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 September 08, 2010



Mr. James Bearzi, Chief
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 New Mexico Environment Department
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Subject: Transmittal of the Waste Isolation Pilot Plant Groundwater Semi-Annual
 Monitoring Report, Sampling Round ~~28~~ 30

Dear Mr. Bearzi:

The purpose of this letter is to submit the Waste Isolation Pilot Plant Semi-Annual
 Groundwater Monitoring Report, Sampling Round 30. This report is required by Module
 V.J.2.a of the Hazardous Waste Facility Permit No. NM4890139088-TSDF.

We certify under penalty of law that this document and all enclosures were prepared
 under our direction or supervision according to a system designed to assure that
 qualified personnel properly gather and evaluate the information submitted. Based on
 our inquiry of the person or persons who manage the system, or those persons directly
 responsible for gathering the information, the information submitted is, to the best of our
 knowledge and belief, true, accurate and complete. We are aware that there are
 significant penalties for submitting false information, including the possibility of fines
 and imprisonment for knowing violations.

Please contact Daniel J. Ferguson at (575) 234-7018 if you have any questions
 regarding this data transmittal.

Sincerely,

David C. Moody, Manager
 Carlsbad Field Office

M. F. Sharif, General Manager
 Washington TRU Solutions LLC

Enclosure(s)

cc: w/enclosures
 S. Zappe, NMED *ED

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 J. Kieling, NMED ED
 *ED denotes electronic distribution



UNITED STATES DEPARTMENT OF ENERGY

**WASTE ISOLATION PILOT PLANT
CARLSBAD, NEW MEXICO**

**WIPP HAZARDOUS WASTE FACILITY
NEW MEXICO ENVIRONMENT DEPARTMENT
PERMIT NUMBER NM4890139088-TSDF**

**WIPP GROUNDWATER DETECTION MONITORING PROGRAM
SEMIANNUAL REPORT**

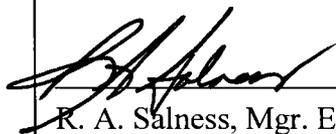
**SAMPLING ROUND 30
MARCH 2010 THROUGH MAY 2010**

**SUBMITTED TO THE
NEW MEXICO ENVIRONMENT DEPARTMENT
AUGUST 2010**

**WIPP GROUNDWATER DETECTION MONITORING PROGRAM
SEMIANNUAL REPORT**

**SAMPLING ROUND 30
MARCH 2010 THROUGH MAY 2010**

This report has been reviewed and approved by:



R. A. Salness, Mgr. EM&H

9/8/10
Date

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List of Abbreviations, Acronyms, and Units

APHA	American Public Health Association
ASTM	ASTM International
AWWA	American Water Works Association
CCC	Calibration Check Compound (for mass spectrometric analysis)
CCV	Calibration Check Verification
CLP	Contract Laboratory Program
DMP	Detection Monitoring Program
EPA	U.S. Environmental Protection Agency
GAC	Granular Activated Charcoal
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
HEAL	Hall Environmental Analytical Laboratory
ICP	Inductively Coupled Plasma Emission Spectroscopy
ICP/MS	Inductively Coupled Plasma Emission Spectroscopy Mass Spectrometry
ICV	Initial Calibration Verification
L	Liter(s)
LCS	Laboratory Control Sample
MS	Matrix Spike
MSD	Matrix Spike Duplicate
µg	microgram(s)
µg/L	micrograms per Liter
µmhos/cm	micromhos per cm
µS	microsiemens
mS	millisiemens
mg	milligram(s)
mg/L	milligrams per Liter
MDL	Method Detection Limit
MRL	Method Reporting Limit
ND	Not Detected
NMED	New Mexico Environment Department
PQL	Practical Quantitation Limit
QA	Quality Assurance
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RL	Reporting Limit
RPD	Relative Percent Difference
RSD	Percent Relative Standard Deviation
SM	Standard Methods for the Examination of Water and Wastewater
SOP	Standard Operating Procedure
SOW	Statement of Work
SPCC	System Performance Check Compound (for mass spectrometric analysis)
SVOC	Semivolatile Organic Compound
TDS	Total Dissolved Solids

TOC	Total Organic Carbon
TOH	Total Organic Halogens (TOX)
TOX	Total Organic Halogens (TOH)
TSS	Total Suspended Solids
UTLV	Upper Tolerance Limit Value
V&V	Verification and Validation
VOC	Volatile Organic Compound
WEF	Water Environment Federation
WIPP	Waste Isolation Pilot Plant
WQSP	Water Quality Sampling Program

Executive Summary

The Permittees at the Waste Isolation Pilot Plant (WIPP) facility collect groundwater quality data semiannually in accordance with the Hazardous Waste Facility Permit (Permit) issued by the New Mexico Environment Department (NMED). As prescribed by the Permit, six monitoring wells completed in the Culebra Dolomite Member of the Rustler Formation and one well completed in the Dewey Lake Redbeds Formation are sampled as part of the Detection Monitoring Program (DMP). This report presents the results of the Round 30 sampling event conducted between March 2010 and May 2010. The Permit requires the groundwater samples to be analyzed for 55 target analytes (Table 1). During Round 30, the Permittees used a contract laboratory for analysis of the required analytes.

These seven wells had each been sampled 29 times prior to this sampling round. The first 10 sampling rounds (all conducted prior to receiving mixed waste at the WIPP site) were used to develop the original baseline for groundwater chemistry at each sampling location. The baseline sample set was used to determine whether statistically significant changes in groundwater chemistry have occurred at any well. The data in this report are presented in both table and graph formats to show the Round 30 results with respect to the established baseline.

The baseline was established incorporating data from three different laboratories. The wide ranges of target analyte concentrations measured in the baseline resulted from difficulties in analyzing the high-brine groundwater from the WIPP site. The contract laboratories used variable dilution factors when analyzing the samples resulting in variable detection limits for some analytes. The current laboratories are encouraged to use the lowest possible dilution factors in order to achieve method reporting limits as low as possible.

Round 30 groundwater analysis results indicate no evidence of groundwater contamination resulting from the disposal and management of radioactive mixed waste at the WIPP site. Examination of time-trend plots for the target analytes revealed no changes in overall groundwater chemistry or the development of concentration trends.

Laboratory analytical results were validated and verified in accordance with WIPP facility procedures and U.S. Environmental Protection Agency (EPA) technical guidance. For this round, strict data verification and validation procedures were used for the general chemistry indicator parameters and major cations/anions as well as the Resource Conservation and

Recovery Act (RCRA) constituents including target volatile organics, semivolatile organics, and trace metals.

1.0 Introduction

The Permittees at the Waste Isolation Pilot Plant (WIPP) facility collect groundwater quality data semiannually in accordance with the Permit, which was issued by the New Mexico Environment Department (NMED) on October 27, 1999. This report documents groundwater quality based upon the chemical analysis results of sampling conducted from March 2010 to May 2010 (Sampling Round 30) and compares the data to the baseline water quality data.

The Detection Monitoring Program (DMP) prescribed by the Permit requires the sampling of six Water Quality Sampling Program (WQSP) monitoring wells (WQSP-1 through WQSP-6) completed in the Culebra Dolomite Member of the Permian Rustler Formation (Culebra); and one additional monitoring well (WQSP-6A), completed in the Permian Dewey Lake Redbeds Formation (Dewey Lake). Figure 1 shows the locations of the monitoring wells. Water level measurements from the DMP monitoring wells and other monitoring wells surrounding the WIPP show that the groundwater flow direction in the Culebra is generally from north to south.

The original DMP baseline includes data from the first 10 sampling rounds. These sampling events provided baseline groundwater quality data for the Culebra and Dewey Lake prior to the first receipt of mixed waste at the WIPP facility on September 9, 2000. The data collected during Round 30 were compared with the target analyte concentration ranges measured during the baseline study. The concentrations of the target analytes were evaluated to determine whether statistically significant changes in water quality have occurred or are occurring compared with the baseline sampling results.

The analytical results for Round 30 indicate no evidence of groundwater contamination resulting from the disposal and management of radioactive mixed waste at the WIPP site. The analytical results were all within the established background concentration ranges, except for chloride in the duplicate sample and TSS in the duplicate sample from WQSP-1; sulfate in the primary sample and duplicate sample, chloride in the duplicate sample and TSS in the duplicate sample from WQSP-3; chloride in the primary sample and duplicate sample, sulfate in the duplicate sample and TSS in the primary sample from WQSP-4; and TSS in both the primary sample and duplicate sample from WQSP-5.

2.0 Background Water Quality Analyses

Sampling of the DMP wells began in August 1995. The WIPP Permittees completed five rounds of background sampling in September 1997. However, mixed waste was not received by the WIPP facility until September 2000. Therefore, five additional rounds of background samples were collected and analyzed. The Permittees performed a groundwater quality baseline analysis for each of the seven monitoring wells using data from these 10 initial sampling rounds.

The WIPP groundwater baseline analysis is presented in the document “Waste Isolation Pilot Plant RCRA [Resource Conservation and Recovery Act] Background Groundwater Quality Baseline Report” (Crawley and Nagy, April 1998), supplemented in November 2000 (DOE, November 2000). Background water quality was established for each individual well because the Culebra water chemistry is spatially highly variable across the WIPP site area, making comparisons of target analyte concentrations among wells of little value.

Techniques were established to compare detection monitoring data generated during the baseline study. A 95th upper tolerance limit value (UTLV) or 95th percentile was determined from those data sets where target analytes were measured at concentrations above the reporting limits. Note that various terms are used for reporting limits including method reporting limits (MRLs), method detection limits (MDLs), and practical quantitation limit (PQLs).

MRLs are used in this report as the primary concentration reporting term. The laboratories reported MRLs for each of their analyses. The MRL was generally the concentration corresponding to the concentration of the lowest calibration standard for a given analysis adjusted for any required dilution factors. The laboratory termed the MRL as the equivalent PQL.

The Statement of Work (SOW) specified a set of target MRLs for the groundwater analyses. These SOW-prescribed MRLs are based on measurable concentrations in relatively clean water and were not always achievable in the high-brine groundwaters from the Culebra due to the need to dilute the samples to avoid overloading the analytical instrumentation.

The MDLs for the current analyses were generally lower than the SOW-prescribed MRLs. MDLs are statistically derived values that assess the performance of the analytical method, the analytical instrumentation, and the analyst. MDLs are typically lower than the low calibration standard and may be less accurate than concentrations measured within the calibration range of the instrument. MDLs are typically two to 15 times lower than MRLs.

