Nye County Department of Natural Resources and Federal Facilities, Nuclear Waste Repository Project Office, pursuant to a Cooperative Agreement funded by the U.S. Department of Energy, and neither Nye County nor any of its contractors or subcontractors nor the U.S. Department of Energy, nor any person acting on behalf of either, assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Department of Energy or Nye County. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Department of Energy.

CONTENTS

1.0 INTRODUCTION	1
2.0 DATA TREND ANALYSES	3
2.1 Correspondence Analysis.....	3
2.2 Tertiary Diagrams	4
2.2.1 Major Anion and Cation Tertiary Diagrams	4
2.2.2 Interpretation of Trends in Tertiary Diagrams.....	5
2.3 Enrichment Plots	6
3.0 ENGINEERED BARRIER SYSTEM GROUNDWATER CHEMISTRY MODELING	9
3.1 Additional Waters Modeled.....	9
3.2 Paintbrush Non-welded Tuff Pore Water	9
3.3 Topopah Spring Welded Tuff Pore Water	10
3.4 Precipitation Water	11
3.5 Precipitation Water and Paintbrush Non-Welded Tuff Pore Water Mixture.....	11
3.6 Conclusions.....	12
4.0 GROUNDWATER CHEMISTRY SAMPLING AND ANALYSIS	13
4.1 Field and Laboratory Performance	13
4.1.1 Sampling and Field Parameter Measurement Problems	13
4.1.2 Laboratory Testing and Shipping Problems	14
4.2 Groundwater Sampling Plan	14
5.0 QUALITY ASSURANCE	17
5.1 Charge Balance Evaluations	17
5.2 Analytical Result Comparisons.....	18
5.3 Blind Field Duplicates	19
5.4 Field Blanks	19
5.5 Nevada Environmental Laboratory Quality Control Analysis.....	19
5.6 Summary	20
6.0 REFERENCES	21

FIGURES

1-1	Location of Early Warning Drilling Program Wells.....	F-1
2-1	Correspondence Analysis for Early Warning Drilling Program Wells	F-2
2-2	Magnetic Lineations in the Early Warning Drilling Program Area.....	F-2
2-3	Tertiary Diagram of Anions for Early Warning Drilling Program Wells.....	F-3
2-4	Tertiary Diagram of Cations for Early Warning Drilling Program Wells	F-3
2-5	Calcium Enrichment Plot.....	F-4
2-6	Fluoride Enrichment Plot.....	F-4
2-7	Nitrate Enrichment Plot	F-5
2-8	Sulfate Enrichment Plot	F-5
2-9	Sodium Enrichment Plot	F-6
2-10	Bicarbonate Enrichment Plot	F-6
2-11	Magnesium Enrichment Plot.....	F-7
2-12	Potassium Enrichment Plot.....	F-7
3-1	Paintbrush Non-welded Tuff Pore Water Evaporation Sequence for Anions	F-8
3-2	Paintbrush Non-welded Tuff Pore Water Evaporation Sequence for Cations.....	F-8
3-3	Paintbrush Non-welded Tuff Pore Water Precipitate Sequence for Anions.....	F-9
3-4	Paintbrush Non-welded Tuff Pore Water Mass of Precipitates for Anions.....	F-9
3-5	Topopah Spring Welded Tuff Pore Water Evaporation Sequence for Anions	F-10
3-6	Topopah Spring Welded Tuff Pore Water Evaporation Sequence for Cations	F-10
3-7	Topopah Spring Welded Tuff Pore Water Precipitate Sequence for Anions	F-11
3-8	Precipitation Water Evaporation Sequence For Anions	F-11
3-9	Precipitation Water Evaporation Sequence for Cations.....	F-12
3-10	Precipitation Water Precipitate Sequence for Anions.....	F-12
3-11	Paintbrush Non-welded Tuff Pore Water Mixed with Precipitation Water Evaporation Sequence for Anions	F-13
3-12	Paintbrush Non-welded Tuff Pore Water Mixed with Precipitation Water Evaporation Sequence for Cations	F-13
3-13	Paintbrush Non-welded Tuff Pore Water Mixed with Precipitation Water Precipitate Sequence for Anions	F-14
5-1	Relative Percent Difference in Gross Chemistry for NWRPO and USGS Samples Collected on the Same Day	F-15
5-2	Relative Percent Difference in Iron for NWRPO and USGS Samples Collected on the Same Day	F-16
5-3	Relative Percent Difference in Aluminum and Molybdenum for NWRPO and USGS Samples Collected on the Same Day	F-17
5-4	Relative Percent Difference in Lithium, Manganese, and Strontium for NWRPO and USGS Samples Collected on the Same Day	F-18

TABLES

1-1	Summary of Nuclear Waste Repository Project Office (NWRPO) Groundwater Chemistry Sampling and Analysis for 1994 through 2002.....	T-1
2-1	Composition of Average Precipitation in the Kawich Range in Nevada.....	T-9
4-1	Well Sampling Prioritization for the First Sampling Phase.....	T-10
5-1	Nuclear Waste Repository Project Office and U.S. Geological Survey Charge Balance Results from November 1999, May 2000, and October 2000 Sampling Sessions	T-11
5-2	Percentage of Deviation from Electroneutral for Nuclear Waste Repository Project Office Analytical Results from the 2002 Sampling Session.....	T-12
5-3	Average Relative Percent Difference between U.S. Geological Survey and Nuclear Waste Repository Project Office Analytical Results for Samples Collected in 1998, 1999, and 2000 Sampling Sessions	T-13
5-4	Relative Percent Differences in Blind Field Duplicate Analyses for 2001 and 2002 Sampling Sessions	T-14
5-5	Summary of Statistical Analysis of Selected Matrix Spike Recovery Data from Nevada Environmental Laboratory	T-15
5-6	Recommendations for Censoring Nuclear Waste Repository Project Office Data	T-16

APPENDIX

A	Physical Separation Processes and EBS Water Chemistry – A Modeling Study
---	--

ACRONYMS AND ABBREVIATIONS

CA	correspondence analysis
DO	dissolved oxygen
DOE	U.S. Department of Energy
EBS	engineered barrier system
EWDP	Early Warning Drilling Program
GWS	groundwater sample
ISIP	Independent Scientific Investigations Program
mg/L	milligrams per liter
NEL	Nevada Environmental Laboratory
NWRPO	Nuclear Waste Repository Project Office
ORP	oxidation/reduction potential
PCA	principal components analysis
PTn	Paintbrush non-welded tuff
QA	quality assurance
QC	quality control
RPD	relative percent difference
TSw	Topopah Springs welded tuff
USGS	U.S. Geological Survey
YSI	Yellow Springs Instrument

Intentionally Left Blank

1.0 INTRODUCTION

This annual report summarizes the results of groundwater chemistry sampling and analysis conducted from April 2002 through March 2003 (fiscal year 2002) as part of the Nye County Nuclear Waste Repository Project Office (NWRPO) Independent Scientific Investigation Program (ISIP). These activities were funded by a cooperative agreement with the U.S. Department of Energy (DOE) to support the evaluation of the high-level nuclear waste repository at Yucca Mountain.

