

Semiannual Monitoring Results of Natural Gas Wells near the Rulison, Colorado, Site September 2017 Monitoring Event

U.S. Department of Energy Office of Legacy Management Grand Junction, Colorado

Date Sampled: September 20, 2017

Background

The Rulison, Colorado, Site is in the Piceance Basin of western Colorado, 40 miles northeast of Grand Junction. The U.S. Atomic Energy Commission (a predecessor agency to the U.S. Department of Energy [DOE]), in partnership with the Austral Oil Company Inc. and the nuclear engineering firm CER Geonuclear Corporation, conducted an underground nuclear test at the site, identified as Lot 11 (Figure 1), on September 10, 1969. The test, known as Project Rulison, was designed to evaluate the use of a nuclear detonation to enhance gas production in a low-permeability sandstone reservoir. This was the second natural gas reservoir stimulation experiment in the Plowshare Program, which was initiated to develop peaceful uses for nuclear energy. The device was detonated in the emplacement well (R-E) at a depth of 8426 feet (ft) and had a reported yield of 40 kilotons (DOE 2015). It created a temporary cavity, a collapse chimney, and a fractured zone surrounding the cavity (collectively known as the detonation zone). A sidetrack hole (reentry well) was drilled off the exploration well (R-Ex) into the chimney in October 1970 and tested to evaluate the success of the detonation at improving gas production. In 1976, the participating parties agreed there would be no gas production at the site in the future, the R-E and R-Ex wells were abandoned, and a deed restriction was established for Lot 11. The deed restriction prohibits penetration or withdrawal of any material below 6000 ft within the boundary of Lot 11 unless authorized by the U.S. government.

Purpose

LM collects samples (natural gas and produced water) from producing natural gas wells near the Rulison site to verify that residual radiological contamination has not migrated from the detonation zone to those locations. The samples are analyzed for radionuclides that are associated with a nuclear detonation. Tritium is the most abundant radionuclide remaining that can be present in the gas and aqueous phases. Its presence in water vapor (a minor constituent of natural gas) is the primary concern, because gas is more mobile than liquid in a gas reservoir. Almost all tritiated methane was removed and flared during the production testing.

The natural gas wells produce some liquids (produced water and hydrocarbon condensate) along with natural gas; these liquids are brought to the surface with the natural gas and are mechanically separated at the wellhead. Produced water is a mixture of water vapor in the natural gas that condenses at the surface, formation water, and remnant water from hydrofracturing well development. Natural gas and produced water samples are collected for analysis.

The Colorado Oil and Gas Conservation Commission (COGCC) requires that operators with gas wells within approximately 2 miles of the Rulison site adhere to the COGCC's *Rulison Sampling and Analysis Plan for Operational and Environmental Radiological Monitoring Near Project Rulison Revision 4*, hereafter called the Rulison Sampling and Analysis Plan (COGCC 2017).

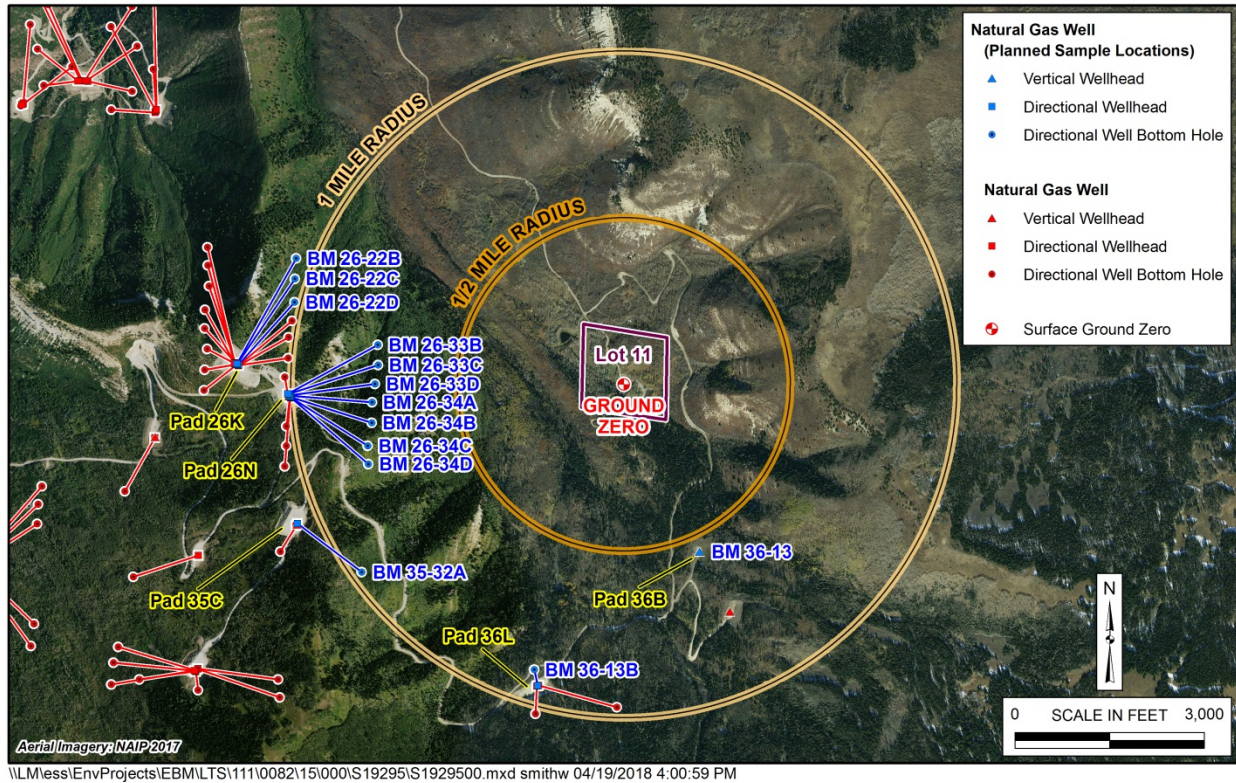


Figure 1. Rulison, Colorado, Site and Well Location Map

Monitoring Plan (Monitoring Plan) (DOE 2010), which samples gas wells within 1 mile of the detonation zone. The Monitoring Plan and analytical results from past monitoring activities are available on the LM website at <https://www.lm.doe.gov/Rulison/Documents.aspx>. Analytical results obtained from LM's September 2017 monitoring event are summarized in the following sections.

Monitoring Protocol

The Monitoring Plan provides guidance on the type of samples collected (natural gas or produced water), the laboratory analyses performed, and the frequency of sample collection that is based on the amount of gas produced and the distance and direction of the well from the Rulison site. It also establishes screening levels or concentrations that, if exceeded in the sample results, require that samples be reanalyzed or additional sampling be done. The natural gas and produced water samples are analyzed for tritium, which is the most mobile contaminant remaining in significant quantities in the detonation zone. Natural gas samples are also analyzed for carbon-14 and produced water samples are also analyzed for gross alpha and beta radiation and gamma-emitting nuclides to obtain background information.

Produced water samples are submitted to a commercial laboratory that provides analytical services in accordance with the *Department of Defense (DoD) Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories* (DoD/DOE 2017) to ensure that data are of known, documented quality. These laboratory analytical data are validated according to Section 8.0, "Standard Practice for Validation of Environmental Data," in the *Environmental Procedures Catalog* (LMS/POL/S04325). Table 1 provides the gas and

Table 1. Rulison Area Natural Gas and Produced Water Sample Screening Levels

Analyte	Sample Matrix	Laboratory Detection Limit	Screening Concentration	Action Concentration
Tritium	Natural gas	10 TU ^a	19,293 TU ^b	TBD ^d
	Produced water	400 pCi/L	800 pCi/L	TBD ^d
Gross alpha radiation	Produced water	2 pCi/L	3 × background ^c	TBD ^d
Gross beta radiation	Produced water	4 pCi/L	3 × background ^c	TBD ^d
¹³⁷ Cs (high-resolution gamma spectrometry)	Produced water	10 pCi/L	20 pCi/L	TBD ^d

Notes:

The screening activities (concentrations) were obtained from the *Rulison Monitoring Plan* (DOE 2010).

^a A tritium unit (TU) is equal to 3.19 picocuries per liter in water.

^b The natural gas screening concentration for tritium assumes a standard temperature (0 °C) and pressure (1 atmosphere).

^c Background concentrations have not been established for gross alpha and beta radiation.

^d Action concentrations have not been established for the analytes of interest.

Abbreviations:

pCi/L = picocuries per liter

TBD = to be determined

TU = tritium unit (1 tritium atom in 1×10^{18} hydrogen atoms)

produced water screening activities (concentrations) for tritium, gross alpha and gross beta radiation, and gamma-emitting nuclides (specifically cesium-137 [¹³⁷Cs]). Background concentrations for gross alpha and beta have not been established.

Sample Collection of Produced Water and Natural Gas

Samples of the water produced from the natural gas wells operating near the site were collected on September 20, 2017. Samples could not be collected from wells BM 26-33B, BM 26-33C, BM26-34A, BM 26-22B, and BM 36-13, because these wells were not in production at the time of the monitoring event (Figure 1) (Table 2). Samples of the produced water were collected from a tap on the dump line connecting the gas–liquid separators and accumulation tank. Before sample collection, the gas–liquid separators that share a dump line were isolated using valves and then purged of produced water and condensate. The samples were contained in 1 gallon plastic containers provided by the laboratory. The produced water samples were submitted to ALS Laboratory Group in Fort Collins, Colorado, for the determination of tritium, gross alpha and beta radiation, and gamma-emitting nuclides. The produced water sample collected from well BM26-33D could not be analyzed for gross alpha and beta radiation, because the sample volume was limited as a result of low water production from the well.