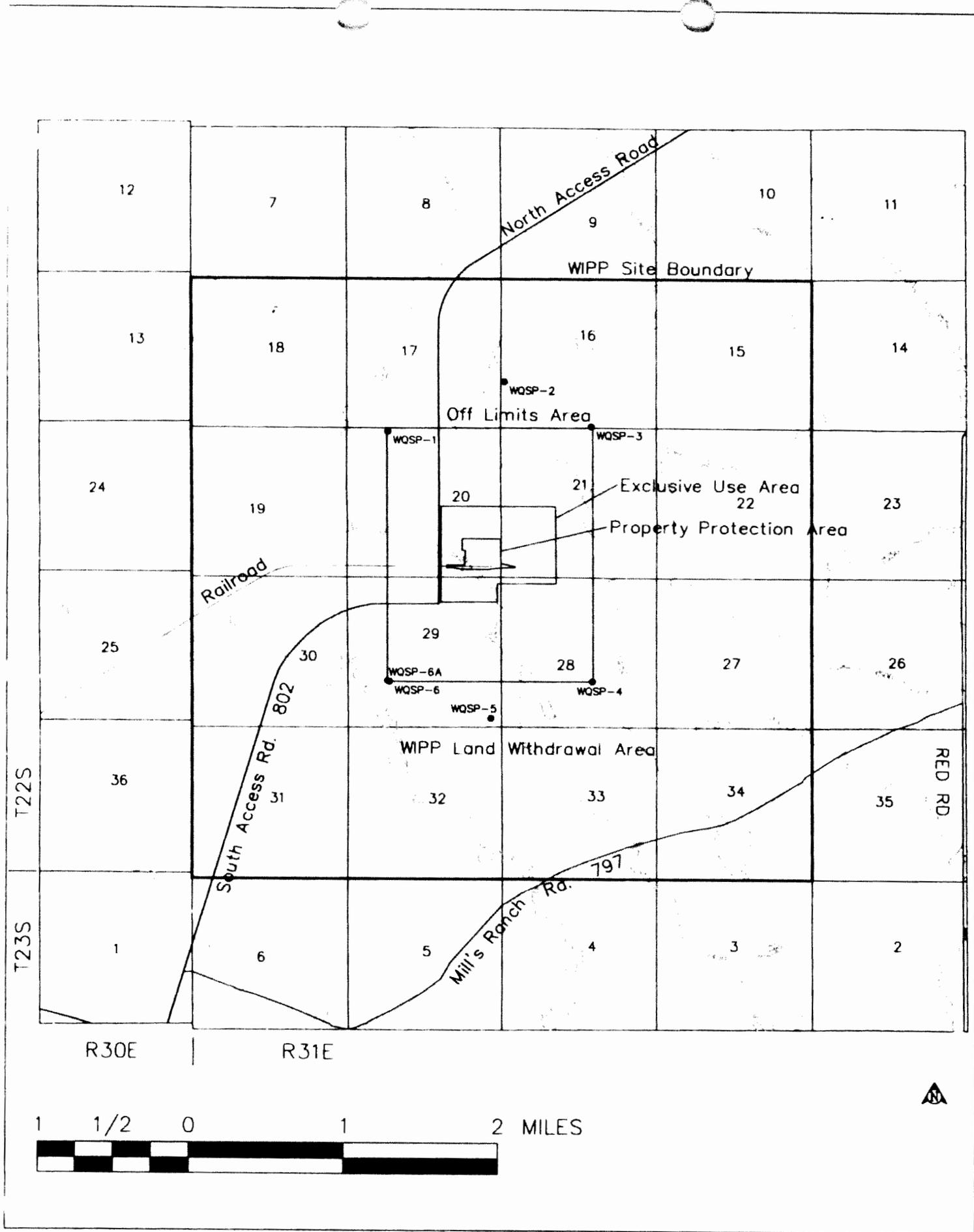


Figure 1

WIPP D... Monitor Well Locations

Concentrations between the MDL and the MRL are measurable and reportable, but are flagged with a “J” flag as estimated concentrations. Some of the concentrations measured in the high-brine samples in this report are J-flagged.

The UTLV is provided for normal or lognormal distributions and a 95th percentile confidence interval is provided for data sets that are nonparametric, which implies the data set had greater than 16 percent non-detects.

The UTLV is defined as:

$$UTLV = \bar{X} + (K) (S)$$

where

- UTLV = Upper tolerance limit value
- \bar{X} = Arithmetic mean of the data set
- K = One-sided normal tolerance factor
- S = Standard deviation of the data set

The UTLV establishes a concentration range that contains a specified proportion of the population with a specified confidence. The proportion of the population included is referred to as the coverage, and the probability with which the tolerance interval includes the proportion is referred to as the tolerance coefficient. The one-sided normal tolerance factor (K) in the above equation is a function of the desired percent coverage, the desired tolerance coefficient, and the number of samples. The U.S. Environmental Protection Agency (EPA) guidelines (EPA, February 1989) recommended a coverage value of 95 percent. A tolerance coefficient value of 95 percent was used to calculate the baseline UTLVs. For lognormal data sets, the calculations were performed on the log-transformed data, and the antilog of the UTLV was calculated using the above procedure. The percentile of a distribution of values is a number, X_p , such that a percentage, p , of the population of values is less than or equal to X_p . For example, the 95th percentile of a variable is a value, X_p , such that 95 percent of the values of the variable fall below this value.

This 95th UTLV or 95th percentile implies that 5 percent, or 1 in 20, of the concentrations from subsequent sampling rounds would be expected to be above the 95th UTLV or 95th percentile and do not necessarily represent contamination.

For analytes with only a few detects (greater than 95 percent non-detects), an accurate 95th percentile cannot be calculated. For these analytes, the maximum detected concentration is used as the baseline value. For analytes that are non-detect in all the samples, the MRL was used as the baseline concentration. These reporting limits for non-detected analytes were evaluated to make sure that an anomalously high reporting limit was not used as the baseline concentration. Previous analyses have shown that Culebra groundwater across the area contains total dissolved solids (TDS) concentrations that range from approximately 12,000 to 280,000 mg/L. These high TDS concentrations require diluting the samples prior to analysis for some analytes. The wide range of TDS concentrations has required various dilution factors between rounds and from well to well over the years of the DMP. This has resulted in MRLs that have not always been consistent between rounds and occasionally have been high compared to the MRLs for the same target analytes in different sampling rounds.

3.0 Round 30 Groundwater Analyses

In accordance with requirements in the WIPP Permit, Module V, and Attachment L, the Permittees sample the seven detection monitoring wells for the chemical analytes listed in Table 1. In addition to the Permit required analytes listed in Table 1, the samples were analyzed for alkalinity; a major cation, sodium; a major anion, sulfate; and for the anion, nitrate.

Round 30 samples were analyzed for these groundwater analytes in accordance with Permit requirements. On August 31, 2001, the WIPP added trans-1, 2-dichloroethene (trans-1, 2-dichloroethylene) and vanadium to the analyte list. Rounds 13 through 16 were used to establish the background for these analytes. Vanadium background concentrations were established in Rounds 1-10, and these are the concentrations used in Table 3.

Table 1
Permit-Required Target Analyte List

Volatile and Semivolatile Organic Compounds	General Chemistry and Major Cations/Anions	Trace Metals (Total)
<p>VOCs: Isobutanol</p> <p>Carbon tetrachloride Chlorobenzene Chloroform 1,1-Dichloroethane 1,2-Dichloroethane</p> <p>1,1-Dichloroethylene cis-1,2-Dichloroethylene trans-1,2-Dichloroethylene Methyl ethyl ketone Methylene chloride 1,1,2,2-Tetrachloroethane Tetrachloroethylene 1,1,1-Trichloroethane 1,1,2-Trichloroethane Toluene Trichloroethylene Trichlorofluoromethane Vinyl chloride Xylenes</p> <p>SVOCs 1,2-Dichlorobenzene 1,4-Dichlorobenzene 2,4-Dinitrophenol 2,4-Dinitrotoluene Hexachlorobenzene Hexachloroethane Cresols (2-, 3-, & 4-Methylphenol) Nitrobenzene Pentachlorophenol Pyridine</p>	<p>General Chemistry: Density (measured as Specific Gravity) pH Specific conductance TDS (Total dissolved solids) TOC (Total organic carbon) TOH, TOX (Total organic halogens) TSS (Total suspended solids)</p> <p>Major Cations: Calcium (Ca⁺⁺) Magnesium (Mg⁺⁺) Potassium (K⁺)</p> <p>Major Anions: Chloride (Cl⁻)</p>	<p>Antimony (Sb) Arsenic (As)</p> <p>Barium (Ba) Beryllium (Be) Cadmium (Cd) Chromium (Cr) Iron (Fe)</p> <p>Lead (Pb) Mercury (Hg) Nickel (Ni) Selenium (Se) Silver (Ag) Thallium (Tl) Vanadium (V)</p>

pH = Hydrogen ion potential (measure of alkalinity or acidity)
SVOC = Semivolatile Organic Compound
VOC = Volatile Organic Compound

Table 2 lists the volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and the trace metal constituents measured in the Round 30 samples along with the corresponding MRLs specified in the Statement of Work (SOW). Chemical synonyms used by the current analytical laboratory, Hall Environmental Analysis Laboratory (HEAL), which deviate from the Permit-listed organic compound nomenclature, are provided in parentheses in Table 2 and will

be used for subsequent discussions of analyses results. The chemical name of an organic compound (i.e., volatile [VOC] and semivolatile [SVOC]) may vary by laboratory because of the use of various chemical synonyms.

Table 2**VOC, SVOC, and Metal Target Constituents and Their Associated SOW-Prescribed MRLs**

Compound^a	MRL, µg/L	Trace Metal	MRL, mg/L
VOCs			
Isobutanol (Isobutyl Alcohol)	5.0	Antimony	0.025
Carbon tetrachloride	1.0	Arsenic	0.050
Chlorobenzene	1.0	Barium	0.020
Chloroform	1.0	Beryllium	0.010
1,1-Dichloroethane	1.0	Cadmium	0.010
1,2-Dichloroethane	1.0	Chromium	0.025
1,1-Dichloroethylene (1,1-Dichloroethene)	1.0	Iron	0.500
cis-1,2-Dichloroethylene (cis-1,2-DCE)	1.0	Lead	0.020
trans-1,2-Dichloroethylene (trans-1,2-DCE)	1.0	Mercury	0.0002
Methyl ethyl ketone (2-Butanone)	5.0	Nickel	0.025
Methylene chloride	5.0	Selenium	0.025
1,1,2,2-Tetrachloroethane	1.0	Silver	0.013
Tetrachloroethylene (Tetrachloroethene)	1.0	Thallium	0.025
1,1,1-Trichloroethane	1.0	Vanadium	0.025
1,1,2-Trichloroethane	1.0		
Toluene	1.0		
Trichloroethylene (Trichloroethene)	1.0		
Trichlorofluoromethane	1.0		
Vinyl chloride	1.0		
Xylenes (Xylenes, Total)	1.0		
SVOCs			
1,2-Dichlorobenzene	5.0		
1,4-Dichlorobenzene	5.0		
2,4-Dinitrophenol	5.0		
2,4-Dinitrotoluene	5.0		
Hexachlorobenzene	5.0		
Hexachloroethane	5.0		
2 ^b -Methylphenol	5.0		
3 ^b -Methylphenol	5.0		
4 ^b -Methylphenol	5.0		
Nitrobenzene	5.0		
Pentachlorophenol	5.0		
Pyridine	5.0		

^aChemical synonyms used by the current analytical laboratory, Hall Environmental Analytical Laboratories, are noted in parentheses.

^b Listed as Cresols in the Permit

µg/L = microgram(s) per liter

mg/L = milligrams per liter

SVOC = semivolatile organic compound

VOC = volatile organic compound

Table 3 summarizes the analytical results for all the target analytes in the Round 30 samples along with their calculated distribution types and the original baseline 95th UTLV or 95th percentile concentrations (DOE, November 2000). Analytical results with analyte concentrations higher than the 95th UTLV or 95th percentile are identified and discussed. The actual laboratory MRLs for each particular sample are shown in parentheses for analytes that were not detected or for which the analytes were detected, but the concentrations were between the MDL and the MRL and are J-flagged as estimated concentrations. The corresponding laboratory MDLs are shown on the WQSP well summary data sheets, on the laboratory data summary sheets in the appendices, and on the time-trend charts for Round 30.

The analytical results from Round 30 are discussed in Sections 3.1 through 3.4 by analyte type including volatile and semivolatile organics, trace metals, general chemistry indicator parameters, and cation-anion balances.

Individual appendices for each well (Appendices 1 through 7) provide data summary spreadsheets with the groundwater sample detections in the duplicate samples along with the averages and precision of the concentrations; the lab-reported sample analysis data along with the quality assurance/quality control (QA/QC) data; a summary narrative of the groundwater sampling and mobile lab (serial sample) analysis results; and data verification and validation narratives and checklists for all the laboratory data from each WQSP well. The appendices also contain time-trend charts comparing the Round 30 chemical analysis results for metals and general chemistry parameters to the historical background data and concentration data from the previous rounds.