Work was conducted in the following areas: 1) groundwater chemistry monitoring in Early Warning Drilling Program (EWDP) wells and 2) prediction of the possible range in water chemistries resulting from the physical separation process occurring near and/or on the engineered barrier system (EBS) proposed for the repository.

The topics discussed in this report include the following:

- An analysis and interpretation of trends in EWDP groundwater chemistry data from 1999 through fiscal year 2002.
- A study that models EBS groundwater chemistry for different conditions.
- The groundwater chemistry sampling and analysis program for fiscal year 2002.
- Quality assurance (QA) analyses of the groundwater chemistry data collected from 1998 through 2002.

Table 1-1 summarizes EWDP groundwater sampling and analysis from 1994 to 2002.

Figure 1-1 shows the locations of all completed wells in EWDP Phases I through III. A description of drilling, lithology, and well completion details for EWDP Phase III wells can be found in NWRPO (2002). Lithology and well completion information for wells from all three phases can be viewed on the NWRPO website (www.nyecounty.com).

Groundwater samples collected from these wells are listed in Table 1-1 as first water encountered, predevelopment/purging samples, and samples collected after well development and purging. Interpretive and QA analyses presented in this report will focus on the third group of samples, although data from several first water samples are included in some QA analyses. First occurrence and predevelopment sample data are not generally considered representative of in situ conditions.

Intentionally Left Blank

2.0 DATA TREND ANALYSES

Three types of trend analyses were performed on groundwater chemistry data: correspondence analysis (CA), tertiary diagrams, and enrichment graphs. Individual data points in the analysis were not averaged but represent distinct samples from different wells taken at different depths and/or on different dates. CA was used to statistically sort the water into three distinct groups. Tertiary diagrams, also known as Piper plots, are a traditional method of displaying data trends. Enrichment graphs illustrate concentrations relative to a hypothetically concentrated precipitation and can provide information on the chemical evolution of the groundwater in the Yucca Mountain area.

Groundwater chemistry data from the following EWDP wells were not included in data trend analyses. (The full EWDP well name includes the prefix “NC-EWDP-;” the full name will not be used in this report for the sake of brevity.) The absence of one or more key analytes in data sets from wells 19D, 19P, 19IM1, and 19IM2 precluded the use of these data sets. The data from wells 2D, 3D, and 3S were not considered to be representative of the true aquifer groundwater chemistry, and were therefore not included in the trend analyses. Samples from wells 2D and 3D were first occurrences of water samples that were collected prior to well development. Data from well 3S exhibits high temporal variability between sample collections, suggesting contamination from drilling fluids and/or grout from a nearby borehole.

2.1 Correspondence Analysis

CA and principal components analysis (PCA) are statistical models intended to reveal underlying trends in data (ter Braak and Smilauer, 1998). PCA is a linear method, whereas CA can reveal unimodal (e.g., Gaussian) responses. In many situations PCA and/or CA will reveal grouping or trends in the data that are caused by external, often unknown, factors. Both PCA and CA separate the columns in the data set using a number of axes derived from the data. Each of the axes is orthogonal, or statistically independent, from the other. In most cases, only the first two axes are shown on the plots in this report.

PCA and CA was applied to the NWRPO groundwater chemistry data using individual chemical parameter results for the rows, and wells for the columns. Chemical parameters included boron, calcium, chloride, fluoride, iron, lithium, manganese, magnesium, molybdenum, nitrate, potassium, sodium, sulfate, zinc, and alkalinity as calcium carbonate. CA was more effective in explaining NWRPO data than PCA. CA results for chemical analyses from selected EWDP wells are shown on Figure 2-1. The first axis accounts for 52 percent of the variance, the second axis for 25 percent. Variance not included in the axis is included in an error term. In total, 95 percent of the variance is explained.

All but one of the EWDP wells (i.e., 23P) fell into three distinct groups. Data from well 23P are outliers, with a chemistry that is clearly different than any other EWDP well, possibly for reasons discussed in Section 2.2.2.

Group I wells consist of 7SC, 7S, 1DX, 1S, and 12PC. In general, waters from these wells have elevated concentrations of bicarbonate, sulfate, and calcium compared to waters from other wells, which can suggest contact with evaporites. It is likely these wells are similar due to the

influence of a paleospring formation present at or near the wells. The groundwater chemistry signature for these wells becomes more dilute as you move away from 7SC in that group (Figure 2-1). The inclusion of 12PC with the evaporite wells may reflect communication across the Highway 95 or Carera Faults, or infiltration and recharge of paleospring pump test waters from 9SX after flowing across the highway.

Group II wells include 4PA, 4PB, 5SB, 9SX, 12PA, 12PB, and 15P. This grouping is possibly due to physical separation from Group III wells by a structural boundary (i.e., the Highway 95 Fault). This boundary appears as the southernmost deep-seated magnetic signature on Figure 2-2.

Group III consists of wells 10S, 10P, 18P, 22S, 22PA, and 22PB. 18P plots closer to Group II wells on Figure 2-1 than other Group III wells, suggesting that its chemistry represents a transition from Group III to Group II waters. This may be in part because it is both physically separated from other Group III wells (i.e., it is located outside of Fortymile Wash, as shown on Figure 1-1) and it is screened in volcanic tuff, whereas other Group III wells are screened in alluvium or underlying volcanic conglomerate (NWRPO, 2002).

In general, these three groups correspond to the groups seen in the tertiary diagrams and enrichment plots as described in the following sections.

2.2 Tertiary Diagrams

As stated, tertiary diagrams are a traditional method of evaluating major ion groundwater chemistry. Data presented in the CA plots are also plotted in tertiary diagrams on Figures 2-3 and 2-4, with blue symbols for Group I, purple for Group II, and red for Group III. The groupings identified in the tertiary diagrams correspond roughly to the groupings in the CA plots.