Natural gas samples were not collected from the gas wells operating near the site because of limited gas production, ranging from 6.2 to 13.1 million cubic feet (MMCF), since the last monitoring event on March 24, 2017. This range in the gas production volume is below the range of 15 to 30 MMCF that is established and recommended for sampling in the Monitoring Plan (DOE 2010). Appendix A includes a chart for each well showing the monthly and cumulative gas production volumes in MMCF.

Table 2. Rulison Area Natural Gas Well Sample Locations

Well Name/Number	Well Pad	API No. 05-045-	Sample Type	
			Gas	Liquid
BM 26-33B	26N	15743	Not sampled	Not sampled
BM 26-33C	26N	15742	Not sampled	Not sampled
BM 26-33D	26N	15739	Not sampled	Sampled
BM 26-34A	26N	15744	Not sampled	Not sampled
BM 26-34B	26N	15745	Not sampled	Sampled
BM 26-34C	26N	15741	Not sampled	Sampled
BM 26-22C	26K	16087	Not sampled	Sampled
BM 26-22D	26K	16074	Not sampled	Sampled
BM 35-32A	35C	10919	Not sampled	Sampled
BM 26-22B	26K	16086	Not sampled	Not Sampled
BM 26-34D	26N	15748	Not sampled	Sampled
BM 36-13B	36L	15469	Not sampled	Sampled
BM 36-13	36B	10840	Not sampled	Not sampled

Abbreviation:

API = American Petroleum Institute

Sample Results for Produced Water and Natural Gas

The produced water samples had no detections of ^{137}Cs above the laboratory minimum detectable concentrations (MDCs). Tritium was detected at an activity (concentration) of 745 picocuries per liter (pCi/L) in the produced water sample collected from well BM36-13B located about 0.9 miles south of the site (Figure 1). The result was qualified as estimated because of the elevated laboratory uncertainty of ± 235 pCi/L associated with the result and the result is below the determination limit established for the laboratory (Appendix B, Table 2). The tritium result is below the screening level of 800 pCi/L established in the Monitoring Plan (DOE 2010) and the Rulison Sampling and Analysis Plan (COGCC 2017). Tritium was not detected above the laboratory MDC in any of the remaining samples. Concentrations of gross alpha and beta radiation were above the MDCs in select samples, but they were consistent with past sample results and within the expected range for background concentrations from naturally occurring radionuclides. The analytical results were validated in accordance with the Section 8.0, “Standard Practice for Validation of Environmental Data,” in the *Environmental Procedures Catalog*. All analyses were completed, and the samples were prepared and analyzed in accordance with accepted procedures for the specified methods. The laboratory radiochemical MDC reported with these data is an a priori estimate of the detection capability of a given analytical procedure rather than an absolute concentration that can or cannot be detected. A copy of the data validation package is provided as Appendix B. Analytical results for produced water samples collected on September 20, 2017, are provided in Table 3.

Table 3. Analytical Results for Rulison Area Produced Water and Natural Gas Samples from March 2017

Well Name/Number	API No. 05-045-	Natural Gas ^a		Produced Water			
		Tritium (TU) ^b	Carbon-14 (pMC) ^c	Tritium (pCi/L)	Gross Alpha (pCi/L)	Gross Beta (pCi/L)	¹³⁷ Cs (pCi/L)
BM 26-33B	15743	NS	NS	NS	NS	NS	NS
BM 26-33C	15742	NS	NS	NS	NS	NS	NS
BM 26-33D	15739	NS	NS	<328	NA	NA	<5.12
BM 26-34A	15744	NS	NS	NS	NS	NS	NS
BM 26-34B	15745	NS	NS	<328	<32.8	75.9	<3.65
BM 26-34C	15741	NS	NS	<325	279	167	<5.02
BM 26-22C	16087	NS	NS	<332	6.13	8.41	<4.59
BM 26-22D	16074	NS	NS	<344	<1.98	3.38	<5.15
BM 35-32A	10919	NS	NS	<324	27.2	95.2	<4.91
BM 26-22B	16086	NS	NS	NS	NS	NS	NS
BM 26-34D ^d	15748	NS	NS	<324	66.1	77.3	<4.6
		NS	NS	<321	25.5	54.2	<4.61
BM 36-13B	15469	NS	NS	745	<25.1	95.5	<4.21
BM 36-13	10840	NS	NS	NS	NS	NS	NS
Screening concentrations		19,293	TBD	800	3 × background ^e	3 × background ^e	20

Notes:

- ^a The natural gas samples were initially analyzed by gas chromatography to determine the composition of the natural gas. The samples were then combusted, and the resulting water was collected for tritium and carbon-14 analysis.
- ^b A tritium unit (TU), 1 tritium atom in 1×10^{18} hydrogen atoms, is equal to 3.19 pCi/L in water.
- ^c pMC is based on the International Radiocarbon Dating Standard, which is 1950 before present.
- ^d Indicates that the sample was provided to the laboratory as a field duplicate.
- ^e Background activities (concentrations) have not been established for gross alpha and beta radiation.

Abbreviations:

- API = American Petroleum Institute
- NA = not analyzed
- NS = not sampled
- pMC = percent modern carbon
- TBD = to be determined
- TU = tritium unit (1 tritium atom in 1×10^{18} hydrogen atoms)

Conclusion

Laboratory results obtained from this monitoring event continue to demonstrate that tritium has not been detected above the screening levels established for produced water or natural gas in the wells within 1 mile of the site. Natural gas wells near the Rulison site have not been impacted by detonation-related contaminants. This report is available on the LM public website at <https://www.lm.doe.gov/rulison/Sites.aspx>. Data collected during this and previous monitoring events are available on the Geospatial Environmental Mapping System (GEMS) website at <https://gems.lm.doe.gov/#site=RUL>.

References

COGCC (Colorado Oil and Gas Conservation Commission), 2017. *Rulison Sampling and Analysis Plan for Operational and Environmental Radiological Monitoring Near Project Rulison, Revision 4*, July.

DoD/DOE (Department of Defense/Department of Energy), 2017. *Department of Defense (DoD) Department of Energy (DOE) Consolidated Quality Systems Manual (QSM) for Environmental Laboratories*, Version 5.1, January.

DOE (U.S. Department of Energy), 2010. *Rulison Monitoring Plan*, LMS/RUL/S06178, Office of Legacy Management, July.

DOE (U.S. Department of Energy), 2015. *United States Nuclear Tests, July 1945 through September 1992*, DOE/NV—209-Rev 16, National Nuclear Security Administration, September.

Environmental Procedures Catalog, LMS/POL/S04325, continually updated, prepared by Navarro Research and Engineering, Inc., for the U.S. Department of Energy Office of Legacy Management.

Appendix A
Gas Well Production Data

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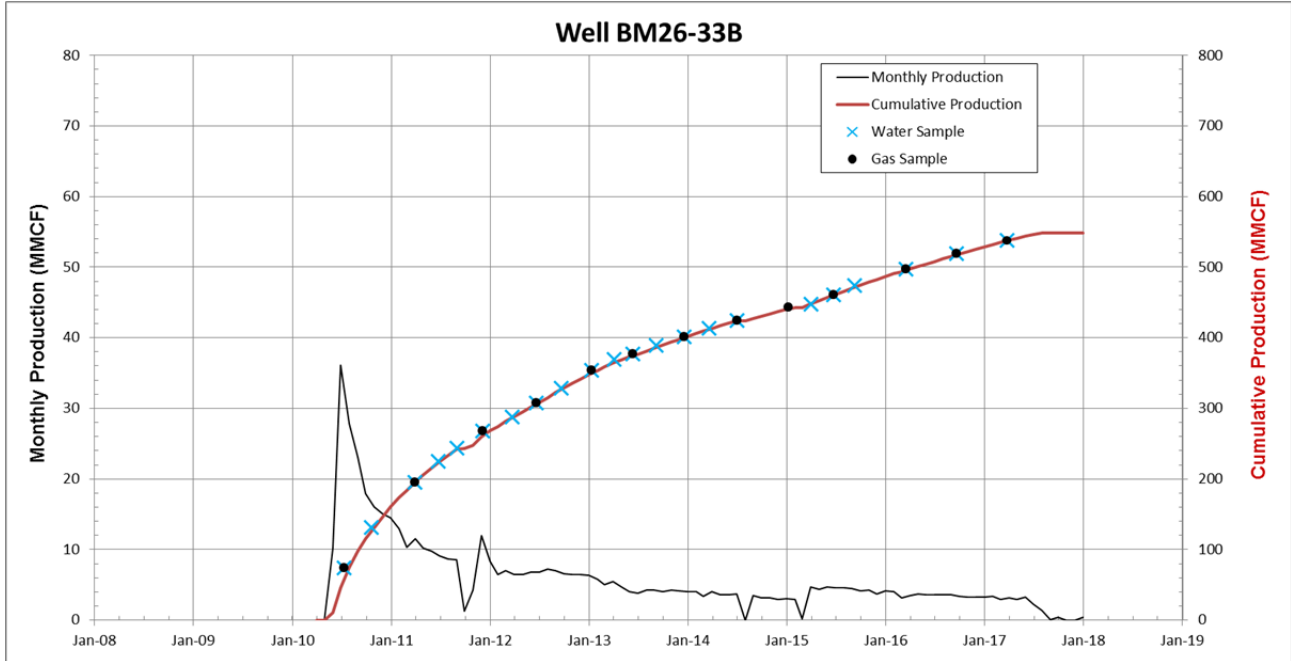


