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Revision 1

100-KW REBOUND STUDY DATA USABILITY ASSESSMENT

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
under Contract 89303320DEM000030

P.O. Box 1464
Richland, Washington 99352

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Terms

CPCCo	Central Plateau Cleanup Company
DQI	data quality indicator
DUA	data usability assessment
EB	equipment (rinsate) blank
FTB	full trip blank
HEIS	Hanford Environmental Information System
LCS	laboratory control sample
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
OU	operable unit
PQL	practical quantitation limit
QA	quality assurance
QC	quality control
RPD	relative percent difference
SAP	sampling and analysis plan
SOP	standard operating procedure

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1 Introduction

This data usability assessment (DUA) report evaluates laboratory data for water samples collected during the 100-KW Rebound Study from May 2021 to July 2022 under DOE/RL-2020-42 Rev. 0, *Parent Rebound Study Sampling and Analysis Plan for the 100-KR-4 Operable Unit* (hereinafter referred to as the 100-KR-4 Rebound sampling and analysis plan [SAP]), and applicable addendum:

- DOE/RL-2020-42-ADD1, *Rebound Study Sampling and Analysis Plan for the 100-KR-4 Operable Unit, Addendum 1*

This DUA completes the U.S. Environmental Protection Agency data quality life cycle (planning, implementation, and assessment).

For this project, a judgmental (focused) sampling design was implemented in the field; therefore, the data quality indicators (DQIs) precision, accuracy/bias, representativeness, comparability, completeness, and sensitivity for the specific datasets are evaluated according to EPA/240/R-02/004, *Guidance on Environmental Data Verification and Data Validation,* and SW-846, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods Compendium.* Data verification and data validation are integral to the DQI evaluation process. The Central Plateau Cleanup Company (CPCCo) will use the results of the DQI evaluation process to interpret the data and determine if the data quality objectives for this activity have been met.

This report documents components of the DUA, including data verification (Chapter 2), data validation (Chapter 3), data quality indicators evaluation (Chapter 4), data quality assessment (Chapter 5), and summary and conclusions (Chapter 6).

1.1 Purpose

The purpose of this DUA is to determine whether the data collected under the 100-KR-4 Rebound SAP (DOE/RL-2020-42) and the associated addendum are the right type and of sufficient quality and quantity to support groundwater remediation decisions. The purpose of the 100-KR-4 Rebound SAP is to detail the groundwater sampling and analysis activities associated with rebound studies within the 100-KR-4 OU. Specific quality control (QC) measures are also provided in the SAP. The purpose of the 100-KR-4 OU SAP Addendum is to provide detailed information to implement an area-specific hexavalent chromium (Cr(VI)) rebound study within the 100-KR-4 Operable Unit (OU).

The DUA process is not intended to be a definitive analysis of a project or problem. Rather, the process provides an initial assessment of the reasonableness of the generated data based solely on the associated QC information and not on the technical interpretations of the data values. The information contained in this report follows guidelines for DUAs established by CPCCo procedures based on EPA/240/R-02/004 and SW-846.

1.2 Scope

This DUA focuses on the chemical data collected by sampling groundwater from nine wells installed in the 100-KR-4 groundwater OU as required by the 100-KR-4 Rebound SAP (DOE/RL-2020-42) and the addendum. The data are evaluated to determine whether they meet the analytical criteria outlined in the SAP and addendum and are adequate to support decision making. The assessment of field analysis data (such as pH or specific conductance) and data collected but not required under the addendum are also not within the scope of this report. The review determined whether the data are the right type, quality, and quantity to support the intended use.

1.3 Project Background

This section describes the sampling design and associated project objectives, including implementation of the sampling design.

1.3.1 Sampling Design

Water samples were collected at predefined frequencies and depths as discussed in the 100-KR-4 Rebound SAP addendum and outlined in Table 1.

1.3.2 Project Objectives

Table 2 presents a summary of the principal study questions for the 100-KR-4 Rebound SAP (DOE/RL-2020-42) groundwater sampling. Principal study questions and data needs are defined in Section 1.3 of DOE/RL-2020-42.

1.3.2.1 Implementation of the Sample Design

Table 1 provides a summary of the wells and the planned frequency of sampling. A review of the applicable analytical data packages indicates all samples were collected and analyzed in accordance with the sampling design except for one sample event during the pre-rebound sample collection on wells 199-K-205 and 199-K-236. The requirement was to take two samples per week for three weeks prior to implementing the rebound study. One of the sample events was collected but the cooler delivery was delayed due to a commercial shipping issue. The samples arrived at the laboratory outside of 2X hold time and out of temperature requirements, so the analysis was cancelled.