2.2.1 Major Anion and Cation Tertiary Diagrams

Major anions are plotted in the tertiary diagram on Figure 2-3 and major cations on Figure 2-4. Anion data from well 23P plot on the left-center portion of the diagram, reflecting close-to-equal concentrations of sulfate and bicarbonate and a low concentration of chloride. The remaining EWDP wells, located in the lower left portion of the diagram, contain predominantly carbonate waters, with some indication of further grouping comparable to those observed in CA plots.

For example, wells 22S, 22PA, 22PB, 18P, 10S, and 10P have the highest concentrations of bicarbonate and the lowest concentrations of sulfate, and plot in a close group. These wells are all located north of the Highway 95 Fault and correspond to CA Group III wells. With the exception of well 4PA, the remaining predominantly bicarbonate wells plot into groups corresponding to CA Groups I and II. For example, wells 12PA, 12PB, 9SX, and 5SB correspond to CA Group II wells and exhibit slightly lower bicarbonate and slightly higher sulfate data than the CA Group III wells. Finally, bicarbonate wells 7S, 7SC, 1S, 1DX, and 12PC plot above the previously mentioned wells and correspond to CA Group I wells.

The tertiary diagram for cations on Figure 2-4 also shows that well 23P plots as a separate water type, with a cation composition close to 100 percent sodium and potassium. Wells 1DX, 1S, 12PC, 7S, and 7SC are grouped low in the center of the diagram, reflecting nearly equal

concentrations of calcium and sodium plus potassium, and the presence of some magnesium. This cation group corresponds to CA Group I wells. Major cations from the remaining wells plot along the bottom right side of the diagram, indicating that sodium and potassium still predominate but that calcium exists in significant concentrations. Within this group, there appears to be an additional grouping corresponding to CA Groups II and III. For example, wells 22S, 22PA, 22PB, 10S, and 10P, which correspond to CA Group III wells, contain notably more calcium than wells 4PA, 4PB, 12PA, 12PB, and 9SX, which correspond to CA Group II wells. Well 18P appears to be the only exception.

2.2.2 Interpretation of Trends in Tertiary Diagrams

Winograd and Thordarson (1975) reported that, based on tertiary diagrams, groundwater in the region, including Yucca Mountain and the EWDP area, could be classified as sodium-potassium-bicarbonate, calcium-magnesium-bicarbonate, calcium-magnesium-sodium-bicarbonate, or sodium-sulfate-bicarbonate. Figures 2-3 and 2-4 show that EWDP groundwater can also generally be classified as one of these regional groups, as expected.

Both major anions and cations for well 23P plot separately in tertiary diagrams, suggesting unique groundwater chemistry. The CA plot for this well also indicated a unique chemistry, which may be related to the significant amount of bentonite drilling fluid lost to the formation during drilling. Residual bentonite not recovered during well development and purging prior to sampling may be responsible for altering the groundwater chemistry in this borehole. Until more data are available, no further trend analyses will be performed on data from this well.

The major anions and especially cations in wells 1DX, 1S, 7SC, 7S and 12PC are similar and differ from other wells. Each of these wells is on the western edge of the EWDP area and most are located on a paleospring deposit. The fact that well 12PC has a significantly higher concentration of calcium and magnesium than the lower screens in wells 12PA and 12PB suggests that the Highway 95 Fault may stop the paleospring water from flowing south toward these wells at depths lower than 100 feet, while the saturated shallow alluvium above transports the spring water across the fault, giving well 12PC a higher calcium and magnesium concentration. It is also possible that the well was contaminated with water produced from well 9SX during aquifer testing. This discharge water was observed to flow across the highway in the direction of well 12PC.

The above trends in groundwater chemistry appear to support water table elevation data, which indicate that the direction of flow for water in the western edge of the EWDP is to the southwest.

Wells 9SX, 15P, 4PA, 4PB, 5SB, 12PA, and 12PB are grouped together on the cation diagram, with the exception of well 4PA, and also appear to be grouped together on the anion diagram. These wells have a common carbonate, sodium, potassium water. The deeper screens in these wells are in volcanic tuff and the shallow screens are in alluvium. Despite the variation in the geology and location, the chemistry remains relatively similar in all screens. An upward hydraulic gradient measured at wells 9SX, 4PA and 4PB, and 12PA and 12PB may be responsible in part for the similar water chemistries in the different aquifers in these wells.

2.3 Enrichment Plots

The following analysis compares ion concentrations in groundwater samples to those in average current precipitation. If it is assumed that 1) the composition of current precipitation is similar to precipitation at the time of recharge of the measured groundwater and 2) the chloride ion behaves conservatively in the system with no sources or sinks, then the relationship between ion concentrations in groundwater and those in current precipitation can provide information on the chemical evolution of the groundwater. Neither of these assumptions is strictly correct; however, the presentation of these data is useful as long as the interpretation is kept at a qualitative level. The average value for precipitation is taken from Meijer (2002) based on data from the Kawich Range, approximately 200 kilometers north of the EWDP area (Table 2-1).

The results of this analysis, plotted by the CA group, are shown on Figures 2-5 through 2-12. The precipitation line shown on these figures is calculated from the ratio of chloride concentration in the sample to that in precipitation (i.e., the concentration factor) times the ion concentration in precipitation. The abscissa is the chloride concentration of the sample in parts per million. The chloride axis indicates the degree of concentration of groundwater. High chloride concentrations are associated with concentrated groundwater and low values with dilute groundwater. The ordinate is the species concentration in parts per million. A conservative ion would follow the modeled precipitation line. For example, ions depleted by chemical precipitation or ion exchange during evaporation and transport would appear below the line; ions dissolved from the solid phase during transport would appear above the line.

Figure 2-5 shows the results for calcium. Calcium is depleted for most Group II and III samples and the value appears to be independent of the degree of evaporation until a very high degree of evaporation occurs. Group I samples, the paleosprings wells, generally have significantly higher calcium enrichment.

Fluoride (Figure 2-6) is enriched for waters with low evaporation but the enrichment declines at a higher degree of evaporation. This type of trend could be caused by initial dissolution of a fluoride-bearing phase followed by precipitation when waters become more concentrated. Group I waters are depleted in fluoride. The lower fluoride abundance in Group I waters may be related to the high calcium concentration.