Figure A-1. Frequency of Sampling with Gas Production Data for Well BM26-33B

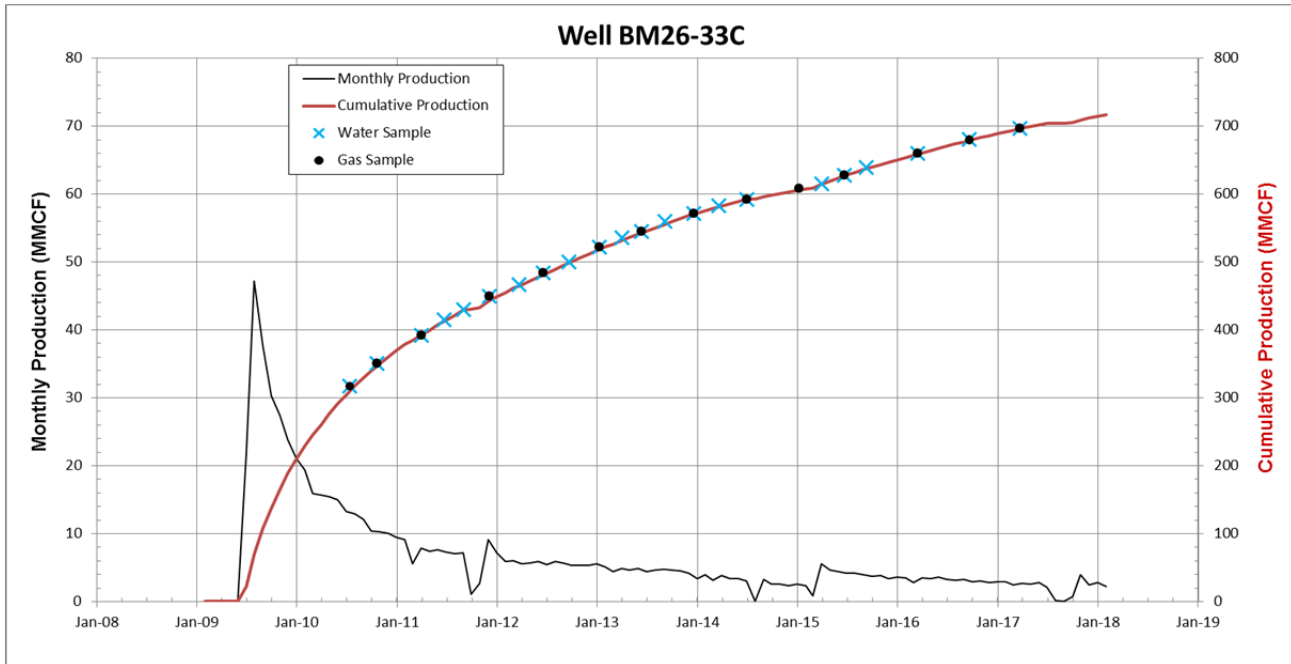


Figure A-2. Frequency of Sampling with Gas Production Data for Well BM26-33C

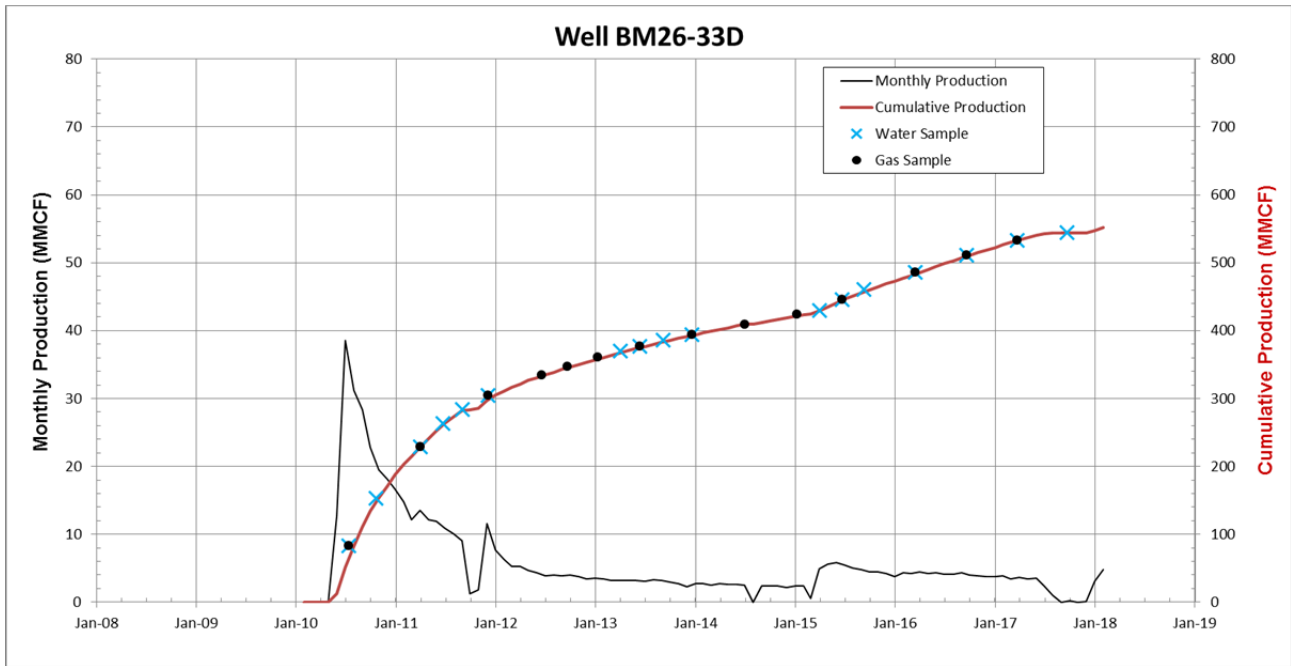


Figure A-3. Frequency of Sampling with Gas Production Data for Well BM26-33D

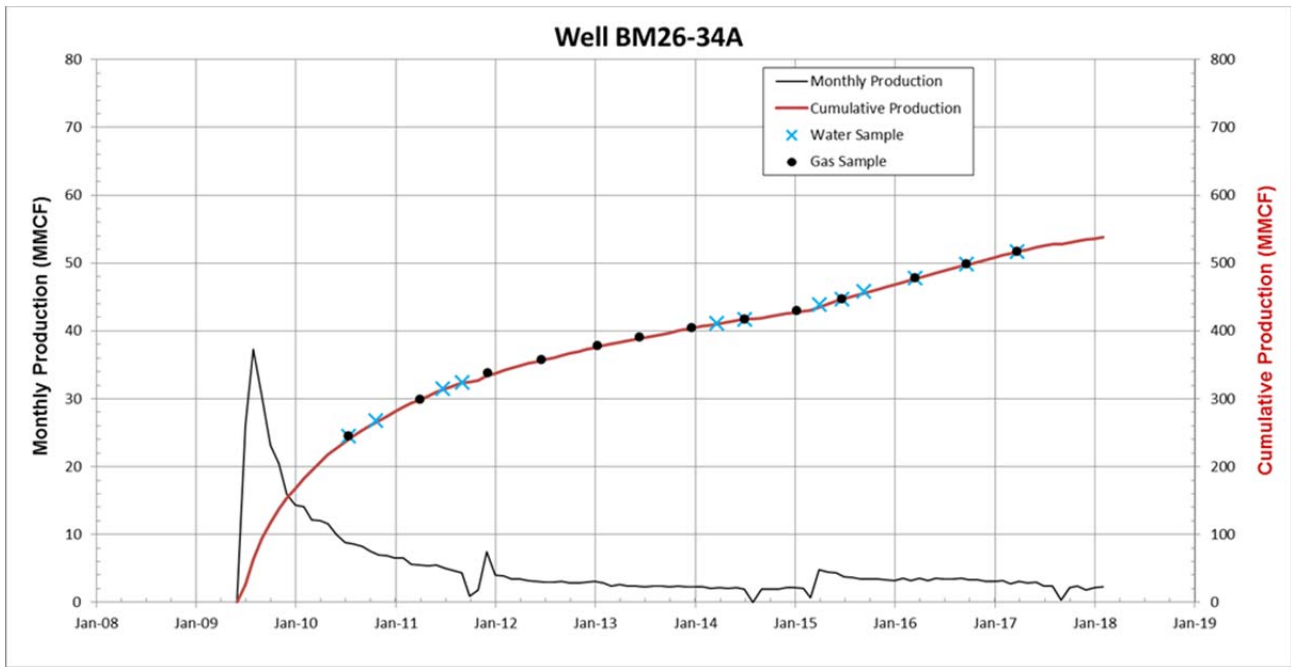


Figure A-4. Frequency of Sampling with Gas Production Data for Well BM26-34A

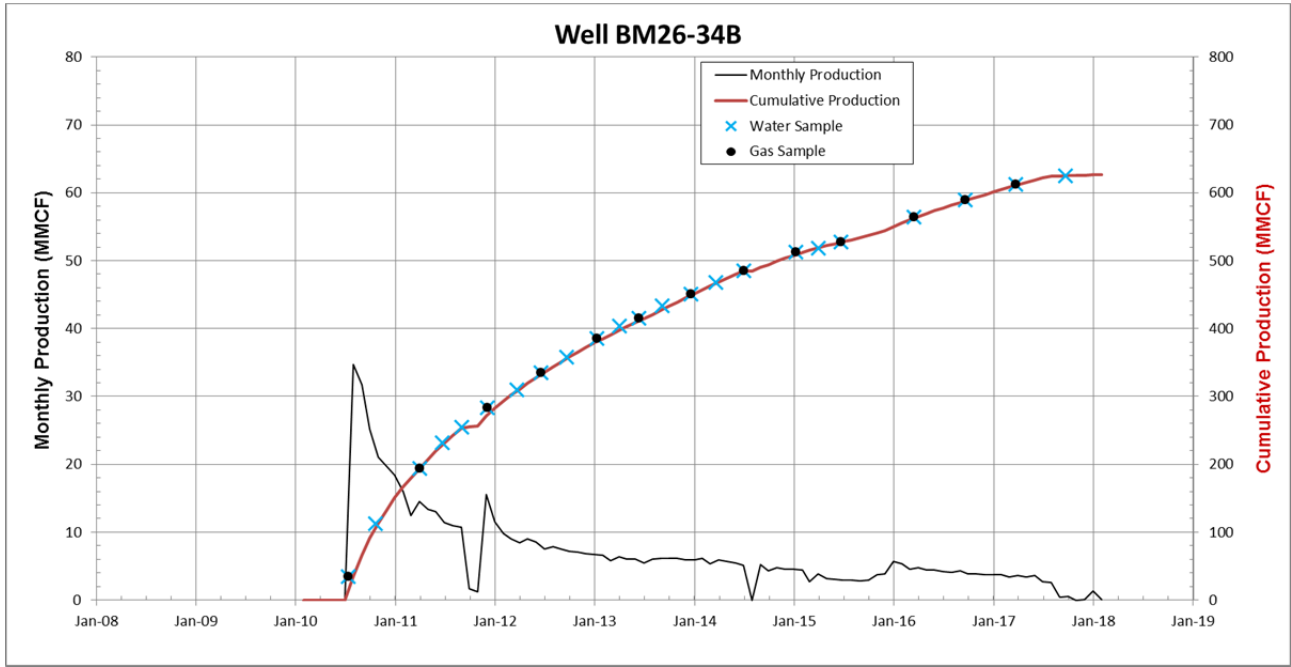


Figure A-5. Frequency of Sampling with Gas Production Data for Well BM26-34B

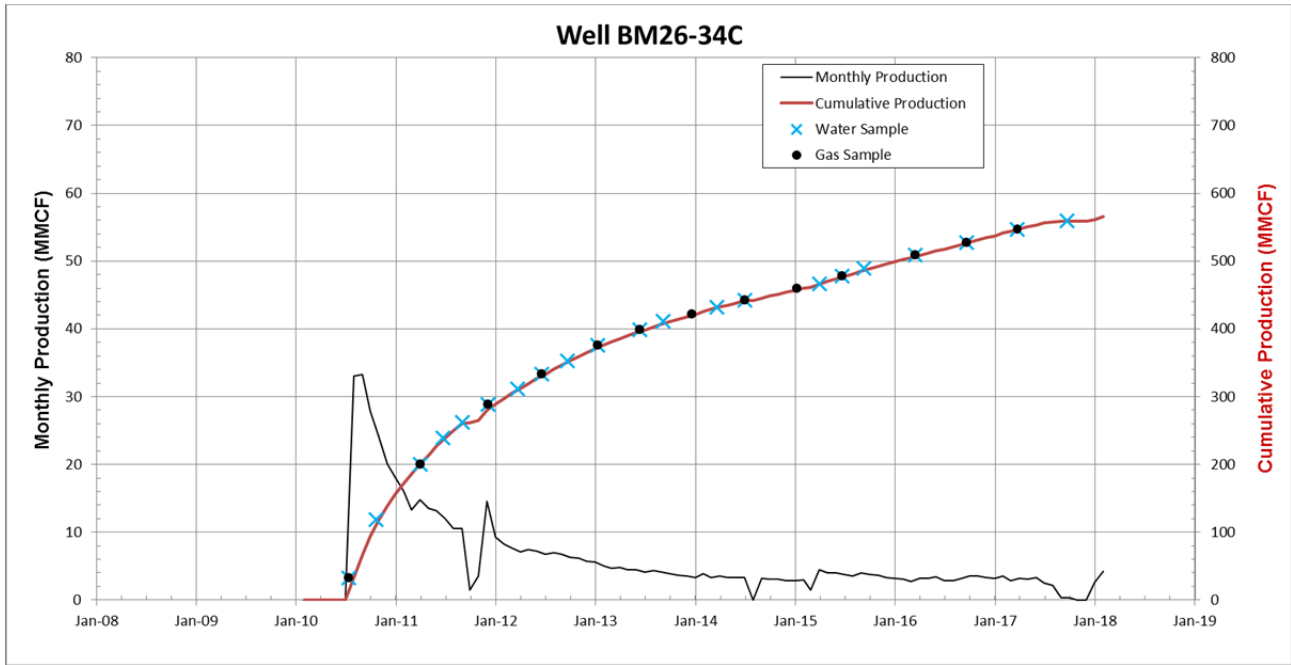


Figure A-6. Frequency of Sampling with Gas Production Data for Well BM26-34C

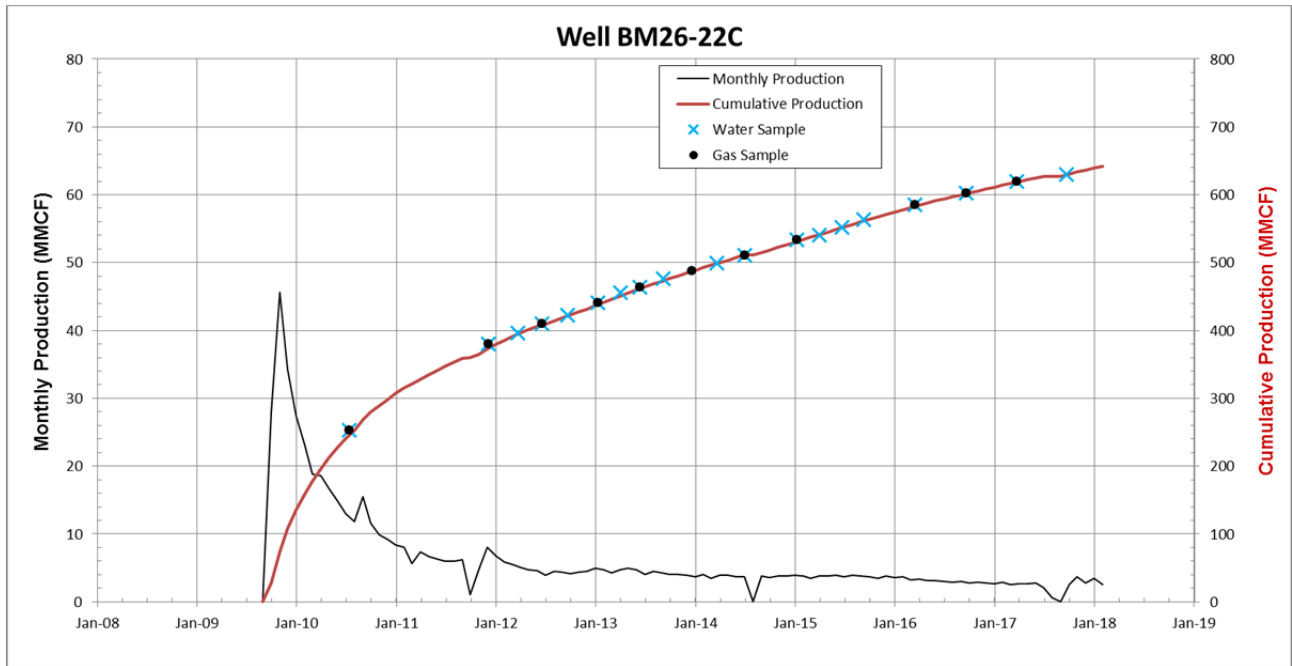


Figure A-7. Frequency of Sampling with Gas Production Data for Well BM26-22C

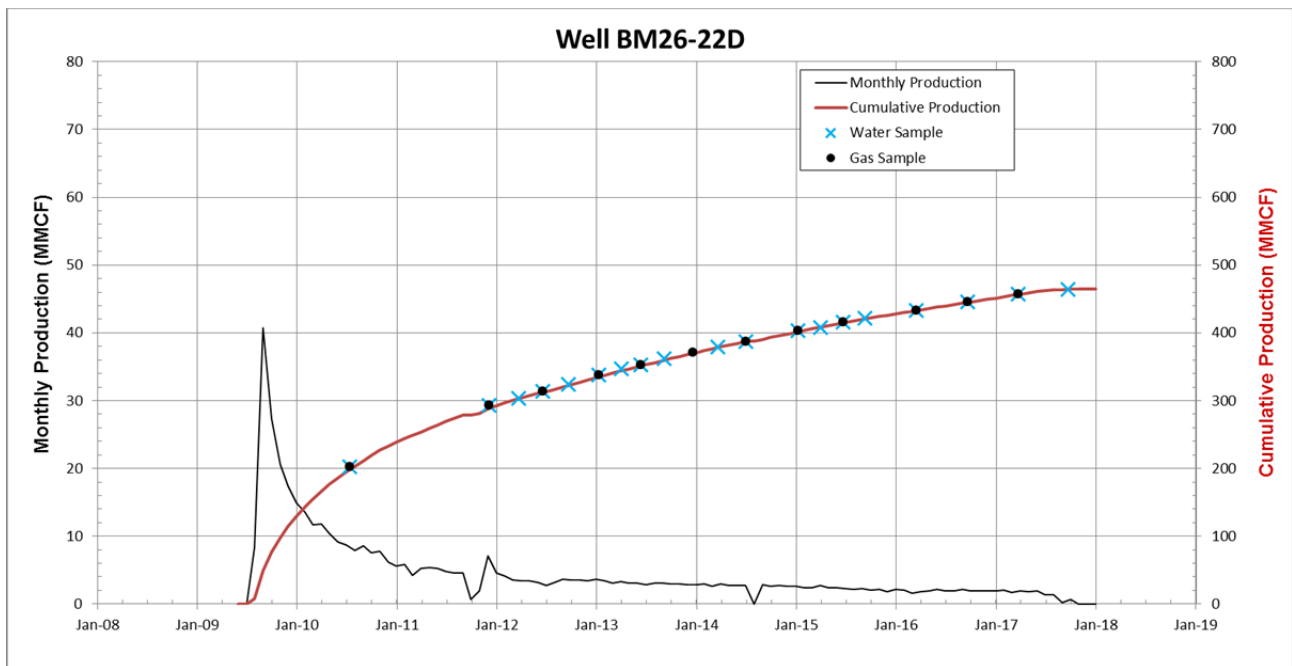


Figure A-8. Frequency of Sampling with Gas Production Data for Well BM26-22D

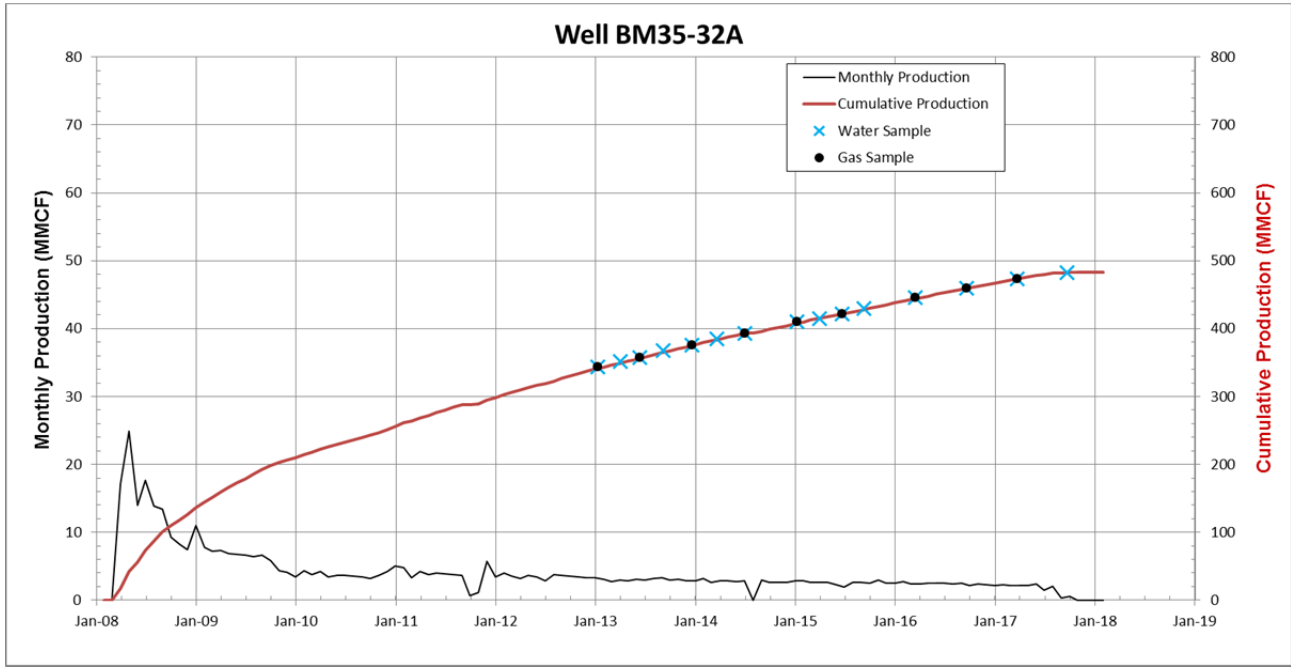