Table 1. Principal Study Question Summary and Sampling Frequency

Well Name	Well ID	Previous Use	PSQ[a]							Groundwater Constituents and Properties[b]									PSQ 3 Vertical Sampling	
			1	2a	2b	3	4	5	6	Hexavalent Chromium (F)	Calcium (F)	Magnesium (F)	Potassium (F)	Sodium (F)	Chloride (UF)	Nitrate (UF)	Sulfate (UF)	Alkalinity (UF)	Hexavalent Chromium (F)	Sample Depth m (ft) bgs[b]
199-K-174	C7061	Injection well	X	--	--	X	X	X	X	BM	BM	BM	BM	BM	BM	BM	BM	BM	2x	WT 34 (110) 38 (126)
199-K-175	C7062	Injection well	X	--	--	X	X	X	X	BM	BM	BM	BM	BM	BM	BM	BM	BM	2x	WT 38 (124) 43 (142)
199-K-205[c]	C8292	Extraction well	X	X	--	X	X	X	X	M	BM	BM	BM	BM	BM	BM	BM	BM	BM	WT 37 (120) 52 (170)
199-K-206	C8293	Injection well	X	--	--	X	X	X	X	BM	BM	BM	BM	BM	BM	BM	BM	BM	2x	WT 42 (138) 54 (178)
199-K-223	C9595	Monitoring well	X	--	X	X	X	X	X	BM	BM	BM	BM	BM	BM	BM	BM	BM	2x	WT 34 (110) 52 (170)
199-K-224	C9596	Extraction well	X	--	X	X	X	X	X	BM	BM	BM	BM	BM	BM	BM	BM	BM	BM[d]	WT 40 (130) 53 (175)
199-K-229	C9713	Monitoring well	X	--	X	X	X	X	X	BM	BM	BM	BM	BM	BM	BM	BM	BM	2x	WT 41 (135) 55 (180)
199-K-235	C9973	Monitoring well	X	X	--	X	X	X	X	M	BM	BM	BM	BM	BM	BM	BM	BM	BM	WT 32 (104) 36 (117)
199-K-236[c]	C9974	Monitoring well	X	X	--	X	X	X	X	M	BM	BM	BM	BM	BM	BM	BM	BM	BM	WT 32 (104) 36 (118)

Reference: DOE/RL-2020-42, *Parent Rebound Study Sampling and Analysis Plan for the 100-KR-4 Operable Unit.*

a. Except for the additional sample depths listed for PSQ 3, all groundwater samples including the WT listed for PSQ 3 were collected from the top, or 1.5 m (5 ft) of the water table.

b. Identified constituents were analyzed using the methods specified in Table 2-3 in the 100-KR-4 Parent Rebound SAP (DOE/RL-2020-42).

c. Prior to the implementation of the rebound study, groundwater samples were collected two times per week for three weeks for the identified wells.

d. If hexavalent chromium concentrations remains less than the groundwater remediation target of 20 µg/L during vertical sampling activity within the first three events, the sampling frequency should be reduced to align with river stage sampling.

-- = no data available or not applicable
2x = During the rebound study, two groundwater sampling events occurred at the identified location for the given constituent. The samples targeted the current high (May or June) and low (September or October) river stage periods.
bgs = below ground surface
BM = bimonthly; constituent will be sampled every other month
F = filtered
ID = identification
M = monthly
PSQ = principal study question
UF = unfiltered
WT = water table

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Table 2. Principal Study Questions

Primary Study Question		Data Need
PSQ 1	In the absence of P&T operations, have Cr(VI) concentrations reached concentrations below the interim action remediation target of 20 µg/L and expected to remain stable or decrease?	Increased frequency of Cr(VI) concentration measurements in groundwater in the absence of P&T operations
PSQ 2a	If rebound of Cr(VI) is observed, does it originate from known or suspected continuing sources of groundwater contamination?	High frequency Cr(VI) concentration measurements in groundwater collected at the top of the unconfined aquifer in the absence of P&T operations
PSQ 2b	If rebound of Cr(VI) is observed, does it originate from areas outside of known or suspected continuing sources of groundwater contamination?	Increased frequency of Cr(VI) concentration measurements in groundwater collected at the top of the unconfined aquifer in the absence of P&T operations
PSQ 3	What is the vertical distribution of Cr(VI) within the unconfined aquifer in the absence of P&T operations?	Cr(VI) concentration measurements in groundwater collected vertically through the saturated screen interval in the absence of P&T operations
PSQ 4	What is the magnitude, gradient, and flow direction of groundwater in the absence of P&T operations?	Manual water level and AWLN measurements collected in the absence of P&T operations
PSQ 5	What are the seasonal effects of changing river stage on Cr(VI) concentrations and groundwater flow in the absence of P&T operations?	High frequency Cr(VI) concentration measurements in groundwater
PSQ 6	In the absence of P&T operations, has groundwater reestablished natural conditions?	Increased frequency of major ions (calcium, chloride, magnesium, nitrate, potassium, sodium, and sulfate), alkalinity, specific conductance, and other field parameter measurements in groundwater in the absence of P&T operations

AWLN = automated water-level network
P&T = pump and treat
PSQ = principal study question

1.4 Quality Assurance and Quality Control Requirements

This section describes the analytical and laboratory quality assurance (QA) and QC requirements identified in 100-KR-4 Rebound SAP (DOE/RL-2020-42).

1.4.1 Laboratory Information

RJ Lee laboratory, TestAmerica St Louis (TASL), ALS laboratory and GEL Laboratories, LLC performed sample analyses.

1.4.2 Analytical Methods

Samples were analyzed using methods listed in Table 3. Both multi- and single-component method-based analyses were used. Multi-component method-based analyses are those typically based on EPA methods, as applicable, that yield concentration data for multiple analytes in a single analysis. The analytes may include both target and nontarget analytes. Single-component method-based analyses are those typically based on EPA methods as applicable, that yield concentration data for a single-target analyte in a single analysis. Sample results were reported in the Hanford Environmental Information System (HEIS) database.

Table 3. Analytical Methods

Parameter	Analytical Method(s)
Water	
Calcium	EPA 6010
Magnesium	EPA 6010
Potassium	EPA 6010
Sodium	EPA 6010
Hexavalent chromium	EPA 7196
Alkalinity	SM-2320
Chloride	EPA 300 or 9056
Nitrate	EPA 300 or 9056
Sulfate	EPA 300 or 9056

Notes: For EPA Method 300, see EPA/600/R-93/100, *Methods for the Determination of Inorganic Substances in Environmental Samples*.
For the four-digit EPA methods, see SW-846, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods Compendium*.

EPA = U.S. Environmental Protection Agency
SM = standard method

1.4.3 Analytical Requirements

Analytical performance requirements for groundwater samples are defined in Table 2-3 and Table 2-5 in the 100-KR-4 Rebound SAP (DOE/RL-2020-42).