Nitrate (Figure 2-7) is depleted in all waters and the degree of depletion generally increases with evaporation, although this is only visible on a log scale. One hypothesis for this behavior is that waters subject to greater amounts of evaporation are likely to have a longer residence time in near-surface zones where biological uptake of nitrate would occur. This observation may have important implications for the EBS groundwater chemistry, where nitrate has been assumed to be conservative.

Sulfate (Figure 2-8) has slight enrichment in most waters with the exception of Group III waters. Within each group the enrichment declines with increased evaporation.

Sodium (Figure 2-9) is significantly enriched in all waters, indicating mass transfer from the solid to the aqueous phase. The degree of enrichment appears to decline as evaporation increases. Bicarbonate (Figure 2-10) behaves in a manner similar to sodium, suggesting that

their behavior may be linked. This could be caused by hydrolysis of silicate minerals releasing sodium and increasing alkalinity.

Magnesium (Figure 2-11) enrichment clearly separates the three water groupings. Group III waters are highly enriched, Group II waters are in the middle, and Group I waters have lower enrichment. Potassium (Figure 2-12) is depleted in most waters and the depletion increases with evaporation. An exception to this occurs in three samples from Group II, where the waters are enriched with potassium.

In summary, the enrichment plots in general fall into the same groupings found in the CA.

Intentionally Left Blank

3.0 ENGINEERED BARRIER SYSTEM GROUNDWATER CHEMISTRY MODELING

Ongoing research with the goal of better evaluating the chemical environment of the EBS was published at the 10th International High Level Radioactive Waste conference (Hall and Walton, 2003). Appendix A presents an initial look at the effect of physical separation processes on EBS groundwater chemistry and a comparison of models with laboratory results. Additional results are presented in Sections 3.2 through 3.5. These results will be submitted for publication in the near future.

The physical separation of ions in a source water can occur by several mechanisms. The first is water movement during the evaporation process, causing different minerals to precipitate at different locations based on relative differences in solubility. The second is the natural tendency for Gibb's free energy minimization, for minerals to precipitate as relatively pure phases. The third is gravity separation of precipitates from the water leading to distinct layers (i.e., playa deposits). The first two mechanisms are likely to be important at Yucca Mountain.

The physical separation of ions based upon differential solubility has two end points: maximum possible physical separation and no physical separation. These end points can be easily modeled; the range of results between the two modeled end points is a measure of the importance of physical separation processes. Total physical separation is simulated by the infinite cell mixing tank model; no physical separation is simulated by the single cell model. Using the infinite cell mixing tank assumption, precipitates are physically separated and rehydrate independently of one another. Using the single cell mixing tank, the once wetted area rehydrates in unison and, as more water is added, the wetted area begins to look more like the starting water composition. These modeled scenarios are analyzed for different waters in the following sections.

3.1 Additional Waters Modeled

Historically, water from DOE water supply well J-13 has been assumed to be a convenient proxy for perched water in the Yucca Mountain area; however, the likelihood that perched water will form above the repository and affect EBS corrosion is low (DOE, 2001d). It is probably more reasonable to assume that 1) pore water alone, 2) pore water mixed with condensate, 3) pore water mixed with infiltrating waters, or 4) other unsaturated zone water will contact the EBS in the future. Paintbrush non-welded tuff (PTn) pore water is present in the horizon above the repository. Topopah Spring welded tuff (TSw) pore water exists in the repository horizon. These two waters may be more likely than perched water (i.e., J-13 water) to contact the EBS in the future. Rainwater, subsequent to varying degrees of interaction with pore waters, also has the possibility of contacting the EBS through infiltration after large precipitation events. These waters present a broad range of chemistries that may influence corrosion of the EBS. The simulations below represent a total concentration factor of 10^6 taken in 52 model steps.

3.2 Paintbrush Non-welded Tuff Pore Water

PTn pore water is rich in calcium, sulfate, and chloride, and is different in composition from J-13 water, which is more typical of saturated zone waters in the region.

Assuming a single cell mixing tank model, the evaporation sequence to a brine concentration of 10^6 of the original waters is shown on Figure 3-1. The sequence is shown as a composition percentage of major anions in the remaining liquid phase brine. For the single cell mixing tank assumption, the rehydration sequence is an exact reversal of the evaporation sequence. Sulfate and bicarbonate anions are removed from the brine during initial concentration steps as the result of the precipitation of gypsum and calcite, respectively. The removal of calcium, primarily as gypsum and calcite, is shown on Figure 3-2, which illustrates the evaporation sequence for cations. After these initial concentration steps, the brine composition is dominated by chloride leading to potentially increased EBS corrosion risk. That is, the anion ratio of five parts chloride to one part nitrate is exceeded. Chloride does not precipitate within the extent of evaporation shown due to a lack of adequate sodium and potassium and the relatively high solubility of halite, hydrophilite, and chloromagnesite. For example, the concentrations of sodium and potassium in the source water are only 9 and 0.01 milligrams per liter (mg/L), respectively.

The precipitation sequence for PTn in an infinite cell mixing tank is shown on Figure 3-3. The sequence is shown as a composition percentage of the total precipitates. The concentration step at which anions begin to precipitate is shown on Figure 3-4 and the first step of the precipitation of an ion accounts for the largest mass precipitated. Figure 3-3 shows that bicarbonate is the first anion to precipitate. It precipitates as calcite, due in part to the large concentration of calcium present in the initial source water (Figure 3-2). The middle portion of the precipitation sequence is dominated by the precipitation of sulfate as gypsum and chloride precipitates, primarily as halite at the end of the precipitation sequence (i.e., near the wetted fringe). Niter and soda-niter precipitate in small quantities relative to halite. This is due to the lower aqueous solubility of halite, which limits soda-niter precipitation by depleting the aqueous concentration of sodium. Potassium is present in very low concentrations in PTn pore water, which limits the mass of niter that can precipitate. The resulting precipitates form an area at the end of the evaporation sequence that is very high in chloride concentration. After rehydration this area, in particular, will present an increased localized corrosion risk because there is no nitrate or sulfate to mitigate the effects of the large mass of chloride.

3.3 Topopah Spring Welded Tuff Pore Water

TSw is the geologic unit where the Yucca Mountain repository will be located. TSw pore water is bicarbonate-, sodium-, chloride-rich water.