Table 3
Round 30 Analytical Data Summary

WQSP-1 Culebra				
Chemical	Concentration (mg/L)		Distribution Type^a	95th UTLV or 95th Percentile
	Sample	Duplicate		
WQSP-1 General Chemistry				
Specific Gravity ^b	1.043	1.045	Normal	1.07
pH (su)	7.19	7.20	Lognormal	5.6 – 8.8
Specific Conductance (µmhos/cm)	113,000	114,000	Lognormal	175,000
Total Dissolved Solids	64,200	66,100	Lognormal	80,700
Total Organic Carbon	0.66 J (1.0)	0.80 J (1.0)	Nonparametric	<5.0
Total Organic Halogens	0.25	0.13	Nonparametric	14.6
Total Suspended Solids	31	35	Nonparametric	33.3
WQSP-1 Total Trace Metals				
Antimony	ND (0.010)	ND (0.010)	Nonparametric	0.33
Arsenic	0.0238 (0.010)	0.0224 (0.010)	Nonparametric	<0.1
Barium	0.032 J (0.05)	0.029 J (0.05)	Nonparametric	<1.0
Beryllium	0.0021 J (0.015)	0.0023 J (0.015)	Nonparametric	<0.02
Cadmium	ND (0.015)	ND (0.015)	Nonparametric	<0.2
Chromium	ND (0.03)	ND (0.03)	Nonparametric	<0.5
Iron	0.19 J (0.25)	ND (0.25)	Nonparametric	0.91
Lead	ND (0.025)	ND (0.025)	Nonparametric	0.105
Mercury	ND (0.0040)	ND (0.0040)	Nonparametric	<0.002
Nickel	ND (0.05)	ND (0.05)	Nonparametric	0.490
Selenium	0.0398 (0.010)	0.0301 (0.010)	Nonparametric	0.150
Silver	ND (0.025)	ND (0.025)	Nonparametric	<0.5
Thallium	ND (0.010)	ND (0.010)	Nonparametric	0.98
Vanadium	0.023 J (0.25)	0.024 J (0.25)	Nonparametric	<0.1
WQSP-1 Major Cations, Dissolved				
Calcium	1,820	1,790	Normal	2,087
Magnesium	1,210	1,200	Normal	1,247
Potassium	575	557	Lognormal	799
Sodium	21,700	21,600	Lognormal	22,090
WQSP-1 Major Anions				
Alkalinity	48.7	48.8	Lognormal	55.8
Chloride	40,400	40,800	Normal	40,472
Nitrogen, NO ₃ (As N)	ND (1.0)	ND (1.0)	Nonparametric	<10.0
Sulfate	5,030	4,780	Normal	5,757

Refer to footnotes at end of table.

Table 3 (Continued)
Round 30 Analytical Data Summary

WQSP-2 Culebra				
Chemical	Concentration (mg/L)		Distribution Type^a	95th UTLV Or 95th Percentile
	Sample	Duplicate		
WQSP-2 General Chemistry				
Specific Gravity ^b	1.044	1.042	Lognormal	1.06
pH (su)	7.19	7.23	Normal	7.0–7.6
Specific Conductance (µmhos/cm)	112,000	112,000	Lognormal	124,000
Total Dissolved Solids	65,200	64,900	Normal	80,500
Total Organic Carbon	0.34 J (1.0)	0.53 J (1.0)	Nonparametric	7.97
Total Organic Halogens	0.078	0.162	Lognormal	202
Total Suspended Solids	37	38	Nonparametric	43.0
WQSP-2 Total Trace Metals				
Antimony	ND (0.010)	ND (0.010)	Nonparametric	<0.5
Arsenic	ND (0.010)	ND (0.010)	Nonparametric	0.062
Barium	0.028J (0.10)	0.027 J (0.10)	Nonparametric	<1.0
Beryllium	0.0054 J (0.03)	0.0059 J (0.03)	Nonparametric	<1.0
Cadmium	ND (0.02)	ND (0.02)	Nonparametric	<0.5
Chromium	ND (0.06)	ND (0.06)	Nonparametric	<0.5
Iron	ND (0.5)	0.15 J (0.5)	Nonparametric	0.91
Lead	ND (0.05)	ND (0.05)	Nonparametric	0.163
Mercury	ND (0.0008)	ND (0.0008)	Nonparametric	<0.002
Nickel	ND (0.10)	ND (0.10)	Nonparametric	0.37
Selenium	ND (0.010)	ND (0.010)	Nonparametric	0.150
Silver	ND (0.05)	ND (0.05)	Nonparametric	<0.5
Thallium	ND (0.010)	ND (0.010)	Nonparametric	0.980
Vanadium	0.036 J (0.50)	0.037 J (0.50)	Nonparametric	<0.1
WQSP-2 Major Cations, Dissolved				
Calcium	1,590	1,550	Lognormal	1,827
Magnesium	1,080	1,070	Normal	1,244
Potassium	492	493	Lognormal	845
Sodium	20,800	19,500	Normal	21,900
WQSP-2 Major Anions				
Alkalinity	45.3	45.8	Normal	70.3
Chloride	38,200	37,500	Normal	39,670
Nitrogen, NO ₃ (As N)	ND (20)	ND (20)	Nonparametric	<10.0
Sulfate	5,710	5,700	Normal	6,590

Refer to footnotes at end of table.

Table 3 (Continued)
Round 30 Analytical Data Summary

WQSP-3 Culebra				
Chemical	Concentration (mg/L)		Distribution Type^a	95th UTLV Or 95th Percentile
	Sample	Duplicate		
WQSP-3 General Chemistry				
Specific Gravity ^b	1.144	1.144	Normal	1.17
pH (su)	6.78	6.78	Lognormal	6.6 – 7.2
Specific Conductance (µmhos/cm)	301,000	305,000	Normal	517,000
Total Dissolved Solids	232,000	222,000	Lognormal	261,000
Total Organic Carbon	0.28 J (1.0)	1.61	Nonparametric	<5.0
Total Organic Halogens	0.50	0.38	Nonparametric	55.0
Total Suspended Solids	96	115	Nonparametric	107
WQSP-3 Total Trace Metals				
Antimony	ND (0.010)	ND (0.010)	Nonparametric	<1.0
Arsenic	ND (0.010)	ND (0.010)	Nonparametric	<1.0
Barium	0.063 J (0.50)	0.051 J (0.50)	Nonparametric	<1.0
Beryllium	0.020 J (0.15)	ND (0.15)	Nonparametric	<0.1
Cadmium	ND (0.10)	ND (0.10)	Nonparametric	<0.5
Chromium	ND (0.30)	ND (0.30)	Nonparametric	<2.0
Iron	0.89 J (2.5)	0.34 J (2.5)	Nonparametric	<4.0
Lead	ND (0.25)	ND (0.25)	Nonparametric	0.800
Mercury	ND (0.004)	ND (0.004)	Nonparametric	<0.002
Nickel	ND (0.50)	ND (0.50)	Nonparametric	<5.0
Selenium	ND (0.010)	ND (0.010)	Nonparametric	<2.0
Silver	ND (.25)	ND (0.25)	Nonparametric	0.310
Thallium	ND (0.010)	ND (0.010)	Nonparametric	5.800
Vanadium	0.12 J (2.5)	0.067 J (2.5)	Nonparametric	<5.0
WQSP-3 Major Cations, Dissolved				
Calcium	1,430	1,540	Normal	1,680
Magnesium	2,320	2,530	Lognormal	2,625
Potassium	1,430	1,560	Lognormal	3,438
Sodium	74,400	70,300	Nonparametric	140,400
WQSP-3 Major Anions				
Alkalinity	30.7	29.9	Lognormal	54.5
Chloride	140,000	150,000	Lognormal	149,100
Nitrogen, NO ₃ (As N)	ND (20)	ND (20)	Nonparametric	<12.0
Sulfate	8,070	8,080	Normal	8,015

Refer to footnotes at end of table.

Table 3 (Continued)
Round 30 Analytical Data Summary

WQSP-4 Culebra				
Chemical	Concentration (mg/L)		Distribution Type^a	95th UTLV Or 95th Percentile
	Sample	Duplicate		
WQSP-4 General Chemistry				
Specific Gravity ^b	1.074	1.074	Lognormal	1.09
pH (su)	7.17	7.17	Lognormal	6.8 – 7.6
Specific Conductance (µmhos/cm)	181,000	183,000	Lognormal	319,800
Total Dissolved Solids	100,000	107,000	Normal	123,500
Total Organic Carbon	0.84 J (1.0)	0.28 J (1.0)	Nonparametric	<5.0
Total Organic Halogens	0.20	0.25	Lognormal	17.0
Total Suspended Solids	131	46	Nonparametric	57.0
WQSP-4 Total Trace Metals				
Antimony	ND (0.0050)	ND (0.0050)	Nonparametric	<10.0
Arsenic	0.0067	0.0055	Nonparametric	<0.5
Barium	0.028 J (0.50)	0.036 J (0.50)	Nonparametric	1.00
Beryllium	ND (0.15)	ND (0.15)	Nonparametric	0.25
Cadmium	ND (0.10)	ND (0.10)	Nonparametric	<0.5
Chromium	ND (0.30)	ND (0.30)	Nonparametric	<2.0
Iron	0.48 J (2.5)	0.29 J (2.5)	Nonparametric	2.245
Lead	ND (0.25)	ND (0.25)	Nonparametric	0.525
Mercury	ND (0.0010)	ND (0.0010)	Nonparametric	<0.002
Nickel	ND (0.50)	ND (0.50)	Nonparametric	<5.0
Selenium	0.0062	0.0083	Nonparametric	2.009
Silver	ND (0.25)	ND (0.25)	Nonparametric	0.519
Thallium	ND (0.0050)	ND (0.0050)	Nonparametric	1.00
Vanadium	0.066 J (2.5)	0.066 J (2.5)	Nonparametric	<5.0
WQSP-4 Major Cations, Dissolved				
Calcium	1,660	1,500	Lognormal	1,834
Magnesium	1,300	1,180	Lognormal	1,472
Potassium	808	739	Lognormal	1,648
Sodium	35,600	36,100	Normal	38,790
WQSP-4 Major Anions				
Alkalinity	37.0	38.0	Normal	47.1
Chloride	65,500	69,000	Normal	63,960
Nitrogen, NO ₃ (As N)	ND (5.0)	ND (5.0)	Nonparametric	<10.0
Sulfate	7,410	8,490	Normal	7,927

Refer to footnotes at end of table.

Table 3 (Continued)
Round 30 Analytical Data Summary

WQSP-5 Culebra				
	Concentration (mg/L)			
Chemical	Sample	Duplicate	Distribution Type^a	95th UTLV Or 95th Percentile
WQSP-5 General Chemistry				
Specific Gravity ^b	1.017	1.016	Normal	1.04
pH (su)	7.48	7.49	Normal	7.4 – 7.9
Specific Conductance (µmhos/cm)	49,100	49,800	Lognormal	67,700
Total Dissolved Solids	32,900	29,900	Nonparametric	43,950
Total Organic Carbon	1.22	1.62	Nonparametric	<5.0
Total Organic Halogens	0.038	0.035	Lognormal	8.37
Total Suspended Solids	11	11	Nonparametric	<10
WQSP-5 Total Trace Metals				
Antimony	ND (0.010)	ND (0.010)	Nonparametric	0.073
Arsenic	ND (0.010)	ND (0.010)	Nonparametric	<0.5
Barium	ND (0.25)	0.012 J (0.25)	Nonparametric	<1.0
Beryllium	ND (0.075)	ND (0.075)	Nonparametric	<0.02
Cadmium	ND (0.050)	ND (0.050)	Nonparametric	<0.05
Chromium	ND (0.15)	ND (0.15)	Nonparametric	<0.5
Iron	0.51 J (1.3)	0.32 J (1.3)	Nonparametric	0.795
Lead	ND (0.13)	ND (0.13)	Nonparametric	<0.05
Mercury	ND (0.0020)	ND (0.0020)	Nonparametric	<0.002
Nickel	ND (0.25)	ND (0.25)	Nonparametric	<0.1
Selenium	ND (0.010)	ND (0.010)	Nonparametric	<0.1
Silver	ND (0.13)	ND (0.13)	Nonparametric	<0.5
Thallium	ND (0.010)	ND (0.010)	Nonparametric	0.209
Vanadium	ND (1.25)	ND (1.25)	Nonparametric	2.70
WQSP-5 Major Cations, Dissolved				
Calcium	977	1040	Lognormal	1,303
Magnesium	464	472	Nonparametric	547
Potassium	317	324	Lognormal	622
Sodium	9,430	9,910	Normal	11,190
WQSP-5 Major Anions				
Alkalinity	45.1	45.0	Lognormal	56
Chloride	16,000	16,000	Lognormal	18,100
Nitrogen, NO ₃ (As N)	ND (5.0)	ND (5.0)	Nonparametric	<10.0
Sulfate	5,760	5,700	Normal	6,129

Refer to footnotes at end of table.