Figure A-9. Frequency of Sampling with Gas Production Data for Well BM35-32A

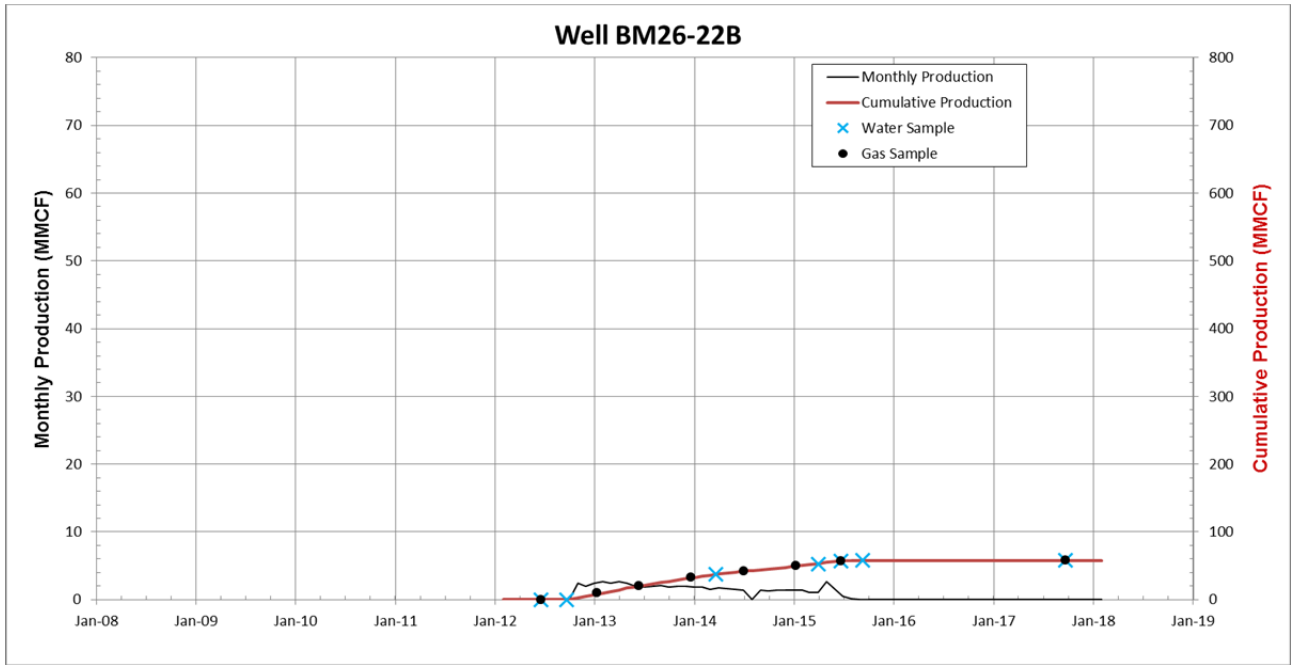


Figure A-10. Frequency of Sampling with Gas Production Data for Well BM26-22B

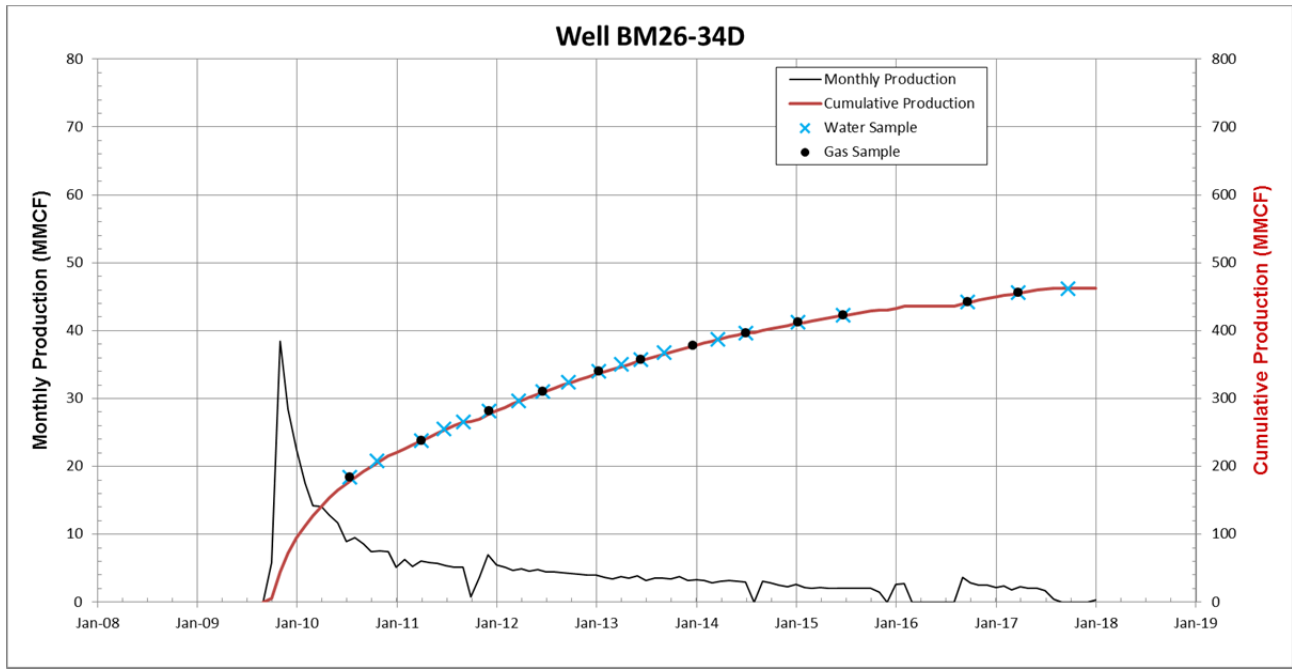


Figure A-11. Frequency of Sampling with Gas Production Data for Well BM26-34D

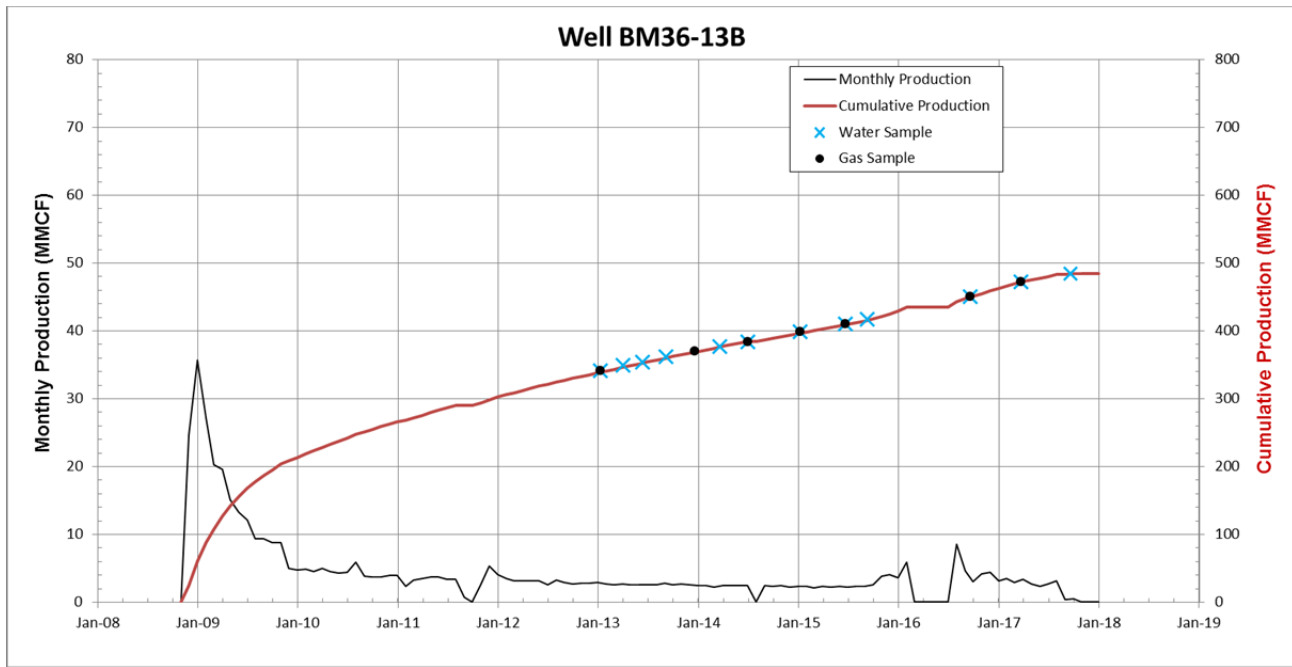


Figure A-12. Frequency of Sampling with Gas Production Data for Well BM36-13B

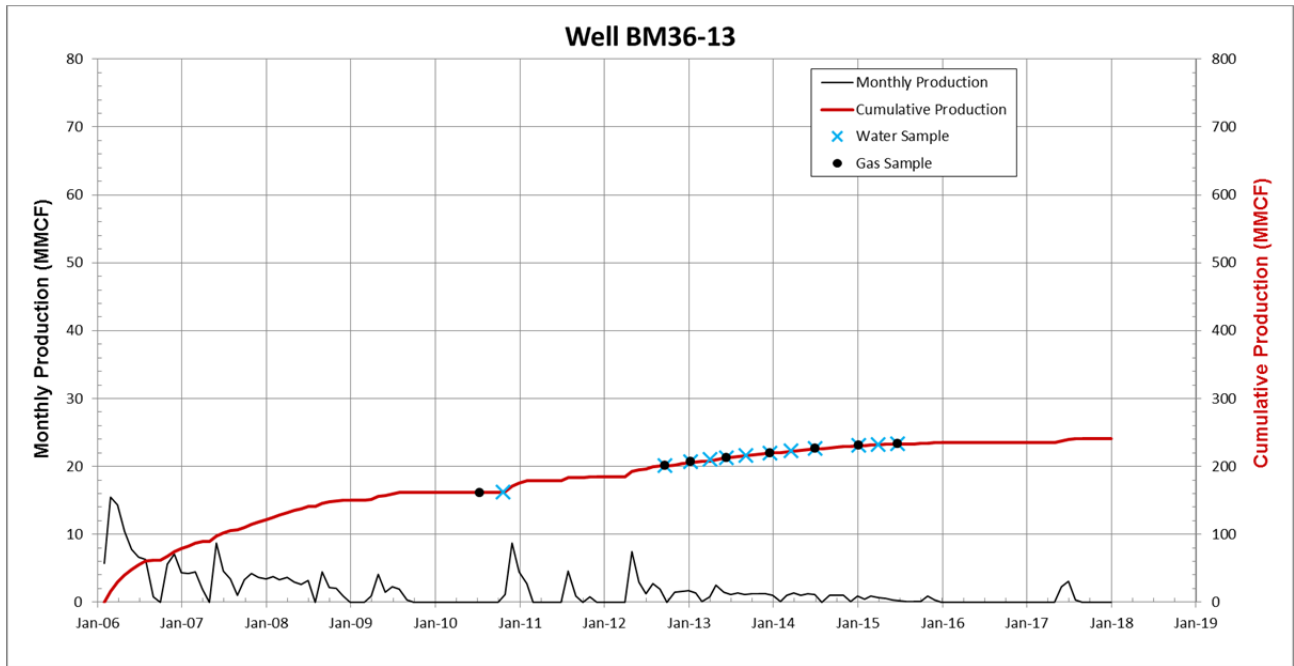


Figure A-13. Frequency of Sampling with Gas Production Data for Well BM36-13

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Appendix B
Data Validation Package

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memo



To: Rick Findlay, Navarro
From: Stephen Donovan, Navarro
CC: Janice McDonald, Navarro
Date: December 6, 2017
Re: Validation of September 2017 Produced Water Data from the Rulison Site