The evaporation sequence of this water produces brine dominated by nitrate and chloride. Figure 3-5 displays the evaporation sequence for TSw pore water. Concentration of the solution rapidly removes bicarbonate and calcium as calcite. The removal of calcium is shown on Figure 3-6. At the point where bicarbonate and calcium are completely removed from solution, chloride dominates the brine composition and exceeds the ratio of five parts chloride to one part nitrate. This corrosive anion ratio in the brine lasts until sulfate is precipitated and nitrate becomes a larger portion of the solution.

Physical separation under the infinite cell mixing tank assumption presents a different brine composition upon rehydration. The precipitation sequence of TSw pore water (Figure 3-7) removes bicarbonate first, in the form of magnesite and calcite. Most of the mass of bicarbonate and calcium precipitate during this period. Sulfate precipitation follows the intermediate stage of

concentration, where it precipitates as thenardite and small amounts of gypsum. Gypsum precipitation is limited by low aqueous concentrations of calcium. Closer to the wetted area fringe, chloride precipitates as halite just before nitrate precipitates as soda-niter, due to the higher solubility of soda-niter. The band of nearly pure halite contains most of the mass of chloride. This band is of particular interest under the infinite cell mixing tank assumption because it is physically separated from corrosion-inhibiting anions and the chloride to nitrate ratio exceeds 5 to 1. The precipitates nearest the wetted area fringe contain significant quantities of nitrate and are not likely to be corrosive.

3.4 Precipitation Water

Precipitation water could be an important component of the water that may contact the EBS or the repository. Large, long-term precipitation events may infiltrate through fast flow paths above the repository and lead to a relatively unchanged but concentrated form of precipitation water. Precipitation water studied for this report was concentrated 100 times before it was entered into the model. The beginning aqueous concentrations of all ions were very low and had to be increased to provide stable numerical results from the model. Although the precipitation events leading to large amounts of infiltration may seldom recur, they may be important hydrochemically and impact EBS corrosion processes.

The evaporation sequence (Figure 3-8) begins with dominant and nearly equal concentrations of nitrate, bicarbonate, and sulfate, and lesser amounts of chloride in the brine. Bicarbonate is quickly removed from solution and precipitated as magnesite and calcite. At this point, nitrate and sulfate dominate the brine solution and the solution inhibits localized corrosion. The next change in the brine is the removal of sulfate through gypsum and thenardite precipitation. At this point, nitrate is the principal component of the solution, with chloride in lower concentrations. Large amounts of sodium (Figure 3-9) in solution at this stage of evaporation allow for much of the nitrate to precipitate as soda-niter with some halite. The end brine solution is one that is composed of 80 percent chloride.

The precipitation sequence for anions under the infinite cell mixing tank assumption is very diverse in terms of banding and the physical separation of precipitates (Figure 3-10). Initially, bicarbonate is precipitated as calcite and magnesite, and fluoride is precipitated as fluorite. Sulfate then precipitates, forming gypsum and thenardite, with an area near the middle of the separation sequence where the precipitation of fluoride (i.e., fluorite) and bicarbonate (i.e., magnesite) again increase. Although fluorite is close to 40 percent of the precipitate composition, the total mass present in this area is very small. Nitrate then forms a band of niter and soda-niter. Low concentrations of potassium limit the amount of niter that can form but soda-niter precipitation is relatively unrestricted. Due to this fact, nitrate precipitates soda-niter and with chloride as halite at the wetted area fringe. Upon rehydration under the infinite cell mixing tank assumption, the nitrate inhibits the corrosion risk.

3.5 Precipitation Water and Paintbrush Non-Welded Tuff Pore Water Mixture

Pure precipitation groundwater chemistry may be unrealistic due to the likelihood of mixing and matrix diffusion prior to reaching the repository. One example of mixing precipitation water with in situ pore water was modeled. This involved mixing equal parts of PTn pore water with

ten times concentrated precipitation water. This case mixes water with very different chemistries.

Evaporation of this mixed composition water under the single cell mixing tank assumption is different from that of both PTn pore water and precipitation water, despite the relatively small contribution precipitation water makes to the overall chemistry. The evaporation sequence begins with bicarbonate removal through calcite precipitation (Figure 3-11). Calcium in this water, as shown on Figure 3-12, is not as limiting as in most cases shown previously. Fluoride cannot be seen in Figure 3-11 because of its low concentrations relative to other anions, but there is a small amount of fluoride present. Since calcium is not limiting, fluoride precipitates and is removed from solution just as sulfate begins to precipitate, approximately one third of the way through the evaporation sequence. Sulfate precipitates as gypsum, again due to large amounts of calcium. Halfway through brine evolution, chloride and nitrate are the dominant species in the brine. Chloride at this point could be corrosive. Some nitrate is present in the solution but may not be adequate to inhibit corrosion until near the end of the concentration sequence, where nitrate concentration increases slightly.

The precipitation sequence for the mixed composition water under the infinite cell mixing tank assumption is presented on Figure 3-13. Bicarbonate is precipitated as calcite near the water source. The formation of this band of calcite is different from most cases previously described, due to the fact that bicarbonate is limiting. Sulfate and fluoride then precipitate as gypsum and fluorite, respectively, over most of the remaining separation sequence. Fluorite constitutes a small portion of the precipitates, due to the large amount of gypsum that forms at the same time. Last to precipitate is chloride as halite, followed by nitrate as soda-niter. A thin band of pure halite forms near the wetted area fringe and contains the largest mass of chloride. The band of pure halite, physically separated from inhibiting anions, increases the corrosion risk to the EBS during rehydration.

3.6 Conclusions

The modeling described in this section is not intended to exactly predict the groundwater chemistry associated with the EBS, but rather to investigate the potential importance of physical separation processes on groundwater chemistry. The results suggest that physical separation is likely to be important. The variety of results implies that the brines created by varying degrees of separation may behave differently in the context of EBS corrosion. The exact results are not as critical as the range of predicted chemistries that exceeds current DOE assumptions. Future work will attempt to evaluate conditions when physical separation is most likely to occur.

4.0 GROUNDWATER CHEMISTRY SAMPLING AND ANALYSIS

4.1 Field and Laboratory Performance

Collecting high-quality data is the primary goal of the NWRPO water quality monitoring program. During 2001 and 2002, water quality sampling procedures and monitoring equipment were reviewed and updated after comparison with U.S. Geological Survey (USGS) guidelines (USGS, 1997). These changes are reflected in a major revision to NWRPO QA technical procedure TP-8.1, *Field Collection and Handling of Water Samples*.