Table 3 (Continued)
Round 30 Analytical Data Summary

WQSP-6 Culebra				
	Concentration (mg/L)			
Chemical	Sample	Duplicate	Distribution Type^a	95th UTLV Or 95th Percentile
WQSP-6 General Chemistry				
Specific Gravity ^b	1.013	1.011	Normal	1.02
pH (su)	7.65	7.69	Normal	7.5 – 7.9
Specific Conductance (µmhos/cm)	24,000	19,900	Lognormal	27,660
Total Dissolved Solids	15,400	15,300	Lognormal	22,500
Total Organic Carbon	1.02	1.12	Nonparametric	10.14
Total Organic Halogens	0.016	0.019	Lognormal	1.54
Total Suspended Solids	13	10	Nonparametric	14.8
WQSP-6 Total Trace Metals				
Antimony	ND (0.0050)	ND (0.0050)	Nonparametric	0.140
Arsenic	ND (0.0050)	ND (0.0050)	Nonparametric	<0.5
Barium	0.0103	0.0105	Nonparametric	<1.0
Beryllium	ND (0.0030)	ND (0.0030)	Nonparametric	<0.02
Cadmium	ND (0.0020)	ND (0.0020)	Nonparametric	<0.05
Chromium	ND (0.0060)	ND (0.0060)	Nonparametric	<0.5
Iron	0.0985	0.0924	Nonparametric	3.105
Lead	ND (0.025)	ND (0.025)	Nonparametric	0.150
Mercury	ND (0.00002)	ND (0.00002)	Nonparametric	<0.002
Nickel	ND (0.050)	ND (0.050)	Nonparametric	<0.5
Selenium	ND (0.0050)	ND (0.0050)	Nonparametric	0.10
Silver	ND (0.005)	ND (0.005)	Nonparametric	<0.5
Thallium	ND (0.0050)	ND (0.0050)	Nonparametric	0.560
Vanadium	0.0056 J (0.05)	0.0057 J (0.05)	Nonparametric	0.070
WQSP-6 Major Cations, Dissolved				
Calcium	670	681	Normal	796
Magnesium	210	220	Lognormal	255
Potassium	160	164	Lognormal	270
Sodium	4,290	4,460	Lognormal	6,290
WQSP-6 Major Anions				
Alkalinity	44.4	38.7	Normal	55.8
Chloride	5,510	5,890	Nonparametric	15,800
Nitrogen, NO ₃ (As N)	ND (0.2)	ND (0.2)	Nonparametric	7.45
Sulfate	4,480	4,820	Lognormal	5,557

Refer to footnotes at end of table.

Table 3 (Continued)
Round 30 Analytical Data Summary

WQSP-6A Dewey Lake				
Chemical	Concentration (mg/L)		Distribution Type^a	95th UTLV Or 95th Percentile
	Sample	Duplicate		
WQSP-6A General Chemistry				
Specific Gravity ^b	1.0000	0.9994	Nonparametric	1.01
pH (su)	7.43	7.43	Normal	6.8 – 8.0
Specific Conductance (µmhos/cm)	3,550	3,570	Lognormal	5,192
Total Dissolved Solids	3,520	3,570	Nonparametric	11,000
Total Organic Carbon	0.40 J (1.0)	0.29 J (1.0)	Nonparametric	15.45
Total Organic Halogens	ND (0.01)	ND (0.01)	Normal	0.19
Total Suspended Solids	ND (10)	2 J (10)	Nonparametric	91.0
WQSP-6A Total Trace Metals				
Antimony	ND (0.0010)	ND (0.0010)	Nonparametric	0.480
Arsenic	ND (0.0010)	ND (0.0010)	Nonparametric	<0.5
Barium	ND (0.010)	ND (0.010)	Nonparametric	<0.1
Beryllium	ND (0.003)	ND (0.003)	Nonparametric	<0.01
Cadmium	ND (0.002)	ND (0.002)	Nonparametric	<0.5
Chromium	ND (0.006)	ND (0.006)	Nonparametric	<0.5
Iron	0.045 J (0.05)	0.035 J (0.05)	Nonparametric	0.505
Lead	ND (0.005)	ND (0.005)	Nonparametric	<0.05
Mercury	ND (0.0002)	ND (0.0002)	Nonparametric	<0.002
Nickel	0.0044 J(0.01)	0.0045 J(0.01)	Nonparametric	0.284
Selenium	0.023	0.024	Nonparametric	0.220
Silver	ND (0.005)	ND (0.005)	Nonparametric	<0.5
Thallium	ND (0.0010)	ND (0.0010)	Nonparametric	<0.058
Vanadium	0.057	0.056	Nonparametric	<0.50
WQSP-6A Major Cations, Dissolved				
Calcium	563	558	Normal	733
Magnesium	160	157	Normal	188
Potassium	3.87	3.92	Lognormal	10.1
Sodium	224	221	Lognormal	369
WQSP-6A Major Anions				
Alkalinity	102	103	Lognormal	113
Chloride	329	331	Nonparametric	6,723
Nitrogen, NO ₃ (As N)	6.37	6.72	Normal	12.2
Sulfate	2,130	2,160	Lognormal	2,543

Refer to footnotes at end of table.

Table 3 (Continued)
Round 30 Analytical Data Summary

Note: Values in **bold** exceed, or are outside of the range for, the 95th UTLV or 95th percentile.

^aBaseline sample distribution type based upon Rounds 1 through 10. The 95th UTLV is used in cases where the sample distribution type is either normal or lognormal. The 95th percentile value is used in cases where the sample distribution type is nonparametric or had greater than 16 percent non-detects.

^bSpecific Gravity is compared to Density (g/mL) as presented in Addendum 1 (DOE 2000).

J = Estimated concentration. The calculated concentration is between the laboratory's MDL and the MRL for the particular sample.

µmhos/cm = Micromhos per centimeter.

mg/L = Milligram(s) per liter.

ND () = The target analyte was analyzed for but not detected. The analytical result is less than the laboratory's MRL or PQL for that sample, which is shown in parentheses.

pH (su) = Potential of hydrogen (measure of alkalinity or acidity) standard unit.

UTLV = Upper tolerance limit value in mg/L.

WQSP = Water Quality Sampling Program.

3.1 Volatile and Semivolatile Organic Compounds

All of the Round 30 VOC and SVOC concentrations reported for man-made organic compounds were less than the MRL in the groundwater samples. The MRLs were 1.0 µg/L for all target VOCs except for isobutanol, 2-butanone, and methylene chloride, which had MRLs of 5.0 µg/L. The reason for the higher MRLs for these three compounds is that isobutanol and 2-butanone have poor purging efficiencies and methylene chloride has a background concentration due to its ubiquity in a laboratory environment. The only detection of any VOCs was in WQSP-5, and the concentrations were the same as detected in the field blank suggesting the compound was not a component of the groundwater. There were no SVOC detections in any of the groundwater samples either above or below the MRL of 5.0 µg/L.

The lowest point on the initial calibration curve usually establishes the laboratory's reporting range and thus the MRL for each target analyte. The low calibration point on the calibration curves for the Round 30 VOC samples was 0.5 µg/L, and the low point on the curve for the SVOCs analyses was 2.5 µg/L.

MRLs for VOCs and SVOCs can be influenced by the TDS concentration of water samples. The Round 30 analyses did not show any adverse effects from the high TDS samples for the organics. The area counts for the internal standards were in the normal range, and the SVOC samples did not foam during extraction during this round. The matrix spike (MS) and matrix spike duplicate (MSD) recoveries were also in the normal range for the VOCs and SVOCs.

3.2 Trace Metals

Groundwater samples were analyzed for a suite of trace metals as required by the Permit. Historically, most of these target analyte metals have not been detected in the DMP samples although the detection limits have varied. The updated baseline analysis results (DOE,

November 2000) show nonparametric distributions for most of the trace metals, based upon the small number of samples analyzed and the high percentage of non-detects.

The MRLs listed in the SOW do not take into account dilution requirements for samples with high concentrations of dissolved salts. The SOW-prescribed MRLs could not be met for some of the target metals analyzed by ICP in WQSP-1, WQSP-2, WQSP-3, WQSP-4, and WQSP-5 due to the high native salt concentrations and the associated dilution factors required to be able to analyze the samples. The metals Sb, As, Se, and Tl were analyzed separately by inductively coupled plasma emission spectroscopy combined with mass spectrometry (ICP/MS), and the SOW-prescribed MRLs were readily met for these metals.

For those samples where the MRL could not be met, the MDL concentrations were generally lower than the SOW reporting limit concentrations, and the metal concentrations could still be estimated if detected in the samples. The specific SOW-prescribed MRLs, the laboratory's actual MRLs (PQLs), and the laboratory's actual MDL for each analysis are listed on the data summary spreadsheets in the appendix for each WQSP well.

The trace metal analysis results for Round 30 were reported as Not Detected (ND) with the exceptions of the bulleted items below. In most cases the metals detected and their concentrations were very similar to detections in previous rounds.

- WQSP-1 contained detects for barium at concentrations of 0.032 mg/L in the primary sample and 0.029 mg/L in the duplicate sample. Beryllium was detected at the very low concentrations of 0.0021 and 0.0023 mg/L in the primary and duplicate sample, respectively. Iron was detected in the primary sample at 0.19 mg/L but was not detected in the duplicate sample. Vanadium was detected at 0.023 mg/L in the primary sample and 0.024 mg/L in the duplicate sample. All the trace metal concentrations were between the MDL and MRL and are J flagged as estimated.
- WQSP-2 contained detects for barium at concentrations of 0.028 mg/L in the primary sample and 0.027 mg/L in the duplicate sample. Beryllium was detected at the very low concentrations of 0.0054 and 0.0059 mg/L in the primary and duplicate sample, respectively. Iron was detected in the duplicate sample at 0.15 mg/L but was not detected in the primary sample. Vanadium was detected at 0.036 mg/L in the primary sample and 0.037 mg/L in the duplicate sample. All the trace metal concentrations were between the MDL and MRL and are J flagged as estimated.

- WQSP-3 contained detects for barium at concentrations of 0.063 mg/L in the primary sample and 0.051 mg/L in the duplicate sample. Beryllium was detected at 0.020 mg/L in the primary sample but was not detected in the duplicate sample. Iron was detected in the primary sample at 0.89 mg/L and the duplicate sample at 0.34 mg/L. Vanadium was detected at 0.12 mg/L in the primary sample and 0.067 mg/L in the duplicate sample. All the trace metal concentrations were between the MDL and MRL and are J flagged as estimated.
- WQSP-4 contained detects for barium at concentrations of 0.028 mg/L in the primary sample and 0.036 mg/L in the duplicate sample. Iron was detected in the primary sample at 0.48 mg/L and the duplicate sample at 0.29 mg/L. Vanadium was detected at 0.066 mg/L in both the primary and duplicate sample. All the trace metal concentrations were between the MDL and MRL and are J flagged as estimated.
- WQSP-5 contained a detect for barium at 0.012 mg/L in the duplicate sample, but it was not detected in the primary sample. Iron was detected at 0.51 mg/L in the primary sample and 0.32 mg/L in the duplicate sample. The concentrations were between the MDL and MRL and are J flagged as estimated.
- WQSP-6 contained detects for barium at concentrations of 0.0103 mg/L in the primary sample and 0.0105 mg/L in the duplicate sample. Iron was detected in the primary sample at 0.0985 mg/L and in the duplicate sample at 0.0924 mg/L. Vanadium was detected at 0.0056 mg/L in the primary sample and 0.0057 mg/L in the duplicate sample. The Ba and V concentrations were between the MDL and MRL and are J flagged as estimated. The Fe concentration was above the lab's PQL, but was over five times lower than the SOW-prescribed MRL.
- WQSP-6A contained detects for iron at 0.045 mg/L and 0.035 mg/L. Nickel was detected at 0.0044 mg/L in the primary sample and 0.0045 mg/L in the duplicate sample. Vanadium was detected at 0.0571 mg/L in the primary sample and 0.0563 mg/L in the duplicate sample. Selenium was detected at 0.023 mg/L in the primary sample and 0.024 mg/L in the duplicate sample. The Fe and Ni concentrations were between the MDL and MRL and are J flagged as estimated. The V and Se concentrations were just above the lab's PQLs.

