

types of ecological data collected at the Site. The SED is a Microsoft Access® database that contains all quality-assured ecological data for RFETS from early 1993 through the end of 2001. Data that did not meet the QA objectives are not included in the database. Ecology data in the SED include vegetation monitoring, weed control and controlled burn vegetation monitoring, wildlife surveys (including birds, small mammals, frogs, insects, and fish), Preble's meadow jumping mouse habitat characterization and telemetry tracking, a small amount of soil characterization survey data (for revegetation issues), and a few other types of ecological data. The SED does not contain data on potential contaminants nor is it linked to any GIS or other spatial tool. The data in the SED are primarily observational or catch-and-release; they are considered raw data taken directly off of field logbooks and datasheets. The SED is not intended as a reference for the layperson. It is a repository of quality-assured raw field data collected by Site ecologists and cannot be taken out of context of the methods used to collect the data. Data collection methods are not stored in the database, they are described in reports and field sampling plans.

From 2002 to the present, the ecology data have been stored as separate data sets by sample type, event, and year. Depending on the data set, the data may be in a Microsoft Access® database or in a Microsoft Excel® spreadsheet format. The nonspatial electronic ecology data are stored on the Robin server at the Site in Westminster, Colorado, or on backup electronic media.

Spatial ecology data for the Site are available for several data types and are stored in the GIS on the Gull server in Grand Junction, Colorado. The types of ecological spatial data that are available include annual weed distribution data (for select species), annual weed control locations, biocontrol release locations, vegetation and wildlife monitoring locations (transect end points and sample points), vegetation community classifications, Preble's meadow jumping mouse habitat, wetland locations, wildfire/prescribed burn locations, Preble's meadow jumping mouse and wetland mitigation work, and rare plant locations. These data are available in various ArcGIS® compatible formats. In addition to these types of spatial data, orthorectified aerial and satellite imagery is also available for the Site for different timeframes, including pre- and post-closure.

## **3.6 Validation and Data Quality Assessment**

Data validation and verification (V&V) during CY 2008 was performed by LM personnel at the Grand Junction, Colorado, office. Data quality assessment (DQA) is performed by personnel at the Site. The following section distinguishes DQA from data validation, and discusses the technical basis, equations, and criteria used for DQA of water.

### **3.6.1 General Discussion**

Data validation is the principal means of assessing the usability of water analytical data. Validation also improves overall data quality by allowing the laboratory coordinator to closely monitor laboratory performance and to provide feedback to each laboratory regarding its ability to produce quality data that meets subcontract requirements. The laboratory coordinator may also use the results of data validation to direct analytical work to laboratories that demonstrate superior performance by generating timely, high-quality analytical data for the Site.

Data validation is a rigorous data review performed by the laboratory coordinator or designee on all of the water analytical data generated by the Site. Additionally, the Site lead may request a secondary detailed validation on a case-by-case basis. Data validation is currently performed as specified in Stoller procedure *Environmental Procedures Catalog* (LMS/POL/S04325), “Standard Practice for Validation of Laboratory Data,” GT-9(P). This procedure is based on the following EPA documents:

- EPA 2002, *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*, EPA540/R-01/008, July;
- EPA 1999, *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, EPA540/R-99/008, October;
- EPA 2001, *USEPA Contract Laboratory Program National Functional Guidelines for Low Concentration Organic Data Review*, EPA540/R-01/006, June; and
- EPA 1997, *Evaluation of Radiochemical Data Usability*, Office of Environmental Management, ES/ER/MS-5, April.

All water analytical data collected by the Site are considered valid unless data validation identifies analytical problems that require the data to be qualified. When it is necessary to qualify individual data records, standard qualifier codes (alphanumeric validation codes) are applied.

Common data qualifiers used by LM are defined below. Refer to *Environmental Procedures Catalog*, “Standard Practice for Validation of Laboratory Data,” GT-9(P) for formal definitions.