Data collection in 2001 and 2002 was performed for the first time by NWRPO personnel rather than contractors. In general, high quality samples were collected, processed, stored, shipped, and analyzed in a technically defensible manner by strictly following TP-8.1. Minor complications arose with implementation of the revised TP-8.1 and data reporting by the testing laboratories. The issues and their resolutions are detailed in the following sections. Most of these issues will be avoided in future by additional training, the use of sample management test plans, and the inclusion of additional reporting instructions in procurement documents. A sample management test plan for each sampling session will be generated before sampling to provide supplemental detail to TP-8.1. Implementation of a sample management test plan for each sampling session will help reduce problems during sample collection.

4.1.1 Sampling and Field Parameter Measurement Problems

Problems were encountered during the collection of field rinsate blank samples. Pump rinsate blanks were intended for the assessment of the contamination of the wells by the pump and attached tubing. Rinses were performed using water from Garlic Well (i.e., potable water), rather than the deionized water specified in TP-8.1. Consequently, rinsate samples have Garlic Well chemistry and analytical results are inconclusive regarding contamination from the pump/hose system. The system was washed with a non-phosphate detergent, rinsed thoroughly with the Garlic Well water, and allowed to drain prior to being lowered into each borehole; as a result residual contamination is believed to be minimal. In future sampling sessions, TP-8.1 instructions regarding rinsate blank sample collection will be followed explicitly.

The revised procedures in TP-8.1 include the use and calibration of a Yellow Springs Instrument (YSI) 6-Series water quality monitoring sonde and meter. The YSI sonde allows for onsite collection of perishable water quality parameters, including temperature, dissolved oxygen (DO), oxidation/reduction potential (ORP), electrical conductivity, turbidity, and pH. Field measurement of water quality parameters facilitates the interpretation of laboratory analyses and provides an essential indicator of well purging. The equipment performed well during testing, training, and the first few weeks of sampling. Toward the end of the August 2002 session, however, equipment performance problems were encountered. Values for DO decayed over the course of a day and many readings for other parameters, including turbidity and ORP, were unstable or inaccurate. The DO decay was likely the result of increasing water temperatures caused by increasing air temperatures and solar radiation on the exposed plastic tubing (i.e., part of the pump/hose system) stored on the delivery hose reel. The unstable readings and inaccurate values for turbidity and ORP were traced to leaking O-rings in the sonde housing. Lubrication of the O-rings corrected the leaks and restored reading stability and accuracy.

4.1.2 Laboratory Testing and Shipping Problems

Several problems were encountered with the chemical analytical testing laboratories used. Nevada Environmental Laboratory (NEL) was the laboratory responsible for inorganic chemistry analyses. The NWRPO requested that NEL report analytical results for metals at instrument detection limits; however, the laboratory had difficulty producing these data. Delivery of the data packages was delayed 6 to 12 months while NEL resolved internal data reporting issues. Future procurement documents will include a penalty clause for late delivery or data that are not reported as specified. Finally, alkalinity measurements from well 19IM1 were never obtained because the NWRPO did not clearly specify this analyte in the purchase order. In the future, procurement and chain-of-custody documents will be carefully reviewed to ensure that they accurately reflect sample management plans.

Geochron Laboratory (Geochron) was responsible for isotope analyses. Sample shipping instructions supplied by Geochron proved to be inadequate and resulted in the loss of a significant number of samples. Sample bottles leaked during shipping and in some cases broke open. In the future, highly conservative sample packing instructions will be included in sample management test plans for each sample session. In addition to shipping problems, Geochron encountered labor and equipment problems, resulting in long delays in completing analyses. Alternate laboratories will be considered for future sampling and analysis events.

4.2 Groundwater Sampling Plan

Future groundwater sampling and analysis will be conducted in two phases. The first phase is designed to build confidence in initial data quality; the second to investigate the temporal and spatial variations in groundwater chemistry by sampling EWDP wells over time and depth. The objective of the first phase of sampling is to produce from each well two valid data sets separated by at least a year. Once this objective is met, the second phase will include the following sampling schedule:

- Wells containing one or more sampling interval less than 200 feet deep will be sampled every 2 years.
- Wells containing intervals deeper than 200 feet will be sampled every 3 to 4 years.

A priority scheme has been developed to guide groundwater sampling during the first phase of EWDP sampling. All wells that have been completed with screens and sand or gravel packs, and are judged to be adequately developed, have been included in one of three priority groups for Phase I sampling. Multiple-screen wells are considered to be one well in the following classification scheme, since logistical considerations dictate simultaneous sampling of all screens.

- Group 1 (first priority) – wells that meet one or more of the following criteria:
 - Wells that have not been previously sampled.
 - Wells, or groups of wells, that require immediate sampling to answer critical technical questions and/or before they are used for other purposes.

- Wells that have been sampled and analyzed at least once, but data quality is lacking.
- Group 2 (second priority) – wells that have been sampled only once and do not meet Group 1 criteria.
- Group 3 (third priority) – wells that have been sampled more than once, with sampling events separated by less than 12 months.

Table 4-1 summarizes the prioritization of previously completed and developed EWDP wells for the first sampling phase activities conducted in the summer and fall of 2003. All wells that have not been classified as one of the first sampling phase priority groups are eligible for the second sampling phase. These wells include 1DX, 1S, and 9SX. The sample management plan described in this section has been formalized as an NWRPO QA work plan (i.e., WP-11, *Groundwater Chemistry Sampling and Analysis*).

Intentionally Left Blank

5.0 QUALITY ASSURANCE

All groundwater chemistry data collected by the NWRPO have been compiled and stored electronically to facilitate data analysis, and to serve as the basis for the future groundwater chemistry database. The QA analyses described in the following include groundwater chemistry data from five sampling sessions following well development (November 1999, May 2000, October 2000, October through November 2001, and August through October 2002) and two sampling sessions involving first water encountered (December 1998 and January 1999).

During these sampling sessions, the NWRPO supplied split groundwater samples to several other government agencies, including the USGS, which has subsequently published its analytical results (DOE, 2001a; 2001b; 2001c). The existence of NWRPO and USGS groundwater analytical data for the same wells and sample dates provides a unique opportunity to compare results for water samples collected and analyzed by different agencies. Comparisons are made in the following sections using both charge balance calculations and direct analytical results. Evaluations of NWRPO field QA samples (i.e., blind field duplicates and field blanks) are then presented, followed by a summary of QA analyses conducted by the primary testing laboratory.