3.3 General Chemistry Parameters Including Major Cations and Anions

In addition to the 55 target analytes listed in Table 1, the concentrations of alkalinity, sodium, sulfate, and nitrate were measured in the DMP groundwater samples. Total Kjeldahl Nitrogen was also measured in the primary sample of WQSP-6A. The target analyte concentrations in Round 30, including those of the major cations, were all below the 95th UTLV or 95th percentile concentrations from the baseline studies with the following exceptions:

- WQSP-1: The chloride concentration in the duplicate sample was 40,800 mg/L, just above the 95th UTLV concentration of 40,472 mg/L. (The primary sample concentration was 40,400 mg/L.) The TSS concentration in the duplicate sample was 35 mg/L, just above the 95th percentile of 33.3 mg/L. (The primary sample concentration was 31 mg/L.)
- WQSP-3: The sulfate concentrations of 8,070 mg/L in the primary sample and 8,080 mg/L in the duplicate sample were higher than the 95th UTLV concentration of 8,015 mg/L. The chloride concentration of 150,000 mg/L in the duplicate sample was higher than the 95th UTLV concentration of 149,100 mg/L. The TSS concentration of 115 mg/L in the duplicate sample was higher than the 95th percentile concentration of 107 mg/L. (The concentration in the primary sample was 96 mg/L.)
- WQSP-4: The chloride concentrations of 65,500 mg/L in the primary sample and 69,000 mg/L in the duplicate sample were both higher than the 95th UTLV concentration of 63,960 mg/L. The sulfate concentration of 8,490 mg/L in the duplicate sample was higher than the 95th UTLV concentration of 7,927 mg/L.
- WQSP-5: The TSS concentrations of 11 mg/L for both the primary and duplicate samples were higher than the 95th percentile concentration of <10 mg/L.

The exceptions listed above are similar to those of Round 29 when both sulfate concentrations exceeded the 95th UTLV in WQSP-3 and both chloride concentrations exceeded the 95th UTLV in WQSP-4. The TSS concentrations are difficult to measure and vary significantly from well to well and round to round due to the solubility and very fine nature of the particles.

3.4 Cation-Anion Balance Analyses

The major constituents, including calcium, magnesium, potassium, sodium, chloride, sulfate, and bicarbonate, generally comprise the majority of dissolved solids in groundwater. The sum of the

cation equivalent weights of these should be close to or equal to the anion equivalent weights. The comparison of the two values indicates the general quality and reliability of the general chemistry indicator parameter analysis data.

The method of evaluating the charge balance according to the standard method (SM 1030E, 2005) is to determine the percent difference, which is equivalent to the absolute value of the total cation meq/L minus the total anion meq/L divided by the sum of the two values times 100. The groundwater analysis data for wells WQSP-1 through WQSP-6A was evaluated for cation-anion equivalent balance by Hall Environmental Analysis Laboratories (HEAL). Table 4 presents the results of these evaluations for the primary samples (the Round 29 values are shown in parentheses for comparison.). The cation-anion charge balances for the duplicate samples are provided on the individual cation-anion balance calculation sheets located in the summary data packets in the appendices to this report. Charge balance percent differences ranged from 1.67 percent (WQSP-6, Culebra) to 7.62 percent for WQSP-3, Culebra).

Table 4
Summary of Analytical Cation-Anion Balances for Round 30 Samples^a

Well	Total Cations (meq/L)	Total Anions (meq/L)	Percent Difference
WQSP-1 Culebra	1160.36 (1078.83) ^b	1233.43 (1229.88)	3.05 (6.54)
WQSP-2 Culebra	1085.55 (993.48)	1197.36 (1214.72)	4.90 (10.02)
WQSP-3 Culebra	3535.07 (3843.00)	4117.86 (4119.02)	7.62 (3.47)
WQSP-4 Culebra	1758.99 (1728.71)	2002.69 (2054.18)	6.48 (8.60)
WQSP-5 Culebra	505.23 (504.90)	572.17 (587.01)	6.21 (7.52)
WQSP-6 Culebra	241.41 (229.82)	249.59 (230.49)	1.67 (0.2)
WQSP-6A Dewey Lake	51.10 (50.47)	56.12 (56.04)	4.68 (5.23)

^aHall Environmental Analysis Laboratory, Albuquerque, NM data. Individual cation-anion balance calculation sheets are provided in the summary data packets for each well in the appendices to this report. The cation-anion data for the duplicate samples are also included on the sheets.

^bRound 29 results in parentheses.

meq/L = Milliequivalents per liter in filtered samples analyzed for cations and anions.

WQSP = Water Quality Sampling Program.

The Round 30 cation-anion balance results were remarkably precise considering the multiple chemical analyses used to generate the sample concentrations. The Round 30 total anion and cation concentrations also agree well with the Round 29 concentrations. A 10-percent difference in cation-anion balance is generally acceptable for the analyses of potable water with low TDS. No individual percent difference value for the total cation-anion balances was equal to or greater

than 10 percent suggesting that the analysis results used to calculate the cation-anion balances were accurate and reliable.

The total anion concentrations were higher than the total cation concentrations for all samples, as is typically the case. The data for the cation analyses was generated using a single analysis technique, and the calibration curves covered a wider range of concentrations than the anion analysis curves. A possible source of analytical error with the anions is that their analyses require multiple dilutions in order to achieve concentrations within the calibration range of the ion chromatograph.

3.5 Data Verification and Validation

The quality and usability of the data generated by the DMP are prescribed in the Verification and Validation (V&V) Procedures implemented with each set of samples. The DMP groundwater and QC data were rigorously evaluated against a checklist which covers most aspects of the sample preservation, preparation and analysis procedures, the associated calibration standards, documentation, chain of custody, QC sample analysis results, and groundwater sample analysis results. The checklist items were taken from various standard methods as well as from guidance provided in USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, 1991, and USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, 1988 (later versions of both of these documents have since been published) and incorporated into WIPP Procedure, WP 02-EM3003, Revision 6, "Data Validation and Verification of RCRA Constituents" (WIPP, September 25, 2009). The data review process provides information on analytical limitations of the data based on specific quality control criteria specified in the standard methods used to analyze the samples. In cases where a quality assurance objective may not have been met, the guidelines prescribe that the reviewer should use professional judgment to determine if data are acceptable or need to be qualified or rejected.

Data validation was performed for the Permittees by staff from the Environmental Monitoring and Hydrology Group of Washington Regulatory and Environmental Services, URS Corp. The data were evaluated against the quality assurance objectives established in the standard methods used to analyze the samples as well as the lab's Standard Operating Procedures (SOPs).

Formerly only the data for the RCRA target analytes (constituents) as measured by analytical methods described in EPA SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, was subjected to the Verification and Validation procedure. The

general chemistry parameters were initially included in the data verification and validation process during Round 27. The general chemistry parameters were analyzed using standard methods from a variety of sources including methods published by the EPA, ASTM International (ASTM) and methods published in *Standard Methods for the Examination of Water and Wastewater* (SM), a joint publication of the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF). The EPA methods were from *Methods for Chemical Analysis of Water and Wastes* (EPA, November 1986) and from SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*.

The general chemistry parameter data were thoroughly reviewed relative to adherence to a standard method, comparability to previous sampling rounds, reasonableness of the data, and how readily the quality assurance/quality control (QA/QC) data met acceptance criteria prescribed in the standard method. A Verification and Validation Checklist was also filled out for each general chemistry indicator parameter method, and the data for the general chemistry parameters is also addressed in the narrative report for each well if there were any issues with the data.

Table 5 shows the standard analytical methods that were used for each of the general parameter analyses. HEAL contracted the analysis of four of the trace metals, Tl, As, Se, and Sb, to another laboratory, Anatek Labs Inc., where the samples were analyzed by ICP-MS according to EPA SW-846 Method 6020A in order to achieve the required MRLs in the high-TDS groundwater samples. HEAL also contracted out the TOX analyses for WQSP-1 through WQSP-6 to Columbia Analytical Services, Inc. since HEAL does not possess this analytical capability (the TOX analyses for WQSP-6A were also performed by Anatek Labs, Inc.).

Table 5
Summary of Analytical Methods Used for the DMP Samples

Target Analyte(s)	Standard Analytical Method
Volatile Organic Compounds	EPA SW-846 Method 8260B
Semivolatile Organic Compounds	EPA SW-846 Method 8270C
Metals	EPA SW-846 Method 6010B
Mercury	EPA SW-846 Method 7470A
ICP/MS Metals (Sb, As, Se, and Tl)	EPA SW-846 Method 6020A
pH	SM 4500-H ⁺ B
Total Organic Carbon	SM 5310B
Total Dissolved Solids	SM 2540C
Total Suspended Solids	SM 2540D
Alkalinity	SM 320B
Anions	EPA Method 300.0
Specific Conductance (Conductivity)	EPA Method 120.1
Total Organic Halides	EPA SW-846 Method 9020
Total Kjeldahl Nitrogen (WQSP-6A Only)	EPA Method 351.1
Specific Gravity	SM 2710F
Cation-Anion Charge Balance	SM 1030E

The remainder of this section provides a general discussion of the data quality requirements associated with each of the Round 30 WQSP wells. Quality control (QC) samples were prepared and analyzed with each analytical batch (termed Sample Delivery Group (SDG) by the analytical laboratory). The purpose of the QC samples was to measure the accuracy and precision and thus the reliability of the chemical analyses.

Accuracy

The accuracy was checked by analyzing initial and continuing calibration standards, method blanks, laboratory control samples (blank spikes), matrix spikes, and matrix spike duplicates as specified in the standard methods and in the corresponding lab SOPs. The daily calibration standards were used to confirm that the response in the daily standard closely matched the corresponding response during the initial calibration. The method blanks were used to confirm that the accuracy of the groundwater sample analyses was not affected by the presence of any of the target analytes that may have been introduced during sample preparation and analysis. The laboratory control sample (LCS) was analyzed to check that the analytical method was in control

by measuring the percent recoveries of the target analytes spiked into clean water. The LCS samples were analyzed in duplicate to check the precision of the measurement techniques.

MS and MSD samples were prepared and analyzed to check the effect of the groundwater sample matrix on the accuracy of the analytical measurements. The MS and MSD samples were generated by spiking the target constituents and general chemistry indicator parameter analytes into separate portions of the primary groundwater samples. The samples were analyzed, and the recoveries of the constituents and parameters measured and reported. Every calibration standard, sample, and quality control sample analyzed by GC/MS served as a surrogate spike sample in that the surrogate recovery compounds were spiked into the samples prior to analysis, and their recoveries were measured and reported with the sample data.

Precision

The precision of the replicate samples analysis data was compiled and reported as part of the data validation process. The primary measure of precision was the agreement of the analysis results from the duplicate groundwater samples collected simultaneously at each DMP well. The agreement of the measured concentrations was very good as can be seen by reviewing the data in Table 3 for those analytes detected in the samples. Precision data was evaluated according to the relative percent difference (RPD) which is the agreement between two measurements and calculated as the difference between the two values divided by the average of the two values times 100. The RPDs of all the duplicate sample measurements were calculated and are provided in the data summary spreadsheets in the appendices for each well. Most of the RPDs were less than 10 indicating good analytical precision. There were just a few individual cases in which the RPD was greater than 20. These analyses were associated with methods that are challenged by the high-brine samples such as TOX and TSS with low concentrations near the MRL of the analytical method. These analyses are addressed in the narrative sections for each DMP well later in this section.

For most types of analyses the LCS sample was reanalyzed to measure the precision of the determinative analysis step as RPD without consideration of any imprecision associated with the sample preparation. The precision of the LCS and duplicate LCS analyses was calculated by the laboratory and is provided in the QA/QC Summary Reports in the appendices for each DMP well. The precision of the LCS pairs readily met the precision objective for each analytical method.

The precision of the MS/MSD analyses was reported by the laboratory on the QA/QC Summary Reports located in the appendices. The MS/MSD data were generally precise and met the quality assurance objective of ≤ 20 RPD as shown on the QA/QC Summary Reports. The only exceptions were for the SVOCs hexachlorobenzene in WQSP-1; pentachlorophenol in WQSP-2; 9 of the 11 SVOC target analytes in WQSP-3, pentachlorophenol in WQSP-4; the SVOCs 2,4-dinitrophenol and pentachlorophenol in WQSP-6; and all 11 SVOCs in WQSP-6A. The poorer precision was due to unusually high recoveries for the SVOCs in some of the samples. No SVOCs were detected in any of the groundwater samples and thus there was no impact on the usability of the data.