Validation of data generated from the September 2017 produced water sampling event at the Rulison, Colorado, Site has been completed. This Level 2 validation was conducted according to the “Standard Practice for Validation of Environmental Data” in the *Environmental Procedures Catalog* (LMS/POL/S04325).

The samples were submitted for analysis identified by Task Code RUL01-02.1709001. Planned monitoring locations are shown in the Rulison sampling email (Enclosure 1). Samples were collected at 8 of the 13 planned locations. See the trip report (Enclosure 2) for additional details.

All environmental data from this sampling event are considered validated and available for use. Site data are available for viewing with dynamic mapping via the Geospatial Environmental Mapping System (GEMS) website at <http://gems.lm.doe.gov/#>. The field data assessment (Enclosure 3) includes discussion of the field data and field quality control samples. The laboratory performance assessment (Enclosure 4) documents the review of the laboratory data. Summaries of enclosures 3, 4, and 5 are presented below.

Rulison Sampling Email (Enclosure 1)

Trip Report (Enclosure 2)

Field Data Assessment (Enclosure 3)

Verification of Field Activities

A *Field Activities Verification Checklist* was completed with no issues identified.

Assessment of Field Quality Control Samples

A duplicate sample was collected from location 05-045-15748. All duplicate results met the acceptance criteria, demonstrating acceptable precision, with the exception of the gross alpha result. The associated sample and duplicate gross alpha results are qualified with a “J” flag as estimated values.

Laboratory Performance Assessment (Enclosure 4)

All laboratory analytical quality control criteria were met. As shown in the laboratory performance assessment, several analytical results were qualified as estimated values based on the low concentrations observed. Analytical data and the associated qualifiers can be viewed in reports from the environmental database.