1.4.4 Laboratory Quality Assurance and Quality Control Requirements

The QA/QC requirements govern nearly all aspects of analytical laboratory operation, including instrument procurement, maintenance, calibration, and operation. Laboratory requirements for internal QC checks are performed as appropriate for the analytical method at a rate of one per analytical batch or 1 in 20 (5%), whichever is more frequent. Laboratory internal QC checks include the following:

- **Laboratory Contamination**. As appropriate to the method, each analytical batch contains a laboratory method blank (material of composition similar to that of the samples with known or minimal contamination of the analytes of interest) carried through the complete analytical process. The method blank is used to evaluate false positive results in samples caused by contamination during handling at the laboratory.
- **Analytical Accuracy**. A laboratory control sample (LCS) is typically run with every analytical batch. The percent recovery of the LCS is used to evaluate analytical accuracy. In addition, for most analyses, a known quantity of representative analytes of interest (matrix spike [MS]) is added to a separate aliquot of a sample from the analytical batch. The known amount added is compared to the actual measured amount to calculate the percent recovery. The recovery percentage of the added MS is used to evaluate analytical accuracy. For analyses not amenable to MS techniques (such as gamma energy analysis) or where analytical recovery is evaluated from recovery of the tracers or carriers, the accuracy of the laboratory preparation and analysis evaluation defaults to the LCS.

- **Analytical Precision**. Separate aliquots removed from the sample containers (duplicate samples) are analyzed for each constituent as appropriate to the analytical method. The duplicate sample results are compared to the original sample results, which are evaluated as relative percent differences (RPDs) and are used to assess analytical precision. Alternately, a matrix spike duplicate (MSD) may be used for assessing precision. For a MSD, a separate aliquot is removed from the same sample container and spiked in the same manner as the MS. The results, not recoveries, from the MS/MSD are used to calculate a RPD and to assess precision.

Laboratories are also subject to periodic audits of laboratory performance, systems, and overall program. Audits check that the laboratories are performing to laboratory contract requirements. No audits were performed specific to the data analyses performed as part of this project.

1.4.4.1 Qualification Flags

During the generation of environmental analytical data, any of several qualification flags may be assigned to an individual result. The HEIS database carries qualification flags applied by three sources: the laboratory, third-party data validator, or a data user or reviewer. The tables of data within this report show all of these applied qualification flags. Potential flags and their meaning are provided in Table 4.

Table 4. Qualification Flags

Flag	Definition
	Laboratory-Applied Flags
>	WETCHEM – Result greater than quantifiable range or greater than upper limit of the analysis range.
*	INORGANICS – Duplicate analysis not within control limits.
+	INORGANICS – Correlation coefficient for MSA is <0.995.
A	ORGANICS – Valid for TICs only. The TIC is a suspected aldol-condensation product.
B	INORGANICS and WETCHEM – The analyte were detected at a value <PQL but ≥MDL. ORGANICS – The analyte was detected in both the associated QC blank and in the sample, and the blank concentration exceeded the customer's contractual requirements. RADIONUCLIDES – The associated QC sample blank has a result ≥2x the MDA; after corrections, result is ≥MDA for this sample.
C	INORGANICS and WETCHEM – The analyte were detected in both the sample and the associated QC method blank, and the blank concentration is >5% of the sample result. ORGANICS (PESTICIDE only) – The identification of a pesticide confirmed by GC/MS.
D	All – Analyte was reported at a secondary dilution factor, typically DF>1 (i.e., the primary preparation required dilution to either bring the analyte within the calibration range or to minimize interference). Required for organics/wetchem if the sample was diluted.
E	INORGANICS – Reported value is estimated because of interference. See comment on cover page, hardcopy case narrative, or specific inorganic hardcopy data sheet.
J	ORGANICS – Estimated value constituent detected at <PQL and ≥MDL and estimated concentration of TICs.
M	INORGANICS – Duplicate precision criteria not met.
N	All (except GC/MS based analysis) – Spike and/or spike duplicate sample recovery is outside control limits. ORGANICS (GC/MS only) – Presumptive evidence of compound based on mass spectral library search.
O	All: The laboratory control sample recovery is outside control limits.
P	ORGANICS (PCB only) - Aroclor target analyte with >25% difference between column analyses.

Table 4. Qualification Flags

Flag	Definition
	Laboratory-Applied Flags
Q	ORGANICS (dioxins & PCB-congeners only) – Estimated maximum concentration. Used if one of the qualitative identification criteria is not met (e.g., chlorine isotopic ratios outside theoretical range).
S	INORGANICS – Reported value determined by the MSA.
T	ORGANICS (GC/MS only) – Spike and/or spike duplicate sample recovery is outside control limits.
U	All – The constituent was analyzed for and was not detected. The data should be considered usable for decision making purposes.
W	INORGANICS– Post-digestion spike recovery for GFAA out of control limit. Sample absorbance <50% of spike absorbance.
X	All – The result-specific translation of this qualifier code is provided in the data report and/or case narrative. Additional result-specific translation information may also be found in the result comment field in HEIS for this record.
Y	Same as X if more than one flag is required.
Z	Same as X and Y if more than two flags are required.
Third-Party Validation Applied Flags	
UJ	The constituent was analyzed for and was not detected. Because of a QC deficiency identified during data validation, the value reported may not accurately reflect the RL. The data should be considered usable for decision making purposes.
J	Indicates the constituent was analyzed for and detected. The associated value is estimated because of a QC deficiency identified during data validation. The data should be considered usable for decision making purposes.
J+	Indicates the constituent was analyzed for and detected. The result is an estimated quantity, but the result may be biased high. The data should be considered usable for decision making purposes.
J-	Indicates the constituent was analyzed for and detected. The associated value is estimated with a suspected negative bias due to QC deficiency identified during data validation. The data should be considered usable for decision making purposes.
NJ	The analysis indicates the presence of an analyte that has been tentatively identified and the associated numerical value represents its approximate concentration.
C	The target pesticide or Aroclor analyte identification has been confirmed by GC/MS.
X	The target pesticide or Aroclor analyte identification was not confirmed when GC/MS analysis was performed. The data should be considered unusable for decision making purposes.
UR	Indicates the constituent was analyzed for and not detected. However, due to an identified QC deficiency, the data should be considered unusable for decision-making purposes.
R	Rejected value: The value may not reflect true concentrations. The ability to establish detection/nondetection may be questionable. Validation activities identified major QC deficiency/ies or sample matrix interferences. The data should be considered unusable for most purposes. Any use of this data should be undertaken with great care. The data should not be used for certain regulatory decision-making purposes.
Data User-Applied Flags	
A	Indicates an issue with the chain of custody that could affect data usability.
F	Result is undergoing further review. (This review qualifier is assigned when a RDR is first processed).
G	Record has been reviewed and determined to be correct, or the record has been corrected with laboratory confirmation or other supporting information.