The precision of several of the general chemistry parameters, including specific conductance, pH, TDS, and TSS, was generated by analyzing the primary groundwater sample in duplicate as specified in the standard method. The duplicate precision data were quite precise and generally met the quality assurance objectives of ≤ 20 RPD as shown on the QA/QC Summary Reports provided by the laboratory for each DMP well. One exception was for the duplicate analysis of the primary groundwater sample for TSS in WQSP-4. This observation is in line with the difficulty analyzing high-TDS samples discussed above and some imprecision of the TSS analyses in the primary and duplicate groundwater samples as shown in Table 3.

Another type of precision data generated during analysis of samples by GC/MS for VOCs and SVOCs was the agreement of the concentration measured compared to the concentration injected during analysis of the continuing calibration verification standards (CCVs). The measured concentrations were based on the weighted linear or quadratic regression curves from the initial calibration. The CCV precision was measured by percent difference (not relative percent difference-RPD). The CCV precision, also termed bias, is equal to the CCV measured concentration minus the expected concentration divided by the expected concentration times 100. This precision was the determining factor for whether samples could be analyzed or re-calibration was required as prescribed in the lab SOPs and in the standard analytical methods.

The Saturn ion trap gas chromatograph/mass spectrometers used by HEAL to analyze the DMP samples were factory loaded with proprietary quantitation software that used RRFs that were similar to but slightly different from the average RRFs over the calibration range. The RRFs used for quantitation were based on a regression curve where each point on the curve was weighted by the square of the concentration. Some compounds provided linear regression curves and some compounds required quadratic regression curves. In each case the correlation coefficients of the curves for the individual compounds were better than 0.995 (often >0.999)

and provided superior quantitation to using simple average RRFs. The average RRFs are included in the laboratory's raw data packets, but the proprietary linear regression RRFs are not included.

Quality Assurance Objectives

The data quality was evaluated by how well quality assurance objectives were met. The quality assurance objectives are provided in the standard analytical methods and the associated laboratory SOPs. The quality assurance objectives are generally tighter for the general chemistry indicator parameters than for the constituent organics and metals. Typical data quality assurance objectives for general chemistry parameters include recoveries of 80-120 percent for spiked samples and RPDs ≤ 20 for duplicate samples.

The quality assurance objectives for the organic constituents included recoveries of 75-125 percent for LCS samples; recoveries of 60-140 percent for MS/MSD samples; RPDs of ≤ 20 for MS/MSD pairs; agreement of daily calibration standards to within 20 percent difference (bias) from the initial calibration curve; and method blanks with any detected analytes at concentrations less than the MRL and preferably not detected at all. Organic methods also included the recovery of the spiked surrogate compounds. The surrogate recovery objectives were in the range of 30-130 percent for base/neutral compounds and 15-110 percent for acidic compounds according to EPA guidance. HEAL evaluated the recoveries of the surrogates as well as the recoveries of the target analytes against the lab's historical control chart limits, which were generally tighter than the EPA guidance limits.

Hall Environmental Analysis Laboratory, as well as the former laboratory, used a cocktail of compounds that included more compounds than the DMP target VOC and SVOC compounds during calibration of the GC/MS systems. Some of the compounds are termed "Calibration Check Compounds" or CCCs and some are termed "System Performance Check Compounds" (SPCCs). Two of the target DMP SVOC compounds, 1, 4-dichlorobenzene and pentachlorophenol, are CCCs. One of the DMP SVOC target compounds, 2,4-dinitrophenol, is a SPCC. In addition to allowing the lab to use historical control chart limits as the basis of recovery acceptance limits, EPA SW-846 allows that 10 percent of the compounds do not have to meet the initial RRF calibration criteria (<15 percent RSD over the calibration range) as long as the CCC and SPCC compounds meet the criteria. Some DMP target compounds did not meet the <15 percent RSD objective for the average RRFs over the calibration range, but as discussed above, the GC/MS software provided linear and quadratic regression curves with very good correlation coefficients that provided accurate quantitation of the DMP target compounds.

The quality assurance objectives for the metal constituents were generally 80-120 percent recovery for LCS samples, 75-125 percent recovery for MS/MSD samples, and RPDs ≤ 20 for MS/MSD samples. The major cations, calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) required significant dilution to yield analysis results within the calibration range of the instrument. The cations were analyzed separately from the trace metals because of the different dilution factors required. The cations were measured in the diluted samples both as total metals in unfiltered samples and as dissolved metals in filtered samples for the cation-anion balance calculations.

DMP groundwater samples were used to prepare the MS/MSD samples for all the constituents and general parameters. However, for some of the major cations the standard matrix spike concentrations were generally much lower than the native groundwater concentrations. When the spike concentration is < 25 percent of the native sample concentration, the EPA does not require that matrix spike recoveries be reported or the recovery objectives be met. Because of the high native concentrations, the MS/MSD recoveries for sodium and some recoveries for Ca, Mg, and K were not reported. Likewise the native groundwater concentrations of chloride, sulfate, and TDS were very high in the samples, and most of the MS/MSD recoveries were not reported.

The laboratory MRLs (PQLs) could not meet the MRLs listed in the laboratory SOW for some trace metals in some of the Round 30 WQSP groundwater samples due to the high native salt concentrations. The samples needed to be diluted to avoid overloading the analytical instrumentation. However, in most cases the lab's MDL for the analyses was lower than the SOW-prescribed MRLs. MDLs are generally 2-15 times lower than MRLs. These higher MRLs for some Round 30 samples were consistent with the MRLs for the same metals in previous sampling rounds. Sb, As, Se, and Tl were analyzed by ICP/MS, and the MRLs for these metals were 0.010 mg/L or lower in all the DMP groundwater samples.

Additional Information

A data validation narrative was prepared for each WQSP well, which in part described any situations where a QC objective may not have been met and whether there may be an associated impact on the overall quality and usability of the DMP data. The data validation narratives are summarized in the following sections for each WQSP well.

Note that the DMP samples were collected in the order of WQSP-6A first followed by WQSP-6, WQSP-5, WQSP-4, WQSP-3, WQSP-2, and WQSP-1. However, the data are presented in reverse order below starting with WQSP-1.

The bulleted comments below apply to all the wells, except as noted. Inclusion of these summary comments here will reduce the amount of text in the sections for the individual wells that follow.

- DMP groundwater samples were used as the sample matrix for matrix spike and matrix spike duplicate samples (for parameters requiring MS/MSD analyses). The two groundwater samples taken from each well are referred to as the “primary” sample and the “duplicate” sample. The primary samples were used for the MS/MSD.
- The MS and MSD recoveries were often higher than the laboratory objective of 70-130 percent recovery and sometimes higher than the EPA guidance of 60-140 percent recovery for isobutanol, 2-butanone, and 1,1,2,2-tetrachloroethane. It is likely that the purging efficiencies of isobutanol and 2-butanone are higher in the high-TDS spiked groundwater samples than in the clean calibration standards. The 1,1,2,2-tetrachloroethane appears to be a partial degradation product of tetrachloroethylene during the purge and trap analysis of the spiked high-TDS samples. These compounds were not detected in the groundwater samples except that 2-butanone was detected in the WQSP-5 samples at a concentration below the MRL and similar to the concentration detected in the trip blank.
- There were no impacts on groundwater sample data due to method blank contamination for any of the methods to analyze constituents and general chemistry parameters.
- The GC/MS Saturn software used special linear regression software to calculate the RRFs used to quantify the VOC and SVOC compounds in the samples. A standard calibration curve was run but instead of the average RRF over the calibration range being used, each point was weighted by the square of the given concentration. Some compounds yielded linear fits and some compounds yielded quadratic fits. The correlation coefficients were generally better than 0.999. The curve contained a high proportion of calibration standards in the mid range of the curve corresponding to the concentrations of the LCS and MS/MSD samples analyzed for VOCs and SVOCs.

- Quality assurance objectives for precision and accuracy were met for the analyses unless they are specifically addressed in the sections below (all constituents and general chemistry parameters).
- When the native concentration of a given analyte is higher than 3-4 times the spike concentration for the MS/MSD samples, the recovery data are not generally usable according to EPA guidance and as observed with the DMP data. This generally applies to the cations Ca^{++} , Mg^{++} , and Na^{+} , the anions Cl^{-} and SO_4^{-} , and TDS, although some matrix spike data were able to be calculated for these analytes even with the high native concentrations.
- For most VOCs, SVOCs, and trace metal constituents, there was no response for the analytes in the DMP groundwater samples and no validation actions were required. However, any unmet quality assurance objectives are discussed in the sections below.
- VOC and SVOC GC/MS data were searched for the presence of any non-target organic compounds that may be in the samples. The mass spectra and library search results for all peaks in the baseline, including trace peaks greater than 1% of the internal standard, were printed and reviewed by the data validator. Some trace peaks were observed in the groundwater samples but they were also present in the method blank samples. Some of the peaks were attributed to column bleed from the capillary gas chromatography columns used to separate the compounds. Others were not identified by the GC/MS software. However, no peaks were present in the groundwater samples that were not present in the method blank samples.
- TSS and TOX (total organic halogen) are the two analysis methods that are most challenged by the high TDS samples. The detection of TSS appears to be a function of how long the high-TDS samples are allowed to settle before an aliquot of sample is taken for analysis. TOX analyses are affected by the high chloride concentrations in the DMP groundwater samples. The quality assurance objectives for precision and accuracy of the QC samples for these analyses have not always been met. In addition, the QC objective of retaining 90% of the measured TOX on the front granular activated carbon (GAC) column has also not been met with the groundwater samples. Since halogenated organic compounds have not been detected in any of the samples by GC/MS, it is unlikely that the groundwater samples contain halogenated organic compounds.

3.5.1 WQSP-1

Summary for VOCs

Methyl ethyl ketone (2-butanone) was detected in the field blank sample below the MRL at 3.7 ug/L. However, it was not detected in either of the groundwater samples or in the trip blank sample.

Recoveries of isobutyl alcohol, 2-butanone, and 1,1,2,2-tetrachloroethane were higher than the 130 percent recovery objective in both the MS and the MSD. The isobutyl alcohol recoveries were 160 percent and 157 percent; the 2-butanone recoveries were 147 percent and 134 percent; and the 1,1,2,2-tetrachloroethane recoveries were 144 percent and 140 percent, respectively. The compounds were not detected in the groundwater samples. The high-TDS sample matrix causes isobutyl alcohol and 2-butanone to purge more efficiently from the spiked samples than from the calibration standards and 1,1,2,2-tetrachloroethane appears to be a partial degradation product of other chlorinated VOCs.

All other quality assurance objectives were met for the VOC analyses.

Summary for SVOCs

A few of the SVOC compounds yielded higher recoveries in the LCS and LCSD than the lab's historical control chart limits, but all but two of the recoveries were <100 percent. The recovery of hexachlorobenzene was 92 percent in the MSD compared to 74.6 percent in the MS yielding a RPD of 20.9, just above the objective of ≤ 20 RPD. No SVOCs were detected in the groundwater samples.

All other quality assurance objectives were met for the SVOC data.

Summary for Metals Analysis

There were no measured concentrations above the 95th UTLV or 95th percentile. All the quality assurance objectives were met for the trace metals, dissolved cations, and mercury analysis data.

Summary for General Chemistry Parameters

Chloride and sulfate recoveries were not measured in the MS and MSD due to the high native concentrations (this is not a quality issue). The lab's MDL was higher than the SOW-prescribed MRL for nitrate because of the required dilution of the sample.

The breakthrough of TOX from the first granular activated column to the second column exceeded the 10-percent objective. TOX was detected in the primary and duplicate samples with low concentrations of 0.25 and 0.13 mg/L, respectively for a RPD of 63. The measured recoveries of TOX for both the MS and MSD were 580 percent, respectively, for a RPD of 0, but poor accuracy. The recoveries showed significant interference from the native chloride in the samples. However, the measured TOX concentrations in the groundwater samples were similar to concentrations in previous rounds and in other WQSP wells. The TOX analyses seldom meet all the quality assurance objectives because of the high chloride content of the groundwater samples.