- U The material was analyzed for but was not detected. The associated numerical value is the sample quantitation limit.
- J The associated numerical value is an estimated quantity.
- R The data are unusable (compound may or may not be present). Resampling and reanalysis are necessary for verification.
- N Presumptive evidence of the presence of the material.
- NJ Presumptive evidence of the presence of the material at an estimated quantity.
- UJ The material was analyzed for but was not detected. The sample quantitation limit is an estimated value.

Data validation includes the evaluation of laboratory QC data such as method blanks, laboratory control samples (LCSs), and spike recoveries. Adherence to sample and extract holding times, standard analytical methods, contractual requirements, and proper documentation are also verified.

Although DQA and data validation examine some of the same QC data, they do so from different perspectives. DQA (in this report) looks at the overall quality of an entire year of water data, in contrast to validation, which looks at the analytical details of individual data packages. Data validation focuses on laboratory performance, while DQA focuses on interpretation of data describing QC samples that originated in the field, such as “field duplicate” samples and “equipment rinse” samples.

In contrast to data validation, the DQA performed by personnel at the Site does not assign data qualifiers to individual analytical results or data packages. DQA is a second level of QA intended to be a general assessment of how well the water data-collection program is operating. The DQA is performed by evaluating water-quality data in terms of the precision, accuracy, representativeness, completeness, and comparability (PARCC) parameters.

### 3.6.2 PARCC Parameters

Use of the PARCC parameters for DQA has been promoted by EPA guidance documents. Accuracy and precision are quantitative measures. Representativeness and comparability are qualitative measures. Completeness is a combination of both quantitative and qualitative measures.

Site personnel evaluate the PARCC parameters by following guidelines published in these former QC documents:

- RMRS 1998, *Procedure for Evaluation of Data for Usability*;
- RMRS 2000b, *Quality Assurance Program Plan for the Automated Surface-Water Monitoring Program*, RF/RMRS-2000-013, Revision 0 ; and
- RMRS 2001, *Quality Assurance Program Plan for the Groundwater Monitoring Program Rocky Flats Environmental Technology Site*.

The following sections discuss the PARCC parameters and the types of data available to assess them.

#### 3.6.2.1 Criteria for Precision

The precision of a measurement is an expression of the mutual agreement between duplicate measurements of the same property taken under similar conditions. Precision can be expressed quantitatively by the relative percent difference (RPD) between real and field duplicate samples for metals, VOCs, polychlorinated biphenyls, and water-quality parameters (WQPs) as defined by the following equation:

$$RPD = \frac{|(S - D)|}{(S + D)/2} * 100$$

where: S = Concentration of analyte in real sample  
 D = Concentration of analyte in duplicate sample  
 RPD = relative percent difference  
 Undetects are not included

The Site uses the duplicate error ratio (DER) to quantify the precision of radionuclide activity data:

$$DER = \frac{|(S - D)|}{\sqrt{[(TPU_S)^2 + (TPU_D)^2]}}$$

where: TPU<sub>S</sub> = Total propagated uncertainty of the sample  
 TPU<sub>D</sub> = Total propagated uncertainty of the duplicate  
 S = Sample result

D = Duplicate (or lab replicate) result  
DER = duplicate error ratio

Because total propagated uncertainty is seldom reported with radionuclide activity data, the two-sigma error or random counting error has been substituted for total propagated uncertainty in the U, Am, and Pu calculations made for this report.

The Site QC criterion for water RPDs is that individual RPDs should be  $\leq 30$  percent. The analogous criterion for DERs is  $\leq 1.96$ . The overall goal for the water data set is to have 85 percent of the RPD and DER values comply with the QC criteria.

### 3.6.2.2 Criteria for Accuracy

Accuracy is the degree of agreement for a measurement with an accepted reference or true value and is a measure of the bias in a system. The closer the measurement is to the true value, the more accurate the measurement. The Site validation process is the principal means for evaluating the accuracy of analytical results.

Because the Site V&V process compares the actual analytical methods used by each laboratory to the contract-required analytical methods, the Site does not repeat this evaluation.