Table 4. Qualification Flags

Flag	Definition
	Laboratory-Applied Flags
H	Laboratory holding time exceeded before the sample was analyzed.
P	Potential problem. Collection/analysis circumstances make the result questionable.
Q	Associated QC sample is out of limits.
R	Do not use. Further review indicates the result is not valid. (This review qualifier is used only when there is documented evidence that the result is not valid. Generally, results that are "R" qualified will be excluded from statistical evaluations, maps, and other interpretations).
Y	Result is suspect. Review had insufficient evidence to show result valid or invalid.
Z	Miscellaneous circumstance exists. Additional information may be found in the result comment field (in the HEIS result table) for this record and/or in the sample comment field in the HEIS sample table.

Note: Wetchem is a group of analytical methods that are associated with "wet" chemical reactions.

DF = dilution factor
GC/MS = gas chromatograph/mass spectrometer
GFAA = graphite-furnace atomic absorption
HEIS = Hanford Environmental Information System
MDA = minimum detectable activity
MDL = method detection limit
MSA = method of standard additions
PCB = polychlorinated biphenyl
PQL = practical quantitation limit
QC = quality control
RDR = request for data review
RL = reporting limit
TIC = tentatively identified compound

1.4.5 Field Quality Control Sampling Requirements

The 100-KR-4 Rebound SAP (DOE/RL-2020-42) required collection of full trip blank (FTB) samples, equipment rinsate blank (EB) samples, and field duplicate samples. Table 5 summarizes the required frequency for each field QC sample type as outlined in Table 2-4 of the 100-KR-4 Rebound SAP (DOE/RL-2020-42).

Table 5. Project Field Quality Control Checks

QC Sample Type	Purpose	Frequency
Equipment rinsate blank	Verify adequacy of sampling equipment decontamination	1 in 20 samples when nondedicated equipment is used[a,b]
Full trip blank	Contamination from containers, preservative reagents, storage, or transportation	1 per 20 sampling events (well trips[c] or other media samples)
Field duplicates	Reproducibility/sampling precision	1 in 20 sampling events (well trips or other media samples[c])

Note: The information in this table does not represent U.S. Environmental Protection Agency or Washington State Department of Ecology requirements; it is intended solely as guidance.

a. For portable Grundfos® pumps, equipment blanks are collected 1 per 20 well trips. Whenever a new type of nondedicated equipment is used, an equipment blank shall be collected every time sampling occurs until it can be shown that less frequent collection of equipment blanks is adequate to monitor the decontamination procedure for the nondedicated equipment.

b. Vendor provided borehole equipment is considered dedicated equipment and equipment blanks are not typically acquired in this instance.

c. A 'well trip' is defined as any time a well is accessed for sampling. For groundwater monitoring, field duplicates and full trip blanks are run at a frequency of 1 in 20 well trips (i.e., 5% of the well trips) for all groundwater monitoring wells sampled within any given month (not just those restricted to a single treatment storage disposal unit). For example, if a month has 181 wells scheduled, then 10 field duplicates will be collected.

Grundfos® is a registered trademark of the Grundfoss Holding A/S Corporation, Bjerringbro, Denmark.

QC = quality control

1.4.5.1 Field Blank Requirements

FTBs are used to monitor for potential sample contamination from the sampling container, preservation reagents, or storage conditions. Trip blanks are prepared and sealed prior to traveling to the sampling site, transported to the sampling site (not opened in the field), and then shipped as part of the sample set to the laboratory. FTBs may be used for all or a subset of the analyses as defined by project-specific standard operating procedures (SOPs), SAP, or other work control document.

EBs, also known as equipment rinsate blanks, are used to monitor the effectiveness of the decontamination process for reusable sampling equipment. EBs are not usually required for dedicated sampling equipment, disposable sampling equipment, or vendor-provided sampling equipment (e.g., used during a borehole drilling event). They are samples of high purity deionized water or silica sand contacted with the sampling surfaces of equipment used to collect samples prior to using that equipment for field sampling. EBs are collected at the frequency specified in the project-specific SOPs, SAP, or other work control documents. An EB shall be collected from each type of reusable sampling equipment to ensure that the decontamination procedures are effective for the specific equipment types. EBs shall be analyzed for the same analytes as samples collected using that equipment or as specified in the project-specific SOPs, SAP, or other work control documents.

For the field blank samples (e.g., FTB, EB), results greater than method detection limit (MDL) are evaluated against the associated sample results. Samples associated with blanks that have detections >5% of the sample result are flagged with a review qualifier of "Q" and are potentially biased.