Enclosures (4)

Enclosure 1

Rulison Sampling Email

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Donivan, Steve (CONTR)

From: Findlay, Rick (CONTR)
Sent: Tuesday, September 19, 2017 7:51 AM
To: Donivan, Steve (CONTR)
Cc: Campbell, Sam (CONTR)
Subject: RE: Rulison sampling

Steve –

I talked with Art yesterday, the plan is now to sample (produced water only) at the following wells:

- BM 26-33B
- BM 26-33C
- BM 26-33D
- BM 26-34A
- BM 26-34B
- BM 26-34C
- BM 26-34D
- BM 26-22B
- BM 26-22C
- BM 26-22D
- BM 35-32A
- BM 36-13
- **BM 36-13A (if available)**
- BM 36-13B
- **BM 36-23C (if available)**

I'll stop by to discuss.

Thanks,

Rick

From: Donivan, Steve (CONTR)
Sent: Monday, September 18, 2017 9:58 AM
To: Findlay, Rick (CONTR)
Subject: RE: Rulison sampling

Rick – Could you provide a listing of the wells to be sampled?

From: Goodknight, Lauren (CONTR)
Sent: Monday, September 18, 2017 9:21 AM
To: Donivan, Steve (CONTR)
Subject: FW: Rulison sampling

See below.

Lauren Goodknight
Environmental Monitoring Operations

Navarro Research and Engineering
Contractor to the U.S. Department of Energy
Office of Legacy Management
2597 Legacy Way
Grand Junction CO 81503
970-248-6560
lauren.goodknight@lm.doe.gov

From: Findlay, Rick (CONTR)
Sent: Friday, September 15, 2017 8:09 AM
To: Goodknight, Lauren (CONTR)
Subject: RE: Rulison sampling

Gas and produced water.

From: Goodknight, Lauren (CONTR)
Sent: Friday, September 15, 2017 7:59 AM
To: Findlay, Rick (CONTR)
Subject: Rulison sampling

Rick,

Question on Rulison sampling next week...is it gas and produced water or just gas sampling?

Lauren Goodknight

Environmental Monitoring Operations
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Enclosure 2

Trip Report

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memo



To: Rick Findlay, Navarro
 From: Jennifer Graham, Navarro
 Date: October 16, 2017
 CC: Steve Donovan, Navarro
 Rex Hodges, Navarro
 EDD Delivery
 Re: Semiannual Gas Well Sampling Event Trip Report

Site: Rulison, Colorado, Site.

Date of Sampling Event: September 20, 2017.

Team Members: Dan Sellers and Jennifer Graham, Navarro.

Number of Locations Sampled: Samples of produced water were collected from 8 of 13 planned natural gas wells during the sampling event. Natural gas was not sampled during this event per the direction of R. Findlay, Navarro.

Locations Not Sampled/Reason: Produced water could not be collected from well locations BM 26-22B and BM 36-13 because the wells have been shut in for economic reasons and did not produce sufficient water. Well locations BM 26-33B, BM 26-33C, and BM 26-34A due to insufficient water.

Quality Control Sample Cross Reference: The following is the false identification assigned to the quality control sample.

False ID	Sample ID	True ID	Sample Type	Associated Matrix
2487	RUL01-02.1709001-012	BM26-34D	Duplicate	Produced Water

Task Code Assigned: Samples were assigned to task code RUL01-02.1709001. Field data sheets can be found at `\\crow\sms\RUL01-02.1709001\FieldData`.

Sample Shipment: The samples were shipped via FedEx from Grand Junction, Colorado. The produced water samples were sent to ALS Laboratories Group in Ft. Collins, CO on September 21, 2017.

Well Inspection Summary: No issues were identified.

Sampling Method: Samples were collected according to the *Sampling and Analysis Plan (SAP) for the U. S. Department of Energy Office of Legacy Management Sites (LMS/PRO/S04351, continually updated)*.

Field Variance: None.

Rick Findlay
October 16, 2017
Page 2

Equipment: All equipment functioned properly.

Stakeholder/Regulatory/DOE: D. Lawton with Caerus Oil and Gas provided access to the natural gas wells.

Safety Issues: None.

Access Issues: None.

General Information: During this event, none of the natural gas wells were in production (“not running”) at the time, due to a production pipeline repair issue. The wells were briefly turned on for collection of produced water samples. Locations BM35-32A and BM 36-13B have both been shut in for economic reasons but were able to be sampled this event.

Immediate Actions Taken: None.

Future Actions Required or Suggested: None.

Enclosure 3

Field Data Assessment

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Water Sampling Field Activities Verification Checklist

Project	<u>Rulison, Colorado</u>	Date(s) of Water Sampling	<u>September 20, 2017</u>
Date(s) of Verification	<u>December 4, 2017</u>	Name of Verifier	<u>Stephen Donovan</u>

	Response (Yes, No, NA)	Comments
1. Is the SAP the primary document directing field procedures? List any Program Directives or other documents, SOPs, instructions.	<u>Yes</u>	
2. Were the sampling locations specified in the planning documents sampled?	<u>No</u>	<u>Produced water could not be collected from well locations BM 26-22B (05-045-16086) and BM 36-13 (05-045-10840) because the wells have been shut in for economic reasons. Wells BM 26-33B (05-045-15743), BM 26-33C (05-045-15742), and BM 26-34A (05-045-15744) were not sampled due to insufficient water.</u>
3. Were field equipment calibrations conducted as specified in the above-named documents?	<u>NA</u>	<u>Field measurements were not required.</u>
4. Was an operational check of the field equipment conducted daily? Did the operational checks meet criteria?	<u>NA</u>	
5. Were the number and types (alkalinity, temperature, specific conductance, pH, turbidity, DO, ORP) of field measurements taken as specified?	<u>NA</u>	
6. Were wells categorized correctly?	<u>NA</u>	<u>This sampling event did not include groundwater.</u>
7. Were the following conditions met when purging a Category I well: Was one pump/tubing volume purged prior to sampling? Did the water level stabilize prior to sampling? Did pH, specific conductance, and turbidity measurements meet criteria prior to sampling? Was the flow rate less than 500 mL/min?	<u>NA</u>	<u>This sampling event did not include groundwater.</u>

Water Sampling Field Activities Verification Checklist (continued)

	Response (Yes, No, NA)	Comments
8. Were the following conditions met when purging a Category II well: Was the flow rate less than 500 mL/min? Was one pump/tubing volume removed prior to sampling?	NA	This sampling event did not include groundwater.
9. Were duplicates taken at a frequency of one per 20 samples?	Yes	A duplicate sample was collected at location BM 26-34D (05-045-15748).
10. Were equipment blanks taken at a frequency of one per 20 samples that were collected with non-dedicated equipment?	NA	An equipment blank was not required.
11. Were trip blanks prepared and included with each shipment of VOC samples?	NA	
12. Were the true identities of the QC samples documented?	Yes	
13. Were samples collected in the containers specified?	Yes	
14. Were samples filtered and preserved as specified?	Yes	
15. Were the number and types of samples collected as specified?	Yes	
16. Were chain of custody records completed and was sample custody maintained?	Yes	
17. Was all pertinent information documented on the field data sheets?	Yes	
18. Was the presence or absence of ice in the cooler documented at every sample location?	NA	Sample cooling was not required.
19. Were water levels measured at the locations specified in the planning documents?	NA	

Data Qualifier Summary

Analytical results were qualified as listed in the following table. Refer to the section below for an explanation of the data qualifiers applied.

Table 1. Field Quality Control Sample Data Qualifiers for Analytical Results

Sample Number	Location	Analyte(s)	Flag	Reason
1709467-5	05-045-15748	Gross Alpha	J	Field duplicate precision
1709467-9	05-045-15748 Duplicate	Gross Alpha	J	Field duplicate precision

Field Duplicate Assessment

Field duplicate samples are collected and analyzed as an indication of overall precision of the measurement process. The precision observed includes both field and laboratory precision and has more variability than laboratory duplicates, which measure only laboratory performance. A duplicate sample was collected from location BM 26-34D (05-045-15748). For radiochemical measurements, the relative error ratio (the ratio of the absolute difference between the sample and duplicate results and the sum of the 1-sigma uncertainties) is used to evaluate duplicate results and should be less than 3. All duplicate results met this criterion, demonstrating acceptable precision, with the exception of the gross alpha result. The associated sample and duplicate gross alpha results are qualified with a “J” flag as estimated values.