The chloride concentration in the duplicate sample was 40,800 mg/L, just above the 95th UTLV concentration of 40,472 mg/L. The TSS concentration in the duplicate sample was 35 mg/L, just above the 95th percentile of 33.3 mg/L.

All other quality assurance objectives were met for the general chemistry indicator parameter analyses.

3.5.2 WQSP-2

Summary for VOCs

Methyl ethyl ketone (2-butanone) was detected in the duplicate sample at 0.98 ug/L, which is below the PQL of 5.0 µ/L. It was not detected in the primary sample or in the trip blank but was detected in the field blank at 2.8 ug/L.

Recoveries of isobutyl alcohol and 2-butanone were higher than the 130 percent recovery objective in the MS and the MSD. The isobutyl alcohol recoveries were 154 percent and 158 percent, and the 2-butanone recoveries were 143 percent and 145 percent. The compounds were not detected in the groundwater samples above the MRL. The high-TDS sample matrix causes isobutyl alcohol and 2-butanone to purge more efficiently from the spiked samples than from the calibration standards.

All other quality assurance objectives were met for the VOC analyses.

Summary for SVOCs

The quality assurance objective for precision of the recoveries of the spiked SVOCs from the MS and MSD samples did not meet the ≤ 20 RPD criterion for pentachlorophenol due to recoveries of 63.8 percent from the MS and 45.2 percent from the MSD for a RPD of 34. The compound was

not detected in the groundwater samples and there was no adverse impact on the quality or usability of the data.

All other quality assurance objectives were met for the SVOC data.

Summary for Metals Analysis

The lab's achievable MDL for Pb (i.e., 0.036 mg/L) was higher than the SOW-prescribed MRL for Pb (i.e., 0.02 mg/L) due to the required dilution of the samples because of the high TDS. The recoveries of calcium, magnesium, and potassium met the recovery objectives in the MS and MSD in the presence of the high native sample concentrations. Sodium was not spiked into the MS and MSD samples.

There were no measured concentrations above the 95th UTLV or 95th percentile. All other quality assurance objectives were met for the trace metals, dissolved cations, and mercury analysis data.

Summary for General Chemistry Parameters

Chloride and sulfate recoveries were not measured in the MS and MSD due to the high native concentrations (this is not a quality issue). The lab's MDL was higher than the SOW-prescribed MRL for nitrate because of the required dilution of the sample.

The breakthrough of TOX from the first granular activated column to the second column exceeded the 10-percent objective. TOX was detected in the primary and duplicate samples with low concentrations of 0.078 and 0.162 mg/L, respectively for a RPD of 70. The MS and MSD recoveries of TOX were 134 percent and 123 percent, respectively, for a RPD of 8.6. The recoveries were higher than the lab's historical control chart objective of 82-121 percent recovery. The TOX analyses usually do not meet all the quality assurance objectives because of the high chloride content of the groundwater samples.

There were no measured concentrations above the 95th UTLV or 95th percentile.

All other quality assurance objectives were met for the general chemistry indicator parameter analyses.

3.5.3 WQSP-3

The WQSP-3 samples were received by HEAL intact the day after sampling, but the temperature of the samples was 8.2°C, which is higher than the objective of $\leq 6^\circ\text{C}$. The samples were immediately transferred to cold storage upon receipt at the lab and analyzed soon thereafter. The high salt concentration of the WQSP-3 samples appears to affect how fast they cool down since the Round 29 samples were also received at the lab at about the same temperature.

The samples typically do not contain organics, and the quality and usability of the sample data should not have been adversely impacted.

Summary for VOCs

Methyl ethyl ketone (2-butanone) was detected at a concentration just above the MRL in the field blank at 5.6 ug/L but was not detected in the trip blank. The compound was not detected in the laboratory method blank, but was detected in the primary and duplicate groundwater samples at a concentration well below the MRL (1.5 ug/L, 1.6 ug/L, respectively).

Recoveries of isobutyl alcohol, 2-butanone, and 1,1,2,2-tetrachloroethane were higher than the 130 percent recovery objective in the MS and the MSD. The compounds were not detected in the samples. The high-TDS sample matrix causes isobutyl alcohol and 2-butanone to purge more efficiently from the spiked samples than from the calibration standards, and 1,1,2,2-tetrachloroethane is produced in small quantities from degradation of other spiked chlorinated organic compounds in the high-chloride aqueous matrix.

All other quality assurance objectives were met for the VOC analyses.

Summary for SVOCs

The quality assurance objective for precision of the recoveries of the spiked SVOCs from the MS and MSD samples did not meet the ≤ 20 RPD criterion for several of the compounds. The recoveries of the compounds were consistently higher from the MSD than from the MS sample. The recoveries of 2,4-dinitrophenol were only about 12 percent, but were higher than the lab's lower limit based on the historical control chart recoveries. No SVOCs were detected in the groundwater samples and there was no adverse impact on the quality or usability of the data.

All other quality assurance objectives were met for the SVOC data.

Summary for Metals Analysis

The lab's achievable MDL was higher than the SOW-prescribed MRL for Cd, Cr, Pb, Ag, and V due to the required dilution of the samples for metals analysis because of the high TDS. Mercury yielded high recoveries of 333 and 327 percent, respectively in the MS and MSD, apparently due to interference from the sample matrix. Mercury was not detected in the groundwater samples. The recoveries of calcium, magnesium, and potassium met the recovery objectives in the MS and MSD in the presence of the high native sample concentrations. Sodium was not measured in the MS and MSD because of its high native sample concentration.

There were no measured concentrations above the 95th UTLV or 95th percentile. All other quality assurance objectives were met for the trace metals, dissolved cations, and mercury analysis data.

Summary for General Chemistry Parameters

Chloride and sulfate recoveries were not measured in the MS and MSD due to the high native concentrations (this is not a quality issue). The lab's MDL was higher than the SOW-prescribed MRL for nitrate because of the required dilution of the sample.

The breakthrough of TOX from the first granular activated column to the second column exceeded the 10-percent objective. TOX was detected in the primary and duplicate samples at 0.50 and 0.38 mg/L, respectively yielding a RPD of 27. The MS and MSD recoveries of TOX were 134 percent and 123 percent, respectively, for an RPD of 8.6. The recoveries were higher than the lab's historical control chart objective of 82-121 percent recovery. The TOX analyses usually do not meet all the quality assurance objectives because of the high chloride content of the groundwater samples.

The TSS concentrations were higher in this sample than the other groundwater samples at 96 mg/L in the primary sample and 115 mg/L in the duplicate sample for a RPD of 18, which meets the precision objective. The laboratory duplicate analysis of the primary sample yielded 102 mg/L for a RPD of 6.1. Although the particle size of the TSS is likely very close to the pore size of the filters, making accurate and reproducible results difficult to achieve, all the TSS quality assurance objectives were met for the WQSP-3 samples.

The sulfate concentrations of 8,070 mg/L in the primary sample and 8,080 mg/L in the duplicate sample were higher than the 95th UTLV concentration of 8,015 mg/L. The chloride concentration of 150,000 mg/L in the duplicate sample was higher than the 95th UTLV concentration of 149,000 mg/L. The TSS concentration of 115 mg/L in the duplicate sample was higher than the 95th percentile concentration of 107 mg/L.

All other quality assurance objectives were met for the general chemistry indicator parameter analyses.

3.5.4 WQSP-4

Summary for VOCs

Methyl ethyl ketone (2-butanone) was detected above the MRL in the field blank sample at 10.7 ug/L, but it was not detected in the trip blank or in the groundwater samples.

Isobutyl alcohol, 2-butanone, and 1,1,2,2-tetrachloroethane recoveries were higher than the 130 percent recovery objective in the MS and the MSD. The compounds were not detected in the samples.

All other VOC quality assurance objectives were met.

Summary for SVOCs

The RPD for the pentachlorophenol recoveries was less than or equal to ≤ 20 RPD objective with recoveries of 38.9 and 49.3 percent. The compound was not detected in the groundwater samples.

All other quality assurance objectives were met for the SVOC data.

Summary for Metals Analysis

The lab's achievable MDL was higher than the SOW-prescribed MRL for Cd, Cr, Pb, Ag, and V due to the need to dilute the high-TDS samples. Vanadium was detected at a trace concentration between the lab's MDL and MRL. The other four metals were not detected. The ICP/MS metals Se and As were detected in the groundwater samples, at trace concentrations well below the SOW-prescribed MRLs.

All other quality assurance objectives were met for the trace metals, dissolved cations, and mercury analysis data.

Summary for General Chemistry Parameters

Nitrate was not detected in the samples, but the MRL was raised to 5.0 mg/L because of the high TDS concentration.

Chloride and sulfate MS and MSD samples are not prepared and analyzed due to the high native concentrations. The lab's MDL of 1.0 mg/L was higher than the SOW-prescribed MRL for nitrate (0.1 mg/L) because of the required dilution of the sample.

TOC concentrations are reported, but the concentrations were lower than the lab's MRL and lower than the SOW-prescribed MRL. The concentrations were quite variable and as a result the precision objective was not met with a RPD of 100. Likewise the TOX concentrations were very low with one concentration above the SOW-prescribed MRL and one concentration lower than the MRL with a resultant RPD of 59. Carryover exceeded ten percent for the TOX analyses as usual for the high-brine samples. However, the accuracy (MS and MSD percent recoveries) and precision quality assurance objectives were met for the MS/MSO analyses with recoveries of 95 percent and 85 percent, respectively.

The TSS analyses yielded imprecise results due to the difficulty of making this measurement in the high-brine samples. The primary and duplicate sample results were 131 mg/L and 46 mg/L, respectively, for a RPD of 96. The TSS tends to be very fine and can re-dissolve or fall out of solution making representative sampling difficult. The TSS concentration of 131 mg/L in the primary sample was higher than the 95th percentile concentration of 57.0 mg/L.

The chloride concentrations of 65,500 mg/L in the primary sample and 69,000 mg/L in the duplicate sample were both higher than the 95th UTLV concentration of 63,960 mg/L. The sulfate concentration of 8,490 mg/L in the duplicate sample was higher than the 95th UTLV concentration of 7,927 mg/L.

All other quality assurance objectives were met for the general chemistry indicator parameter analyses.

3.5.5 WQSP-5

Summary for VOCs

Isobutyl alcohol recovery was higher than the 130-percent objective in the MSD with 141 percent recovery, but the compound met the objective in the MS with a recovery of 125 percent. Methyl ethyl ketone (2-butanone) was detected in the primary and duplicate samples at 2.23 ug/L

and 2.22 ug/L, respectively. The compound was detected just above the MRL in the field blank at 5.1 ug/L and at 2.4 ug/L in the trip blank, a concentration very similar to that detected in the groundwater samples. The detection of 2-butanone in the trip blank at a concentration similar to the duplicate groundwater samples suggests that 2-butanone was not present in the groundwater samples. The trip blank fulfilled its purpose of checking for possible extraneous sources for detection of analytes in a sample, and there was no adverse impact on the quality or usability of the data.

All other quality assurance objectives were met for the VOC analysis data.

Summary for SVOCs

The lab measured one SVOC concentration in the MSD and several SVOC concentrations in the MS and MSD that were higher than the lab's historical control chart limits. The compounds were not detected in the samples, and there was no impact on the quality or usability of the data.

All quality assurance objectives were met for the SVOC analysis data.

Summary for Metals Analysis

The lab's achievable MDL was higher than the SOW-prescribed MRL for Cr, Pb, Ag, and V due to the required dilution of the samples.

There were no measured concentrations above the 95th UTLV or 95th percentile. All other quality assurance objectives were met for the trace metals, dissolved cations, and mercury analysis data.

Summary for General Chemistry Parameters

The MRL for nitrate was raised to 5 mg/L because of the high native anion concentrations. Nitrate was not detected in the samples.

TOX was reproducibly detected in the primary and duplicate samples at 0.038 and 0.035 mg/L, well below the SOW-prescribed MRL of 0.06 mg/L. The MS and MSD recoveries for TOX were 104 and 88 percent, respectively, resulting in a RPD of 17. The TOX analyses seldom meet the quality assurance objectives because of the high chloride content of the groundwater samples. However, the only objective that was not met for these analyses was that the breakthrough of TOX from the first granular activated column to the second column generally exceeded the 10-percent objective.