1.4.5.2 Field Duplicate Requirements

Field duplicate samples are used to evaluate homogeneity of the sample matrix, the precision of field sampling methods and the precision of the analysis processes. Field duplicates are independent samples collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed as independent samples at a single laboratory.

The duplicate should be collected generally from an area expected to have some contamination so that valid comparisons between the samples can be made (e.g., at least some of the constituents will be greater than the detection limit).

Only those field duplicate result pairs with at least one result greater than the practical quantitation limit (PQL) are evaluated. Field duplicate sample results must agree within 20% as measured by the RPD to be acceptable. Large RPDs can be an indication of laboratory performance problems and should be investigated.

1.4.6 Laboratory Quality Control Requirements

In addition to the evaluation performed on field QC data (as described in Section 1.4.5), a broad review of the laboratory QC results (as described in Section 1.4.4) was also conducted. Laboratory QC results are stored electronically in HEIS and were evaluated using various database queries against the acceptance criteria. Table 6 provides a summary of the laboratory QC acceptance criteria used.

Table 6. Laboratory Quality Control Acceptance Criteria

QC Element	Acceptance Criteria
Laboratory duplicate samples (measures analytical precision)	Laboratory duplicate samples with one or both of the measured concentrations ≥PQL (or 5x the MDC for radiochemistry) and the RPD is ≤20% to be considered acceptable.

Table 6. Laboratory Quality Control Acceptance Criteria

QC Element	Acceptance Criteria
Laboratory blank samples (Measures analytical contamination)	If analyte concentration in the laboratory blank is ≥MDL/MDA, no qualification is necessary when the concentration in the associated samples is ≥20x the laboratory blank concentration.
LCSs (measures analytical accuracy)	LCS percent recovery must be between the upper and lower control limits listed in Table 2-5 found in the 100-KR-4 Rebound SAP (DOE/RL-2020-42).
MS/MSDs (where applicable) (measures analytical precision and accuracy)	Where the sample result is ≤4x the spiking concentration, laboratory spikes are evaluated by comparing the percent recovery with the upper and lower accuracy control limits given in Table 2-5 found in the 100-KR-4 Rebound SAP (DOE/RL-2020-42). In addition, where the sample result is ≤4x the spiking concentration, the MS/MSD RPD must have an RPD ≤20%. Spike values not applicable when sample result is >4x the spiking concentration.

References: DOE/RL-2020-42, *Parent Rebound Study Sampling and Analysis Plan for the 100-KR-4 Operable Unit.*

LCS = laboratory control sample
MDC = minimum detectable concentration
MDL/MDA = method detection limit/minimum detectable activity
MS/MSD = matrix spike/matrix spike duplicate
PQL = practical quantitation limit
QC = quality control
RPD = relative percent difference
SAP = sampling and analysis plan

2 Data Verification

Data verification is the process of evaluating the completeness, correctness, conformance, and compliance of a specific data set against the method, procedural, or contractual requirements. The process includes confirmation that the specified sampling and analytical requirements have been completed (i.e., verification that the number, type, and location of all samples identified in the 100-KR-4 Rebound SAP [DOE/RL-2020-42] and addendum have been collected and that all required measurements and analyses were performed). This evaluation is documented in the completeness section (Section 4.1.5), which evaluates the sampling design versus field implementation. In addition, verification is performed for field QC and laboratory QC samples and is documented in the field QC and laboratory QC sections (Sections 2.2 and 2.3, respectively).

2.1 Data Verification Results

Data verification requires the evaluation of collected documentation to verify that key information for subsequent validation and data indicator evaluations are present.

In accordance with CPCCo procedures, data verification is performed, which requires verification of a minimum of 25% of all final analytical data packages. Final analytical data package verification was performed on randomly selected data deliverables. This random selection is not project specific (i.e., the actual percent of data deliverables verified for the 100-KR-4 Rebound project may be more or less than 25%). For the data set addressed in this DUA, 33.0% of the data packages were verified.

The following sections provide an evaluation and description of the sampling design versus field implementation. All discrepancies between the sampling and analysis requirements outlined in the 100-KR-4 Rebound SAP (DOE/RL-2020-42) (and applicable addendum) and what was actually performed are identified. Data verification is performed for field QC and laboratory QC samples.

2.2 Field Quality Control

FTB for groundwater sampling is not established based on individual projects (such as the rebound study). Rather, the number of FTBs are based on the number of sample events (well trips) performed each month for the entire groundwater program. The FTBs evaluated for the KR-4 Rebound study in this DUA, were those that were taken on the same day and sent to the same laboratory for the same constituents as the rebound samples in the DUA data set. The results of the field blanks, and field duplicates are discussed below.

2.2.1 Field Blanks

Field EB samples are analyzed to determine if positive results may be attributed to contaminants introduced as a result of sampling equipment. Any analyte measured above the laboratory detection limits is evaluated for potential impacts to associated sample results.

There were 26 EB samples taken in conjunction with the KR-4 Rebound sampling resulting in 74 results. Of the 74 results, 15 had detections above the MDL as follows: 5 alkalinity results (all below the PQL), 2 chloride results (1 below and 1 above the PQL), 3 nitrate results (all above the PQL), 1 potassium result (below the PQL and associated with a laboratory blank contamination), 2 sodium results (both below the PQL and associated with a laboratory blank contamination), and 2 sulfate results (1 below and 1 above the PQL). Alkalinity is often detected in deionized water due to carbon dioxide adsorption. For this reason, blanks are not required by the alkalinity method, and the detections are not indicative of a method issue or bias. All other EB detections, except one nitrate result, were less than 5% of the associated sample results and met the SAP performance criteria. For the one nitrate blank excursion, there was one associated sample result that had a value greater than 20X the blank and was flagged with a Q to indicate a possible bias.