Matrix spike (MS) and matrix spike duplicate (MSD) recoveries are reported by the analytical laboratories for most nonradionuclide analytical suites. Criteria for acceptable MS recoveries vary between laboratories, depending on the analyte and the analytical method. The Site criterion for acceptable MS results ranges from 75 to 125 percent recovery.

LCS recoveries for radionuclides are often available for water-quality data. Laboratories in practice will commonly accept LCS values in the range of 70 to 130 percent. LCS percent recoveries between the 70 to 130 percent laboratory range and the 75 to 125 percent QC range required by the Site laboratory contracts are examined by data validators for acceptability on an analyte-by-analyte basis. The Site criterion for acceptable LCS recoveries ranges from 75 to 125 percent recovery.

Because some laboratories reported LCS results in pCi/L, while others calculated percent recovery, the Site uses the "relative bias" reporting criterion. The relative bias criterion is defined in the Basic Ordering Agreement by the following formula (see Page J-6 of the National Basic Ordering Agreement, Section 2.3.2.5):

$$\text{Relative Bias} = (\text{Observed} - \text{Known}) / \text{Known}$$

where: Observed = measured activity of LCS standard (pCi/L)  
Known = known activity of LCS standard (pCi/L)

Acceptable values for relative bias results range from  $-0.25$  to  $+0.25$ .

### 3.6.2.3 Criteria for Representativeness

Representativeness in DQA is limited to an evaluation of whether analytical results for field samples are truly representative of environmental concentrations, or whether they may have been influenced by the introduction of contamination during collection and handling. The potential

introduction of contamination is commonly evaluated by examination of the analytical results for equipment rinsates.

Equipment rinsates are used to assess the efficacy of the decontamination process used to clean water sampling equipment. Analytes detected in rinsate samples indicate possible cross-contamination between environmental samples. Rinsates are samples of volatile-free “distilled” water that has been poured over or through decontaminated sampling equipment and subsequently handled in the same manner as environmental samples. For flow-paced composite samples that are collected over time in carboys, a location-specific “rinse carboy” is prepared using distilled water. This carboy is treated the same as other surface-water samples from that location, and analyzed for the same parameters. Analytical data for these rinse carboys are used to assess how well the carboys were cleaned between field deployments and to determine whether contamination was introduced during sample preparation.

Although rinsates are used specifically as indicators of cross-contamination from improper decontamination of equipment, they are carried through the entire sampling, shipping, and laboratory process. Therefore, they are good indicators of potential contamination introduced during any of these steps.

#### 3.6.2.4 Criteria for Completeness

A qualitative measure of completeness is the rate of successful sampling. The DQA verifies that all planned samples were collected, unless insufficient water was available for sampling. The completeness goal for successful sampling is the collection of at least 90 percent of the planned samples. However, the availability of water is outside the control of the Site. If all required stations were visited, sampling completeness is considered acceptable.

Completeness as a quantitative measure of data quality may be expressed as the percentage of valid or acceptable data obtained from a measurement system. The Site tracks analytical laboratory performance through both the shipment of samples to the laboratory and the receipt of data from the laboratory. The Site also evaluates data completeness using the following formula:

$$Completeness = DP_u = \frac{DP_t - DP_n}{DP_t} * 100$$

where:  $DP_u$  = Percentage of usable data points

$DP_t$  = Total number of data points

$DP_n$  = Nonusable (rejected) data points

The completeness criterion is having  $\geq 90$  percent valid samples.

### 3.6.2.5 Criteria for Comparability

Comparability is a qualitative parameter. Consistency in the acquisition, handling, and analysis of samples is necessary for comparing results. Samples are collected in accordance with Site standard operating procedures, transported per Site standard operating procedures and U.S. Department of Transportation shipping regulations, and analyzed using standard EPA or nationally recognized analytical methods. This helps to ensure comparability of results with other analyses performed in a similar manner.

The laboratory coordinator or designee verifies that laboratory analyses are performed according to the standard protocols specified by the Site subcontract to each laboratory. Therefore, the analytical results should be comparable to data produced by similar methods.