5.1 Charge Balance Evaluations

The charge balance method of assessing data compares the relative amounts of positively and negatively charged major ions from the chemical analysis. Since water is electroneutral, any charge balance other than zero indicates an analytical error and/or significant contribution from “minor” ions.

NWRPO and USGS charge balance data for three sampling periods (i.e., November 1999, May 2000, and October 2000) are presented in Table 5-1. The NWRPO data exhibit relatively small deviations (i.e., an average of 2 percent) overall, which suggests relatively low analytical error in the analysis of the major ions. The USGS data display significantly higher variations (i.e., an average of 7 percent) in the charge balance, suggesting higher analytical error in the analysis of major ions.

Data recently received from NEL for sampling conducted in October and November 2001 and August through October 2002 were analyzed using the USGS program PHREEQC (Parkhurst and Appelo, 1999) to check the charge balance and quality of the data. PHREEQC includes an accurate method for checking charge balance and also provides mineral saturation indices. The percentage of deviation from electroneutral by sample is displayed in Table 5-2. All wells shown in this table were drilled as part of the EWDP, with the exception of J-13, which is a DOE water supply well. The charge balance deviation in Table 5-2 for samples from the same wells listed in Table 5-1 ranges from -9.3 to 15 percent, with an average deviation of 6 percent. Pump rinsate blanks, which had above-detection-limit concentrations for most major anions and cations, were included in the range and average calculations. Field blanks were excluded because the samples had very low concentrations that were close to the detection limits for all analytes. The field blanks, which are composed primarily of distilled water, have very low concentrations of aqueous ions and are subject to large errors in charge balance.

In summary, the charge balance analyses presented in Tables 5-1 and 5-2 provide evidence that NWRPO collection and analysis methods for the major anions and cations were of high quality.

5.2 Analytical Result Comparisons

Differences between NWRPO and USGS analytical results collected from the same well on the same date can be due to variations in field procedures for acidification, filtering, and sample handling, as well as in laboratory methods, equipment, and expertise. A high degree of agreement between analytical results from different agencies increases confidence in the data; the reverse is indicative of errors and the need for improved procedures.

Initial graphical analyses comparing NWRPO and USGS data collected on October 26, 2000, from well 4PB indicated great differences in the concentration of major ions. These two samples, although identically labeled, clearly represent different waters and were removed from the following comparison.

The average of relative percent difference (RPD) between NWRPO and USGS analytical results for selected analytes was calculated to illustrate the deviation between agency laboratories for samples collected from the December 1998, January 1999, November 1999, May 2000, and October 2000 sampling sessions (Table 5-3). The small variation in electrical conductivity and pH shows that the data points are matched and the data are not misaligned. The metals analytes iron, aluminum, molybdenum, lithium, and manganese displayed the largest variations. The average concentrations of these analytes are small, so a small change in concentration results in a large amount of variation. Most of the non-metals analytes with concentrations exceeding 1 mg/L displayed much smaller deviations.

RPDs for the same analytical data set evaluated in Table 5.3 are graphed by well on Figures 5-1 through 5-4. Figure 5-1 displays RPDs for major anions and cations and several other analytes. NWRPO and USGS results vary by less than 20 percent for most of the samples and species. The reasons for the generally larger negative deviations in well 15P are unknown. Figure 5-2 illustrates RPDs for iron and Figure 5.3 shows RPDs for molybdenum and aluminum. Values below the detection limit were excluded. Variable readings for iron, molybdenum, and aluminum are attributable to near-detection-limit concentrations.

Figure 5-4 compares RPDs for lithium, strontium, and manganese. Relatively large and constant negative deviations of approximately 175 percent are displayed for lithium and manganese. Direct comparison of the concentrations indicates a difference of a factor of ten in concentration. These consistent differences suggest a systematic error (e.g., in units or improper dilution) in one of the laboratories. Cross-sample comparisons suggest that the problem lies with the NWRPO analyses.

In summary, the comparison of NWRPO analytical data with USGS data generally indicates good agreement, with some exceptions. In nearly all cases, RPDs of major cations, anions, and water quality indicator parameters are less than 20 percent. Larger differences in several trace metals are attributable to near-detection-limit concentrations in samples. Lithium and manganese variations were likely caused by NWRPO laboratory error.

5.3 Blind Field Duplicates

An RPD analysis of the NWRPO analytical results from three blind field duplicates collected in the November 2001 and August through September 2002 sampling events is another QA check of the data (Table 5-4). Deviation was low (i.e., less than 30 percent) for most analytes. However, high RPDs were observed for a number of trace metals and major anions with low average concentrations. High RPDs for substances with such low concentrations are not generally indicative of poor sample collection or analysis procedures. In contrast, the high RPD for sulfate in well 22PA exhibits a high average concentration and is likely due to sampling or laboratory error.

5.4 Field Blanks

Field blanks were obtained by exposing laboratory-grade deionized water to open atmospheric conditions for the same amount of time as groundwater samples. The blanks were then shipped to the laboratory with the samples. The field blanks from wells 10P and 10S indicated small amounts of contamination, possibly from the atmosphere, transportation, bottles, preservation, and/or handling. The field blank from well 10P had above-detection-limit concentrations of barium, iron, chloride, magnesium, boron, calcium, and sodium. The field blank from well 10S had above-detection-limit concentrations of barium, zinc, iron, iodide as I, magnesium, and boron. Field blanks will be collected and analyzed in future sampling events on a limited basis, as determined by the principal investigator.

5.5 Nevada Environmental Laboratory Quality Control Analysis

Analysis of NEL quality control (QC) reports, including method blanks and spike recoveries, provides a means of assessing the quality of the laboratory analysis. All method blanks analyzed by NEL were reported as non-detectable, which indicates minimal cross-sample contamination in the laboratory.

The NWRPO conducted a simple statistical analysis of NEL matrix spike data to provide information on precision and accuracy. A low standard deviation (i.e., a narrow confidence interval) is indicative of high precision. A mean close to the true mean indicates high accuracy.

The results of this statistical analysis are displayed in Table 5-5 for 21 randomly selected matrix spike recoveries for the analytes listed. Concentrations were normalized by dividing all results by the true spike concentration and multiplying by 100. The mean, standard deviation, and a 99-percent confidence interval, using a “t” statistic, were calculated. The true recovery mean (i.e., 100 percent) falls outside the 99-percent confidence interval for the measured recovery percentages for the following analytes: aluminum, arsenic, boron, manganese, potassium, lithium, bicarbonate, fluoride, bromide, nitrite, chloride and iodide, which indicates that the measured recovery means for these analytes were significantly different at the 99 percent confidence level from the true mean.