Seventeen FTB samples were collected in conjunction with the 99 sample events in this dataset, which exceeds the 1 FTB per 20 sample events requirement in the 100-KR-4 Rebound SAP (DOE/RL-2020-42). From the 17 FTB samples, 116 results were reported. Of the 116 FTB results, 9 were detections, all of which were below the associated PQLs. The nine detections are as follows: six alkalinity results, one chloride result and two potassium results. As discussed with the EBs, alkalinity is often detected in deionized water and the detections are not indicative of a method issue or bias. The one chloride and two potassium detections were less than 5% of the associated sample results and are insignificant compared to the associated sample results. All the blank results meet the SAP acceptance criteria.

2.2.2 Field Duplicates

Like FTBs, field duplicate sample frequency for groundwater is not established based on individual projects. It is also based on the number of sample events (well trips) performed each month. The duplicates evaluated for the KR-4 Rebound study in this DUA, were those that were taken on the same day and sent to the same laboratory for the same constituents as the rebound samples in the DUA data set.

There were 14 duplicates taken in conjunction with the 99 sample events in this data set, which exceeds the 1 duplicate per 20 sample events requirement in the 100-KR-4 Rebound SAP (DOE/RL-2020-42). The 14 duplicate samples resulted in 124 sample/dup result pairs reported. Duplicate pair results were evaluated if at least one of the two results was above the associated PQL. For this data set, all duplicate pairs met the evaluation criteria. All of the 124 reviewed RPDs met the 20% RPD criteria except 1 for potassium with an RPD of 20.6%. The potassium sample and duplicate (non DUA data set samples) results were investigated, and both the sample and duplicate results were out of trend as well. There were two (filtered and unfiltered from well 199-K-174) project samples run in the same analytical batch as the

field duplicate pair which showed a high disparity between the filtered and unfiltered results. All four samples had a review qualifier of "Y" (suspect) applied due to an unknown issue.

2.3 Laboratory Quality Control

Laboratory contamination, precision, and accuracy are discussed below.

2.3.1 Laboratory Contamination

CPCCo laboratory contracts require that laboratory method blanks be analyzed with each batch of up to 20 samples.

A total of 209 laboratory blank results were reported for the rebound study data set. Of those blank results, two results (one for sodium; one for potassium) were reported with negative values with the absolute value of the result falling between the MDL and the PQL. Three (two potassium; one sodium) reported detected concentrations above the MDL but below the PQL and three (two sodium; one potassium) had results above the PQL. The potassium and one of the sodium blank results above the PQL were associated with EB results that also had excursions of similar magnitude. For these EB results (flagged with a "C" by the lab) the detected sodium and potassium were likely due to laboratory contamination.

In all cases, the associated sample results (excluding the EB samples discussed above) were greater than 20 times the laboratory blank concentration (or greater than 20X the absolute value for the negative results). This verifies that the blank excursions were insignificant compared to the sample results and that all the blanks meet the SAP acceptance criteria.

2.3.2 Laboratory Precision

Laboratory precision was determined by the difference between duplicate sample pair results, or between MS/MSD results. Evaluation of the duplicate pairs can be performed accurately only when there is sufficient constituent present to be quantified. Therefore, only RPDs where at least one of the samples in the pair was detected above the PQL were evaluated.

For the water samples, a total of 43 duplicate pairs and 312 MS/MSD pairs were reported. 34 duplicate pairs and all the MS/MSD pairs met the evaluation criteria with all evaluated pairs meeting the RPD acceptance criteria.

2.3.3 Laboratory Accuracy

Two types of QC are used to assess accuracy. The LCS is used to assess the accuracy of the laboratory preparation and analysis processes. The MS and MSD samples are used to assess the accuracy of the published method on the sample matrix and evaluate matrix effects that may bias the data.

2.3.3.1 Laboratory Control Samples

A total of 230 LCS results were reported for the rebound sample data set. All LCS recoveries satisfied the evaluation criteria.

2.3.3.2 Matrix Spike Recovery

MS and MSD recoveries are also used as a measure of analytical accuracy. In cases where the sample concentration is greater than four times the spiking concentration, spike recoveries are not evaluated.

There were 395 out of a total 615 reported MS or spike duplicate sample results that met evaluation criteria. Of the spike results that met the evaluation criteria, there were five MS or MSD recoveries that did not meet the 100-KR-4 Rebound SAP accuracy criteria.

A summary of the spike failures and impacted water samples are as follows:

- Sodium and magnesium were below the acceptance criteria on both the filtered and unfiltered sample associated with B43316 (199-K-206). The post-spike recoveries for these two constituents were also below acceptance limits indicating a potential low bias for the associated sample results. All associated results were flagged "N" by the laboratory.
- One MS below the acceptance range for sodium associated with sample B410Y5 (199-N-210 – not a project well). No project samples were flagged because of this excursion.

3 Data Validation

Data validation is an analyte- and sample-specific process that extends the evaluation of data beyond method or contractual compliance (i.e., data verification) to determine the analytical quality of a specific data set, typically data in single analytical batches. Data validation is an independent assessment to ensure that the reliability of data is known by the user. Analytical data validation provides a level of assurance, based on technical evaluation that an analyte is either present or absent. Validation includes verification of required deliverables (e.g., the minimum detection limits), evaluation of analytical results based on method blanks, and the effect of quality deficiencies on the analytical sample data. Third-party validation was performed on a minimum of 5% of the project data and is described in this chapter.

3.1 Data Validation

Analytical Quality Associates, Inc. performed data validation. All validation qualifiers resulting from data validation were entered into HEIS.