### 3.6.3 Water DQA Results for CY 2008

During CY 2008, 118 locations were sampled one or more times. This resulted in a total of 317 water samples collected.<sup>28</sup> During CY 2008, 960 bottles of water were submitted to analytical laboratories for analysis. Table 3–102 breaks this data down by sample type.

*Table 3–102. CY 2008 Sample Type Breakdown*

	Unique Water Samples	Unique Bottle Codes
<b>Primary samples (REALs)</b>	300	854
<b>Field duplicates (DUPs)</b>	17	46
<b>Rinsates (RNSs)</b>	19	60
<b>Totals</b>	336	960

Data used to evaluate the PARCC parameters are included in the available CY 2008 analytical data generated by the laboratories. These include analyses of field duplicate and rinsate QC samples submitted to the laboratory, and laboratory-generated QA/QC samples such as LCSs. This PARCC evaluation is limited to analyses for analytes that are listed in Table 1 of RFLMA Attachment 2.<sup>29</sup> By limiting the evaluation to Table 1 analytes, more targeted and accurate assessment is made for analytes that have water-quality standards applicable to the Site. The DQA of these analyses is discussed below by each PARCC parameter.

#### 3.6.3.1 Precision During CY 2008

DERs are indicators of precision for radionuclide analyses. The QC criterion for precision requires that individual DER values should be  $\leq 1.96$ , and overall the data set should have  $\geq 85$  percent compliance with the criterion. Appendix Table B–1 is a tabulation of the DER values for CY 2008 radionuclide analyses. The table has been sorted by the DER parameter so that the range of values is apparent. The DER range is from 0.01 to 0.71.

<sup>28</sup> This is the sum of real and duplicate samples for unique sampling events.

<sup>29</sup> Hardness and total suspended solids are also included, though these analytes are not listed in Table 1 of RFLMA Attachment 2.

Table 3–103 summarizes the DER findings of Table B–1 and indicates if the 85 percent goal has been met. Overall, 100 percent of the DER data are in compliance with the criterion, indicating excellent precision for radionuclide analyses.

*Table 3–103. Summary of DER Values*

Analyte Group	Total Number of DER Results	Number of Unacceptable Results DER >1.96	Number of Acceptable Results	Percentage Acceptable	Goal Met
Radionuclides	6	0	6	100%	Yes

The RPD between real and field duplicate sample results is an indicator of precision for nonradionuclide analyses. Individual RPD values should be  $\leq 30$  percent and at least 85 percent of the RPDs should comply with the criterion. Appendix Table B–2 tabulates RPD values and is sorted first by analyte suite, then by RPD, in order to highlight the RPD range of each suite. RPD values ranged from 0.0 percent to 47.06 percent for metals, 0.0 percent to 12.50 percent for WQPs, and 0.0 percent to 28.57 percent for VOCs/semivolatile organic compounds (SVOCs).

Table 3–104 summarizes the RPD findings of Table B–2 and indicates if the 85 percent goal has been met. During CY 2008, the RPD goal was met for all analyte groups. Overall, the nonradionuclide data had 98.2 percent acceptable RPDs, and therefore exceeded the 85 percent goal.

*Table 3–104. Summary of RPD Values*

Analyte Group	Total Number of RPD Results	Number of Unacceptable Results RPD >30%	Number of Acceptable Results	Percentage Acceptable	Goal Met
Metals	19	1	18	94.7	Yes
WQPs	6	0	6	100	Yes
VOCs/SVOCs	29	0	29	100	Yes
Totals	54	1	53	98.2	Yes (overall)

### 3.6.3.2 Accuracy During CY 2008

MS recoveries provide another measure of accuracy. Appendix Table B–3 displays recoveries for 1,527 MS and MSD analytical records for metals, VOCs/SVOCs, and WQPs. These data are summarized in Table 3–105. All individual suites met the goal with greater than 90 percent of their spike recoveries falling in the acceptable range. Overall, across all analytical suites, the percentage of acceptable MS/MSD results was 98.4 percent.