The use of these “t” test results to accept or reject data (i.e., censor or qualify data) is complicated by the fact that chemical analyses with a high degree of precision (i.e., a low standard deviation) are more easily rejected than analyses with a low degree of precision (i.e., a high standard deviation). For this reason, the NWRPO QA objectives or criteria specified in TP-

8.1 require only that each spike recovery be within 25 percent of the original spike concentrations. Similarly, NEL QC reports require spike recoveries to be within 20 to 30 percent of the original spike concentrations, depending on the analyte and type of spike. In the majority of NEL spike analyses, the recoveries met these criteria. The NEL QC samples that did not meet laboratory QC specifications include the following:

- One of four matrix spike recoveries of sulfate associated with groundwater sample (GWS) 0010 and 0018 from well 10P.
- One of four matrix spike recoveries of nitrate/nitrite, one of five matrix spike recoveries of sulfate, and two of five matrix spike recoveries of chloride associated with GWS 0026 and 0033 from well 10S.
- One laboratory control spike and one matrix spike recovery of aluminum for GWS 0034 from well 23P.
- One laboratory control spike of lithium and one matrix spike recovery for nitrate associated with GWS 0027, 0028, and 0032 from well 7SC.
- One laboratory control spike and one matrix spike duplicate of aluminum and one matrix spike recovery of lithium associated with GWS 0032 from well 7SC.
- One of three matrix spike recoveries of orthophosphate, one of three matrix spike recoveries of sulfate, and one of two matrix spike recoveries of sodium associated with GWS 0007 and 0008 from J-13.
- Three of three matrix spike recoveries of orthophosphate, two of two matrix spike recoveries of antimony, and one matrix spike recovery duplicate RPD for sodium associated with GWS 0001 through –0006 from well 19IM1.

The fact that these samples did not meet laboratory QC specifications for matrix spike recoveries suggests some minor problems in laboratory methods of detection and/or QC sample handling for sodium, orthophosphate, sulfate, antimony, lithium, aluminum, chloride, nitrate, and nitrite. However, the deviations from laboratory QC specifications were in all cases not large enough to justify censoring these data.

5.6 Summary

The current and past procedures for groundwater chemistry sample collection and analysis have yielded useful data. Exceptions described in Table 5-6 include lithium and manganese data, data from samples contaminated with drilling fluids and/or grout, pre-purging/pre-development data, first occurrence of water data, and several samples exhibiting field and/or laboratory error determined by comparison with duplicate samples. It is recommended that these data should not be made available for public use (i.e., they should be censored) and should be used with caution in the scientific community.

6.0 REFERENCES

- Hall, D. and J. Walton. 2003. *Physical Separation Processes and EBS Water Chemistry – A Modeling Study*. 10th International High Level Radioactive Waste Management Conference. Las Vegas, NV: Amer. Nuc. Soc.
- Meijer, A. 2002. *Conceptual Model of the Controls on Natural Water Chemistry at Yucca Mountain*. Applied Geochemistry, 16, 6, 793.
- NWRPO (Nuclear Waste Repository Project Office). 2002. *Nye County Drilling, Geologic Sampling and Testing, Logging, and Well Completion Report for the Early Warning Drilling Program Phase III Boreholes*. Technical Report No. NWRPO-2002-04. Pahrump, Nevada: Nye County Department of Natural Resources and Federal Facilities.
- DOE (U.S. Department of Energy). 2001a. *Chemical and Isotopic Data for Spring and Well Samples Collected between 1/20/00 and 4/24/01 from Wells in the Yucca Mountain Area*. Technical Data Management System (TDMS) Data Tracking Number (DTN): GS011108312322.007. Accession Number: MOY-011119-19-03.
- DOE (U.S. Department of Energy). 2001b. *Field and Chemical Data Collected between 1/20/00 and 4/24/01 and Isotopic Data Collected between 12/11/98 and 11/6/00 from Wells in the Yucca Mountain Area, Nye County, Nevada*. Technical Data Management System (TDMS) Data Tracking Number (DTN): GS011108312322.006. Accession Number: MOY-011204-06-01.
- DOE (U.S. Department of Energy). 2001c. *Field, Chemical and Isotopic Data from Wells in the Yucca Mountain Area, Nye County, Nevada, Collected between 12/11/98 and 11/15/99*. Technical Data Management System (TDMS) Data Tracking Number (DTN): GS010308312322.002. Accession Number: MOY-010403-03-02.
- DOE (U.S. Department of Energy Office of Civilian Radioactive Waste Management). 2001d. FY01 Supplemental Science and Performance Analysis, Volume 1: Scientific Bases and Analysis. TDR-MGR-MD-000007 Rev. 00.
- Parkhurst, D. and C. Appelo. 1999. *PHREEQ User's Guide*. Water-Resource Investigation Report 99-4259. Denver, Colorado: U.S. Geological Survey.
- Questa (Questa Engineering Corporation). 2002. *Analysis of Pump-Spinner Test and 48-Hour Pump Test in Well NC-EWDP-7SC, Near Yucca Mountain, Nevada*. Pahrump, Nevada: Nye County Department of Natural Resources and Federal Facilities.
- Technical Procedure TP-8.1, Rev. 02. *Field Collection and Handling of Water Samples*. Pahrump, Nevada: Nye County Department of Natural Resources and Federal Facilities.
- ter Braak, C. J. F., and P. Smilauer. 1998. *CANOCO Reference Manual and User's Guide to Canoco for Windows: Software for Canonical Community Ordination* (version 4). Ithaca, New York: Microcomputer Power.

USGS (U.S. Geological Survey). 1997 to present. *National Field Manual for the Collection of Water-Quality Data: U.S. Geological Survey Techniques of Water-Resources Investigations*, book 9, ch. A1-A9, 2 v., variously paged. Chapters originally published from 1997-1999; updates at: <http://water.usgs.gov/owq/FieldManual/mastererrata.html>

Walker, J. 2003. Contract Geologist. Personal Communication. Pahrump, Nevada: Nye County Department of Natural Resources and Federal Facilities.

Winograd, I.J. and W. Thordarson. 1975. *Hydrogeologic and Hydrochemical Framework, South-Central Great Basin, Nevada-California, with Special Reference to the Nevada Test Site*. Professional Paper 712-C. Washington, D.C.: U.S. Geological Survey.