3.2 Data Validation Results

The 100-KR-4 Rebound SAP (DOE/RL-2020-42) specifies that at least 5% (by matrix and analyte group) of all chemical data will undergo validation. Level C data validation includes the evaluation and qualification of sample results based on the following:

- MS, LCS, laboratory duplicate, and chemical recovery criteria (as appropriate to the method)
- Examined field blanks, field duplicates, and field splits (if information is provided)

Table 7 summarizes the samples and constituents that were independently validated for the 100-KR-4 Rebound SAP (DOE/RL-2020-42). As shown in Table 7, the 5% validation of the data required by the 100-KR-4 Rebound SAP requirement was satisfied.

Table 7. Validated Sample Summary

Analyte	Total Number of Samples Analyzed	Total Number of Samples Validated	Percent Validated
Water Samples			
Calcium	142	8	5.6
Magnesium	142	8	5.6
Potassium	142	8	5.6
Sodium	142	8	5.6
Hexavalent chromium	177	9	5.1

Table 7. Validated Sample Summary

Analyte	Total Number of Samples Analyzed	Total Number of Samples Validated	Percent Validated
Water Samples			
Alkalinity	75	6	8.0
Chloride	71	6	8.5
Nitrate	71	6	8.5
Sulfate	71	6	8.5

Percent complete for all categories was 100% with no deficiencies identified.

3.2.1 Major Deficiencies

There were no major deficiencies identified.

3.2.2 Minor Deficiencies

There were no minor deficiencies identified.

3.2.3 Qualification Flags Applied to the Dataset

There were no qualification flags applied to the dataset.

3.2.3.1 Holding Times and Sample Preservation

Holding times are defined as the period of time from sample collection to sample analysis, and the period of time from sample extraction to sample analysis. Holding times are calculated from the date of sample collection as recorded on the chain-of-custody form to determine the validity of the results.

The holding times and preservation requirements for the constituents in water are as follows:

- The holding time requirements for inductively coupled plasma metals are analysis within 180 days of sample collection. Sample preservation requires nitric acid addition to pH <2.
- The holding time requirements for all anions except nitrate are analysis within 28 days of sample collection. The holding time requirements for nitrate is analysis within 48 hours of sample collection.
- Hexavalent chromium requires analysis within 24 hours of sample collection.
- Alkalinity requires analysis within 14 days of sample collection.

All water holding times and preservation requirements for samples analyzed were met, except for hexavalent chromium. Four hexavalent chromium samples were analyzed outside of holding time. Three were analyzed within 2X the holding time, one was analyzed outside of 2X the holding time due to a rerun request by the project.

Hexavalent chromium in the Hanford Site groundwater has been observed to be stable over several months. The sample results for hexavalent chromium missing the holding time are expected to be representative of actual concentrations at the time of sampling.

4 Data Quality Indicator Evaluation

The DQI evaluation process is used to assess data usability for nonstatistical (judgmental) sampling designs. Data verification and data validation reports were reviewed to determine the usability of the data set as a whole and the quality of individual results as appropriate in terms of the following DQIs:

- **Precision** – Discusses the repeatability of field duplicate data and laboratory QC duplicates (e.g., RPDs of laboratory sample duplicates, LCS duplicates, and MS/MSD).
- **Accuracy/Bias** – Discusses evidence of field contamination and laboratory QC (e.g., percent recoveries of LCS, MS and laboratory blank exceedances).
- **Representativeness** – Discusses the extent to which the sampling design was accomplished, the representativeness of the samples, and the design as a whole. Identify any specific measurements not representative of the target condition, explain why they are nonrepresentative, and discuss the impact to the data set.
- **Comparability** – If multiple laboratories were used or if this data set is intended to be combined with others, discuss the nature of differences that may limit the comparability. For example, note that samples were analyzed using recognized standard methods. If multiple laboratories analyzed field QC split samples, discuss how closely the results agreed between the two laboratories.
- **Completeness** – Discusses the accomplishment of all SAP-required data generating activities. Include a comparison of samples actually collected versus those identified in the original sampling design. Include required field QC blanks, duplicates, and splits in the comparison. Also, compares the analyses performed to the analyses identified in the SAP and evaluates the impact to data set usability of any planned samples that were not taken or analyses not performed.
- **Sensitivity** – Discusses any laboratory data that do not meet the SAP-required reporting limits and other decision thresholds as described in the project data quality objectives.

4.1 Data Quality Indicator Evaluation Results

The DQI evaluation step involves assessing whether the samples collected, and the resulting analytical data meet project quality objectives in terms of the DQIs described above. The data verification acceptance rates discussed below are based on the evaluation of QC performance compared to the SAP requirements for the entire data set. Validation acceptance rates are based on the data determined to be legitimate (i.e., not rejected) in the validated data set.

4.1.1 Precision

Laboratory precision is determined by the difference between field and laboratory duplicate sample pair results or between laboratory MS/MSD sample results. The DQI evaluation of laboratory QC showed an overall precision acceptance rate of 100%. Field QC evaluation returned an acceptance rate of 99.2%. No results are deemed unusable based on the DQI review of precision however two potassium results had a review qualifier of “Y” (suspect) applied.

Data validation for the sample set resulted in no flags being applied. Data validation results show an overall data usability rate of 100% for precision.

4.1.2 Accuracy/Bias

Laboratory accuracy and bias are assessed by using two types of QC: LCS and MS/MSD. These QC types are used to determine the accuracy of the laboratory preparation and analysis process and to evaluate matrix effects that may bias the data.

The DQI evaluation for the laboratory QC associated with the data set showed an overall accuracy acceptance rate of 99.2% based on MS recovery. The post-spike results associated with the failed MSs, also failed low. This indicates there was probable analytical issues and the associated data (all flagged "N" by the laboratory) have a possible low bias. All LCS recoveries satisfied the QC criteria giving an overall accuracy acceptance rate of 100% based on LCS recovery. No results are deemed unusable based on the DQI review of accuracy.