Table 3–105. Summary of MS and MSD Recovery Data

Analyte Group	Total Number of MS & MSD Results	Number of Low Results Below 75%	Number of High Results Above 125%	Number Acceptable	Percentage Acceptable	Goal Met
Metals	563	3	0	560	99.5	Yes
WQPs	55	0	0	55	100.0	Yes
VOCs/SVOCs	909	3	19	887	97.6	Yes
Totals	1,527	6	19	1,502	98.4	Yes (overall)

Appendix Table B–4 contains 88 relative bias values for LCSs. These are used by the Site to evaluate the accuracy of radionuclide analyses. The QC criterion for the acceptable range of relative bias values is from –0.25 to +0.25. During CY 2008, the bias ranged from –0.140 to +0.230. All of the data met the QC criterion.

LCS results for nonradionuclide suites were available for metals, VOCs/SVOCs, and WQPs (including anions). These LCS recoveries are tabulated in Appendix Table B–5, which is sorted by analyte group, then by percent recovery. There are 461 LCS data records for metals. The LCS recoveries for metals fell in the range 88.0 percent to 115.0 percent and were all within the 75 percent to 125 percent acceptable QC range. There are 1,321 LCS data records for VOCs/SVOCs. LCS recoveries for VOCs/SVOCs fell between 26.6 percent and 130 percent. One hundred and one (101) records are outside the 75 percent to 125 percent acceptable QC range (92.4 percent acceptable). There are 59 LCS data records for WQPs. LCS recoveries for WQPs fell between 95 percent and 105 percent and were all acceptable. Overall for nonradionuclides, 94.5 percent of the LCS recoveries indicate that CY 2008 water analytical data for metals, VOCs/SVOCs, and WQPs are of high accuracy.

Another aspect of accuracy is “rejected data.” Out of 10,377 analytical records representing reals, duplicates, and rinsates during CY 2008, only 2 records were rejected (R or RJ qualified) during data V&V. Another way to state this is that 99.98 percent of the analytical data collected during the year were considered to be valid and usable. Appendix Table B–6 lists the 2 rejected records.

### 3.6.3.3 Representativeness During CY 2008

As defined earlier, representativeness is an evaluation of the sampling procedure for its ability to reflect the true concentrations of contaminants in water. Equipment rinsate samples ( and “rinse carboys”) are used by the Site to determine whether there is introduced contamination from improper or incomplete decontamination of the sampling equipment.

During CY 2008 a total of 718 rinsate analytical records were generated for metals, radionuclides, VOCs/SVOCs, and WQPs. The majority of these records lack evidence of contamination. The remaining 16 records are tabulated in Appendix Table B–7. Three of these are “B”-qualified metals data which constitute only weak evidence of contamination. The B qualifier for inorganics indicates that the concentrations are above the instrument detection limit, but below the method detection limit. Eleven records are “J”-qualified indicating an estimated quantification/result.

Only two records (less than 1 percent; at the top of Table B–7) provide substantial evidence of inadequate decontamination of a sample carboy or equipment. Overall, there is very little evidence of introduced contamination during CY 2008 water sampling and shipping activities. Most of the 718 rinsate records appear to be clean. Therefore, water-quality data for the year are judged to be representative of the actual water concentrations.

Because all required sampling locations were visited, and the samples that could be collected were analyzed, analyses for the year are judged to be representative with respect to spatial coverage.

### 3.6.3.4 Completeness During CY 2008

If sufficient water is available for sampling, the goal is to have 100 percent successful sampling of all required locations. However, the availability of water is beyond the control of the samplers. Surface-water monitoring during CY 2008 targeted sampling at 17 RFLMA surface-water sampling locations. In actuality, samples were collected at 12 sites and were submitted to the laboratory for analysis; five locations were dry for the entire year. Groundwater monitoring during CY 2008 targeted sampling at 92 wells. In actuality, samples were collected at 88 wells and were submitted to the laboratory for analysis; two locations were dry for the entire year. Sampling of the other two wells during CY 2008 was inadvertently missed. These two wells were subsequently sampled in CY 2009, satisfying the RFLMA-required biennial sampling frequency. Treatment system monitoring during CY 2008 targeted sampling at nine locations; samples were collected at all nine locations and were submitted to the laboratory for analysis. Because dry locations do not count against sampling success rates (being beyond the control of samplers) and the two missed wells were still sampled as required, success rates for surface water, groundwater, and treatment system sampling are all 100 percent.