The TSS concentrations of 11 mg/L for both the primary and duplicate samples were higher than the 95th percentile concentration of <10 mg/L.

All other quality assurance objectives were met for the general chemistry indicator parameter analyses.

3.5.6 WQSP-6

Summary for VOCs

The only quality assurance objectives that were not met for the VOC analyses were that the recovery of isobutyl alcohol was 138 percent in the primary LCS, and the recovery of 2-butanone was just above the high end of the recovery range at 132 percent. Neither compound was detected in the groundwater samples.

All other quality assurance objectives were met for the VOC analyses.

Summary for SVOCs

The only quality assurance objectives that were not met for the SVOC analyses were that the RPD for the MS/MSD recoveries of 2,4-dinitrophenol was 38.4 due to variable 55.6 and 82.0 percent recoveries, and the RPD for the MS/MSD recoveries of pentachlorophenol was 65.5 due to variable 40.6 and 79.9 percent recoveries. The compounds were not detected in the groundwater samples.

All other quality assurance objectives were met for the SVOC analyses.

Summary for Metals Analysis

Sodium, calcium and magnesium recoveries are not required to be reported in the MS and MSD samples due to the high native concentrations (not a quality issue). The lab's PQL was higher than the SOW-prescribed MRL for Pb, Ni, and V, but the lab's MDLs were well below the SOW-prescribed MRLs, so the metals would have been detected if present. Trace concentrations of vanadium were reported at concentrations between the lab MDL and PQL.

There were no measured concentrations above the 95th UTLV or 95th percentile.

All quality assurance objectives were met for the trace metals, dissolved cations, and mercury analysis data.

Summary for General Chemistry Parameters

The lab's MDL (0.2 mg/L) was higher than the SOW-prescribed MRL (0.1 mg/L) for nitrate because of the required dilution of the samples for anion analysis. Nitrate was not detected in the WQSP-6 groundwater samples.

TOX was detected at concentrations above the lab's PQL of 0.01 mg/L, but well below SOW-prescribed MRL of 0.06 mg/L.

There were no measured concentrations above the 95th UTLV or 95th percentile.

All other quality assurance objectives were met for the general chemistry indicator parameter analyses.

3.5.7 WQSP-6A

Summary for VOCs

Methyl ethyl ketone (2-butanone) was detected at a concentration below the MRL in the field blank at 2.7 ug/L, but was not detected in the trip blank or in the groundwater samples.

All quality assurance objectives were met for the VOC analysis data.

Summary for SVOCs

The RPDs for the precision of the recoveries of the matrix spike and matrix spike duplicate were higher than the ≤ 20 RPD quality assurance objective for all the SVOCs. The reason for the high RPDs was that the recoveries of all the compounds from the MS sample were much higher than normal, and some recoveries were higher than the lab's upper control limit, particularly hexachloroethane at 81.6 percent and pentachlorophenol at 113 percent. The reason for the unusually high recoveries in the MS is not known, but there were no adverse effects on the quality or usability of the data since no SVOCs were detected in the samples.

All other quality assurance objectives were met for the SVOC analysis data.

Summary for Metals Analysis

Vanadium and Selenium were the only trace metal detected above the MRL. Trace concentrations of Fe and Ni were detected below the MRL. All the SOW-prescribed detection limits were met for the metals since the samples did not have to be diluted.

There were no measured concentrations above the 95th UTLV or 95th percentile.

All quality assurance objectives were met for the trace metals, dissolved cations, and mercury analysis data.

Summary for General Chemistry Parameters

WQSP-6A was the only well with detectable nitrate as has been the case in previous rounds. TSS was not detected in the primary sample, but was detected in the duplicate sample at a concentration between the MDL and MRL.

There were no measured concentrations above the 95th UTLV or 95th percentile.

All quality assurance objectives were met for the general chemistry indicator parameter analysis data.

4.0 Groundwater Chemistry Analytical Results and Concentration Plots

The WIPP DMP requires that a primary and duplicate sample be collected from each monitoring well and analyzed for each target analyte. The analytical results received from HEAL for each of the samples from each monitoring well (WQSP-1 through WQSP-6A) are presented as individual appendices (Appendices 1 through 7) at the end of this report.

The appendices are divided into sections which include the following information:

- Analytical Results, consisting of the groundwater sampling data summarized in this report as well as the serial sample analysis results generated in the mobile laboratory.
- The laboratory submittals containing the cover sheet as well as sample concentrations and associated QA/QC data for each parameter in each WQSP well including:
 - Sample collection and analysis dates
 - WIPP and laboratory sample numbers
 - Reporting Limits
 - Analyst's initials

- A list of any data qualifiers
- The Chain of Custody Forms and Request for Analysis Forms for each sample
- The Data Verification and Validation Report consisting of:
 - Data Verification and Validation Narrative
 - Verification and Validation Checklists
 - Groundwater concentration and precision summary for trace metals, dissolved cations, and general chemistry indicator parameters including MRLs, MDLs, data flags, duplicate groundwater analysis results, and the precision of the duplicate groundwater analysis results as RPD
- The plots of the concentrations of the metals and the general chemistry parameters for each sampling round.

The concentration plots for the metals and general parameters were reviewed for the presence of existing or developing trends, and no trends are apparent in these data. Other than 2-butanone detected at the same concentration as the trip blank for WQSP-5, no organic compounds were detected in any of the groundwater samples.

5.0 Test for Outliers

An external test was performed on the groundwater monitoring data from the WIPP facility. In the external test, a newly obtained sample value for a selected groundwater target analyte, such as TDS, is simply compared with the established 10 rounds of baseline (background) data to determine whether the suspected outlier is greater, or less, than the 95th UTLV or 95th percentile.

The chemical analysis data from Round 30 showed that four wells contained measured concentrations of target analytes higher than the 95th UTLV or 95th percentile. Three wells involved the concentrations of anions and all four included TSS.

WQSP-1 contained chloride and TSS concentrations just above the 95th UTLV and 95th percentile, respectively in the duplicate groundwater samples but not in the primary groundwater

sample. The chloride concentration was 40,800 mg/L compared to the 95th UTLV concentration of 40,472 mg/L, and the TSS concentration was 35 mg/L, just above the 95th percentile concentration of 33.3 mg/L.

WQSP-3 contained sulfate concentrations just above the 95th UTLV in both the primary and duplicate sample at 8,070 mg/L and 8,080 mg/L, respectively, compared to the 95th UTLV concentration of 8,015 mg/L. The chloride concentration of 150,000 mg/L in the duplicate sample was higher than the 95th UTLV concentration of 149,100 mg/L. The TSS concentration in the duplicate sample of 115 mg/L was just above the 95th percentile concentration of 107 mg/L.

WQSP-4 contained chloride concentrations of 65,500 mg/L and 69,000 mg/L in the primary and duplicate groundwater samples, respectively, compared to the 95th UTLV concentration of 63,960 mg/L. The sulfate concentration of 8,490 mg/L in the duplicate sample was higher than the 95th UTLV concentration of 7,927 mg/L. The TSS concentration of 131 mg/L in the primary sample was higher than the 95th percentile concentration of 57.0 mg/L.

WQSP-5 the TSS concentrations of 11 mg/L for both the primary and duplicate samples were higher than the 95th percentile concentration of <10 mg/L.

6.0 Summary

The WIPP DMP semiannual groundwater sampling at seven WIPP monitoring wells was performed from March 2010 to May 2010 (Sampling Round 30). Six wells, WQSP-1 through WQSP-6, are completed in the Culebra. The seventh well, WQSP-6A, is completed in the Dewey Lake and is located on the same well pad as WQSP-6. Groundwater samples were submitted to HEAL in Albuquerque, New Mexico, for the chemical analyses. HEAL subcontracted the analyses of four metals, Sb, As, Se, and Tl to Anatek Labs Inc. in order to achieve the requisite MRLs and subcontracted the TOX analyses to Columbia Analytical Services, Inc. Sampling and analysis were performed in accordance with requirements specified in the Permit issued by the NMED on October 27, 1999.

The groundwater analysis results from Round 30 were compared with the baseline water quality statistics to determine whether any measurable or statistically significant changes in water quality have, or are, occurring. The concentrations of the Permit-required target analytes in Round 30 were evaluated against the established 95th UTLV or 95th percentile baseline statistic calculated for each monitoring well.

Review of the Round 30 chemical analysis data demonstrated that the applicable Permit required target constituent concentrations were lower than the 95th UTLV or 95th percentile concentration and that all of the general chemistry indicator parameter concentrations were lower than the 95th UTLV or 95th percentile values with the following exceptions:

- WQSP-1 contained chloride and TSS concentrations just above the 95th UTLV and 95th percentile respectively in the duplicate groundwater samples but not in the primary groundwater sample. The chloride concentration was 40,800 mg/L compared to the 95th UTLV concentration of 40,472 mg/L, and the TSS concentration was 35 mg/L, just above the 95th percentile concentration of 33.3 mg/L.
- WQSP-3 contained sulfate concentrations just above the 95th UTLV in both the primary and duplicate sample at 8,070 mg/L and 8,080 mg/L, respectively, compared to the 95th UTLV concentration of 8,015 mg/L. The chloride concentration of 150,000 mg/L in the duplicate sample was higher than the 95th UTLV concentration of 149,100 mg/L. The TSS concentration in the duplicate sample of 115 mg/L was just above the 95th percentile concentration of 107 mg/L.
- WQSP-4 contained chloride concentrations of 65,500 mg/L and 69,000 mg/L in the primary and duplicate groundwater samples, respectively, compared to the 95th UTLV concentration of 63,960 mg/L. The sulfate concentration of 8,490 mg/L in the duplicate sample was higher than the 95th UTLV concentration of 7,927 mg/L. The TSS concentration of 131 mg/L in the primary sample was higher than the 95th percentile concentration of 57.0 mg/L.
- WQSP-5 the TSS concentrations of 11 mg/L for both the primary and duplicate samples were higher than the 95th percentile concentration of <10 mg/L.

In summary, all Permit-required water quality target analytes were measured during the WIPP DMP Sampling Round 30 conducted from March 2010 to May 2010. Evaluation of the resulting water quality data indicates that no contamination of the groundwater has occurred above established baselines.

7.0 *References*

Crawley, M.E., and M. Nagy, April 1998, "Waste Isolation Pilot Plant RCRA Background Groundwater Quality Baseline Report," DOE/WIPP 98-2285, prepared by IT Corporation for Westinghouse Electric Corporation, Waste Isolation Pilot Plant, Carlsbad, New Mexico.

DOE, see U.S. Department of Energy.

EPA, see U.S. Environmental Protection Agency.

U.S. Department of Energy (DOE), November 2000, "Waste Isolation Pilot Plant RCRA Background Groundwater Quality Baseline Report, Addendum 1" DOE/WIPP 98-2285, prepared by IT Corporation for Westinghouse Electric Corporation, WIPP, Carlsbad, NM.

U.S. Environmental Protection Agency (EPA), 2004, "EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review," OSWER 9240.1-45, EPA 540-R-04-004, Office of Superfund Remediation and Technology Innovation, U.S. Environmental Protection Agency, Washington, D.C.

U.S. Environmental Protection Agency (EPA), 1999, "EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review," OSWER 9240.1-05A-P, PB99-963506, EPA 540/R-99/008, Office of Emergency and Remedial Response, U.S. Environmental Protection Agency, Washington, D.C.

U.S. Environmental Protection Agency (EPA), April 1989 and July 1992, "Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities Unified Guidance," EPA/530-SW-89-026, Waste Management Division, Office of Solid Waste, U.S. Environmental Protection Agency, Washington, D.C.

U.S. Environmental Protection Agency (EPA), November 1986, "Test Methods for Evaluating Solid Waste," 3rd ed., Update 3, SW-846, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C.

Waste Isolation Pilot Plant (WIPP), September 25, 2009, "Data Validation and Verification of RCRA Constituents," WP 02-EM3003, Revision 6, Waste Isolation Pilot Plant, Carlsbad, NM.

Standard Methods for the Examination of Water and Wastewater; 21st Edition; American Water Works Association, 2005, ISBN: 0875530478

Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development, Environmental and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information; Cincinnati, OH, 1983; EPA-600/4-79-020

WIPP, see Waste Isolation Pilot Plant.