Data validation resulted in no flags being applied. Data validation results show an overall data usability rate of 100% for accuracy.

In addition to the evaluations discussed above, bias is also assessed by evaluating the laboratory and field blank results. These QC elements are used to determine if there is significant field or laboratory contamination that may bias the data.

The DQI evaluation of the laboratory blanks associated with the data set showed an overall acceptance rate of 100% for the laboratory blanks and 99.5% for the field blanks excluding the field blank alkalinity results. (Since alkalinity will always be present in the deionized water blanks and is not an indication of contamination or laboratory error it is not applicable).

Data validation for the water samples did not result in any flags due to blank excursions. Data validation results show an overall data usability rate of 100% for laboratory contamination.

4.1.3 Representativeness

There were few QC issues noted for this data set and those identified are relatively minor. Associated data for all samples are considered usable for decision making purposes. Overall, DQIs show the data sets to be representative of their respective sample locations with no systemic bias noted.

4.1.4 Comparability

To generate comparable data, sampling was accomplished using the same procedures used uniformly over the Hanford Site for field sampling. To generate comparable results, laboratory analyses were performed using industry-recognized standard procedures (Table 3).

During the sample analysis period for this data set, the laboratories performing the analysis had no systemic analytical issues identified. All laboratories maintained Washington state accreditation, indicating they passed two performance evaluation samples each year.

4.1.5 Completeness

All samples planned for collection and all required data generating activities outlined in the applicable addendum of the 100-KR-4 Rebound SAP (DOE/RL-2020-42) were completed, with the following exception:

- One sample event during the pre-rebound sample collection on wells 199-K-205 and 199-K-236. The requirement was to take two samples per week for three weeks prior to implementing the rebound study. One of the sample events was collected but the cooler delivery was delayed due to a commercial shipping error. The samples arrived at the laboratory outside of 2X hold time and out of

temperature requirements, so the analysis was cancelled. Due to the frequency of sampling during this period, the missing data set is not considered to have a significant impact on the data usability.

As outlined in the addendum, all required constituents were reported.

4.1.5.1 Field Blanks

For the rebound data set, analysis of 26 EBs and 17 FTB were performed. EBs were performed when reusable sampling equipment was used. The 17 FTBs taken met the 1 FTB for every 20 samples requirement.

The overall performance of the field blanks is discussed in Section 2.2.1. No significant issues were noted.

4.1.5.2 Field Duplicates

For the rebound data set, 14 duplicates were taken and analyzed. The 14 duplicates meet the 1 in 20 frequency requirement for water field duplicates.

The overall performance of the field duplicate results is discussed in Section 2.2.2. No significant issues were noted.

4.1.6 Sensitivity

For this data set, the PQL review was done by confirming that all results flagged as detected but below the laboratory PQL ("B") were below the 100-KR-4 Rebound SAP (DOE/RL-2020-42) PQL requirements listed in the 100-KR-4 Rebound SAP Tables 4 and 5.

All sample values met the required PQL values dictated in the 100-KR-4 Rebound SAP.

5 Data Quality Assessment

The 100-KR-4 Rebound SAP (DOE/RL-2020-42) and associated addendum are based on a judgmental sampling design, which does not require a statistical evaluation of the results.

6 Conclusions

Based on the results of this DUA, the sample set is sufficiently complete as there is a very low overall degree of qualified data points. Given the high degree of acceptable data, the analytical results are considered useable for their intended purposes as indicated in Chapter 4. With the exception of one sample event involving sampling at 2 wells, samples were collected and analyzed as specified in the 100-KR-4 Rebound SAP (DOE/RL-2020-42) and the associated addendum. Sample results accurately indicate the presence or absence of target analyte contamination at sample locations.

Laboratory and matrix accuracy and precision were in control overall and no systematic or general discrepancies were obvious. Sample results appear to be representative of site conditions at the time of collection. Results obtained are comparable to industry standards in that collection and analytical techniques followed approved, documented procedures (except as noted in this report and reflected in qualified data points). All results are reported in industry standard units.

Detection limits, precision, accuracy, and data completeness were evaluated to determine whether any analytical data should be rejected because of QA/QC deficiencies. The conclusions of this DUA are that the data that have been collected are of the right type, quality, and quantity for their intended use.

While there was no specific data verification requirement called out in the SAP for the data set addressed in this DUA, 33% of the data packages were verified with no significant issues noted. A DQI evaluation was performed on 100% of the field and laboratory QC associated with this data set and no significant issues were noted. Lastly, the 5% 100-KR-4 Rebound SAP (DOE/RL-2020-42) requirement for data validation was satisfied.

7 References

DOE/RL-2020-42, 2021, *Parent Rebound Study Sampling and Analysis Plan for the 100-KR-4 Operable Unit*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: https://pdw.hanford.gov/document/AR-10889.

DOE/RL-2020-42-ADD1, 2021, *Rebound Study Sampling and Analysis Plan for the 100-KR-4 Operable Unit, Addendum 1* Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: https://pdw.hanford.gov/document/AR-13899.

EPA/240/R-02/004, 2002, *Guidance on Environmental Data Verification and Data Validation*, EPA QA/G-8, Office of Environmental Information, U.S. Environmental Protection Agency, Washington, D.C. Available at: https://www.epa.gov/sites/production/files/2015-06/documents/g8-final.pdf.

EPA/600/R-93/100, 1993, *Methods for the Determination of Inorganic Substances in Environmental Samples*, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. Available at: https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=30002U3P.txt.

SW-846, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods Compendium*, as amended, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C. Available at: https://www.epa.gov/hw-sw846/sw-846-compendium.

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