V&V completeness is summarized in Table 3–106. This table compiles, by analyte group, the total number of data points for reals, duplicates, and rinsate samples. It then subtracts rejected data points as well as points that lack validation qualifiers. The result is the net number of usable validated or verified data points, and this is expressed as percent usable data, or percent V&V completeness. The QC goal for completeness is  $\geq 90$  percent.

*Table 3–106. Summary of V&V Data Completeness*

Analyte Group	Number of Data Points	Number of Unvalidated Points	Number Rejected	Net Usable Points	Percent Completeness	Goal Met
Metals	1,685	0	2	1,683	99.88	Yes
Radionuclides	389	0	0	389	100.0	Yes
WQPs	113	0	0	113	100.0	Yes
VOCs/SVOCs	8,190	0	0	8,190	100.0	Yes
	<b>Sum of Number of Data Points</b>	<b>Sum of Number of Unvalidated Points</b>	<b>Sum of Number Rejected</b>	<b>Sum of Net Usable Points</b>	<b>Overall Completeness</b>	<b>Goal Met</b>
<b>Totals</b>	<b>10,377</b>	<b>0</b>	<b>2</b>	<b>10,375</b>	<b>99.98</b>	<b>Yes</b>

Validation completeness for all suites was 99.98 percent and exceeded the completeness goal. Therefore, from the perspective of V&V completeness, the CY 2008 water data are acceptable.

Another measure of completeness is that an adequate number of QC samples (field duplicates and equipment rinsates) must be collected to meet QC requirements. The recommended frequency for collecting duplicate samples is 1 duplicate (DUP) per 20 or fewer primary (REAL) water samples. In other words, duplicates should be collected at a 5 percent or greater frequency per REAL sample. Like duplicates, rinsate samples (RNS) are also to be collected at a 5 percent or greater rate.

The sample collection frequencies of REAL, DUP, and RNS samples are tabulated by analyte group in Table 3–107. The ratios of REAL/DUP samples shown in Table 3–107 meet water program QC goals with 1 DUP per 12.9 REALs. Although an insufficient number of radionuclide DUPs were collected, across all analyte suites and samples collected during the year, the overall frequency of duplicates was 7.75 percent, exceeding program goals ( $\geq 5$  percent).

The ratios of REAL/RNS samples shown in Table 3–107 meet water program QC goals with 1 RNS per 12.5 REALs. Across all analyte suites and samples collected during the year, the overall frequency of rinsates was 8.01 percent, exceeding program goals ( $\geq 5$  percent).

*Table 3–107. Summary of Field QC Samples and Data Records*

Analyte Group	Number of Locations Sampled for REALs	Number of Locations Sampled for DUPs	Ratio REALs/ DUPs (Goal <20)	Ratio REALs/ RNSs (Goal <20)	Number REAL Records	Number DUP Records	Number RNS Records	Total Records
Metals	79	11	20.8	16.5	1,520	73	92	1,685
Radionuclides	23	3	59.7	14.3	358	6	25	389
WQPs	43	6	16.7	14.3	100	6	7	113
VOCs/SVOCs	94	11	11.5	11.8	6,986	610	594	8,190
		<b>Totals</b>	12.9	12.5	<b>8,964</b>	<b>695</b>	<b>718</b>	<b>10,377</b>
		<b>Percentages</b>				<b>7.75%</b>	<b>8.01%</b>	

### 3.6.3.5 Comparability During CY 2008

No significant changes were made to water sampling or analytical procedures during CY 2008. Therefore, the analytical data generated during the year should be generally comparable to corresponding analyses from previous years.

This page intentionally left blank