Validation Report: Field Duplicates

Page 2 of 3
30-Nov-2017

Project: Rulison Produced Water **Task Code:** RUL01-02.1709001 **Lab Code:** PAR

Analyte	Duplicate: RUL01-02.1709001-012				Sample: RUL01-02.1709001-008 05-045-15748				RPD	RER	Units
	Result	Qualifiers	Uncert	Dilution	Result	Qualifiers	Uncert.	Dilution			
Actinium-228	24.1	U	15.4	1	27.3		10.6	1		-0.3	pCi/L
Americium-241	15.7	U	15.8	1	2.02	U	3.09	1		1.7	pCi/L
Antimony-125	6.23	U	5.39	1	6.82	U	6.11	1		-0.1	pCi/L
Cerium-144	-4.66	U	12.1	1	-0.254	U	10.5	1		-0.5	pCi/L
Cesium-134	-3.04	U	2.74	1	1.22	U	2.74	1		-2.2	pCi/L
Cesium-137	0.667	U	2.74	1	-0.0349	U	2.71	1		0.4	pCi/L
Cobalt-60	-0.459	U	3.25	1	3.08	U	3.05	1		-1.6	pCi/L
Europium-152	-4.08	U	16.5	1	14.1	U	15.6	1		-1.6	pCi/L
Europium-154	-8.52	U	15.1	1	-9.03	U	15.5	1		0.0	pCi/L
Europium-155	0.332	U	6.21	1	1.7	U	4.39	1		-0.4	pCi/L
Gross Alpha	25.5		11	1	66.1		19.8	1		-3.5	pCi/L
Gross Beta	54.2		16.2	1	77.3		18.8	1		-1.8	pCi/L
Lead-212	6.77	U	6.79	1	8.78	U	6.91	1		-0.4	pCi/L
Potassium-40	92.6	U	78.4	1	43.8	U	76	1		0.9	pCi/L
Promethium-144	1.63	U	1.44	1	1.4	U	2.69	1		0.1	pCi/L
Promethium-146	0.851	U	2.94	1	0.943	U	2.86	1		0.0	pCi/L
Ruthenium-106	-6.1	U	23.7	1	-16.9	U	25.4	1		0.6	pCi/L
Thorium-234	18.3	U	71.1	1	29.8	U	46.5	1		-0.3	pCi/L
Tritium	-15.3	U	191	1	-98.2	U	190	1		0.6	pCi/L
Uranium-235	17	U	10.9	1	10.4	U	10.6	1		0.9	pCi/L

QC Checks: RPD: Relative Percent Difference RER: Relative Error Ratio

Validation Report: Field Duplicates

Page 3 of 3
30-Nov-2017

Project: Rulison Produced Water **Task Code:** RUL01-02.1709001 **Lab Code:** PAR

Analyte	Duplicate: RUL01-02.1709001-012				Sample: RUL01-02.1709001-008 05-045-15748				RPD	RER	Units
	Result	Qualifiers	Uncert	Dilution	Result	Qualifiers	Uncert.	Dilution			
Yttrium-88	1.02	U	6.37	1	2.98	U	2.49	1		-0.6	pCi/L

QC Checks: RPD: Relative Percent Difference RER: Relative Error Ratio

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Enclosure 4

Laboratory Performance Assessment

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General Information

Task ID: RUL01-02.1709001
 Sample Event: September 20, 2017
 Site(s): Rulison, Colorado, Site
 Laboratory: ALS Laboratory Group, Fort Collins, Colorado
 Work Order No.: 1709467
 Analysis: Radiochemistry
 Validator: Stephen Donivan
 Review Date: December 5, 2017

This validation was performed according to the *Environmental Procedures Catalog*, (LMS/POL/S04325) “Standard Practice for Validation of Environmental Data.” The procedure was applied at Level 2, Data Verification. See attached Data Validation Worksheets for supporting documentation on the data review and validation. All analyses were successfully completed. The samples were prepared and analyzed using accepted procedures based on methods specified by line item codes, which are listed in Table 1.

Table 1. Analytes and Methods

Analyte	Line Item Code	Prep Method	Analytical Method
Gamma Spectrometry	GAM-A-001	PA SOP713R11	PA SOP713R11
Gross Alpha/Beta	GPC-A-001	PA SOP702R19	PA SOP724R10
Tritium	LCS-A-001	PA SOP700R10	PA SOP704R9

Data Qualifier Summary

Analytical results were qualified as listed in Table 2. Refer to the sections below for an explanation of the data qualifiers applied.

Table 2. Data Qualifier Summary

Sample Number	Location	Analyte	Flag	Reason
1709467-1	05-045-16074	Gross Beta	J	Less than the determination limit
1709467-5	05-045-15748	Actinium-228	U	Nuclide identification criteria
1709467-6	05-045-10919	Gross Alpha	J	Less than the determination limit
1709467-7	05-045-15469	Potassium-40	J	Less than the determination limit
1709467-7	05-045-15469	Tritium	J	Less than the determination limit
1709467-8	05-045-16087	Gross Alpha	J	Less than the determination limit
1709467-8	05-045-16087	Gross Beta	J	Less than the determination limit
1709467-9	05-045-15748 Duplicate	Gross Beta	J	Less than the determination limit

Sample Shipping/Receiving

ALS Laboratory Group in Fort Collins, Colorado, received nine water samples on September 22, 2017, accompanied by a *Chain of Custody* form. The *Chain of Custody* form was checked to confirm that all of the samples were listed with sample collection dates and times and that signatures and dates indicated sample relinquishment and receipt. Copies of the shipping labels were included in the receiving documentation. The *Chain of Custody* form was complete, with no errors or omissions.

Preservation and Holding Times

The sample shipment was received intact at ambient temperature, which complies with requirements. All samples were received in the correct container types and had been preserved correctly for the requested analyses. Sample analysis was completed within the applicable holding times.

Detection and Quantitation Limits

The method detection limit (MDL) was reported for all metal, organic, and wet chemical analytes as required. The MDL, as defined in Title 40 *Code of Federal Regulations* Section 136 (40 CFR 136), is the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The practical quantitation limit (PQL) for these analytes is the lowest concentration that can be reliably measured and is defined as 5 times the MDL.

For radiochemical analytes (those measured by radiometric counting), the MDL and PQL are not applicable, and these results are evaluated using the minimum detectable concentration (MDC), decision level concentration (DLC), and determination limit (DL). The MDC is a measure of radiochemical method performance and was calculated and reported as specified in *Quality Systems for Analytical Services*. The DLC is the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is estimated as 3 times the 1-sigma total propagated uncertainty. Results that are greater than the MDC but less than the DLC are qualified with a “U” flag (not detected). The DL for radiochemical results is the lowest concentration that can be reliably measured and is defined as 3 times the MDC. Results not previously “U” qualified that are less than the DL are qualified with a “J” flag as estimated values.

The reported MDCs for radiochemical analytes met the detection limits requirements with the following exception: The required detection limits were not met for gross alpha and gross beta samples because of the elevated levels of dissolved solids in the samples.

Laboratory Instrument Calibration

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for all analytes. Initial calibration verification demonstrates that the instrument is capable of acceptable performance in the beginning of the analytical run. Compliance requirements for continuing calibration checks are established to ensure that the instrument continues to be capable of

producing acceptable qualitative and quantitative data. All laboratory instrument calibrations were performed correctly in accordance with the cited methods. All calibration and laboratory spike standards were prepared from independent sources.

Gamma Spectrometry

Activity concentrations above the MDC were reported in some instances where minimum nuclide identification criteria were not met. Such tentative identifications result when the software attempts to calculate net activity concentrations for analytes where either one or both of the following criteria are not satisfied: One or more characteristic peaks for a nuclide must be identified above the critical level, or the minimum library peak abundance must be attained. Sample results for gamma-emitting radionuclides that do not meet the identification criteria are qualified with a “U” flag as not detected.

Method and Calibration Blanks

Method blanks are analyzed to assess any contamination that may have occurred during sample preparation. Calibration blanks are analyzed to assess instrument contamination prior to and during sample analysis. All radiochemical method blank results were below the DLC.

Laboratory Control Sample

Laboratory control samples were analyzed at the correct frequency to provide information on the accuracy of the analytical method and the overall laboratory performance, including sample preparation. All control sample results were acceptable.

Laboratory Replicate Analysis

Laboratory replicate sample results demonstrate acceptable laboratory precision. The relative percent difference value for the chloride matrix spike replicate met the acceptance criteria. The radiochemical relative error ratio (calculated using the 1-sigma total propagated uncertainty) for the sample replicates was less than 3 for all duplicates.

Matrix Spike Analysis

Matrix spike and matrix spike duplicate (MS/MSD) samples are used to measure method performance in the sample matrix. The MS/MSD data are not evaluated when the concentration of the unspiked sample is greater than 4 times the spike concentration. The spike recoveries were acceptable for all analytes.

Completeness

Results were reported in the correct units for all analytes requested using contract-required laboratory qualifiers.

Electronic Data Deliverable File

The Electronic Data Deliverable (EDD) file arrived on October 30, 2017. The EDD was examined to verify that the file was complete and in compliance with requirements. The contents of the file were compared to the requested analyses to ensure all and only the requested data are delivered. The contents of the EDD were manually examined to verify that the sample results accurately reflect the data contained in the sample data package.



STEPHEN
DONIVAN (Affiliate)
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Report Prepared By: _____
Stephen Donovan
Laboratory Coordinator

General Data Validation Report

Page 1 of 1

Task Code: RUL01-02.1709001 **Lab Code:** PAR **Validator:** Stephen Donovan **Validation Date:** 11-30-2017

Project: Rulison Produced Water

Samples: 14

Analysis Type: General Chemistry Metals Organics Radiochemistry

Chain of Custody

Sample

Present: <u>OK</u> Signed: <u>OK</u> Dated: <u>OK</u>	Integrity: <u>OK</u> Preservation: <u>OK</u> Temperature: <u>OK</u>
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Check

Summary

Holding Times:	All analyses were completed within the applicable holding times.
Detection Limits:	There were 3 detection limits above the contract required limits.
Field Duplicates:	There was 1 duplicate evaluated.

Radiochemistry Data Validation Worksheet

Page 1 of 3
30-Nov-2017

Project: Rulison Produced Water

Task Code: RUL01-02.1709001

Lab Code: PAR

Sample ID	Analyte	Analysis Date	QC Type	Result Type	Result	Flag	TPU	Spike Recovery	Spike Dup Recovery	Lower Limit	Upper Limit	RPD	RPD Limit	RER	Comments
	Actinium-228	10-05-2017	MB	TRG	8.49	U	9.31								
	Americium-241	10-05-2017	LCS	SC	98700.00		11700	99.19		85	115				
	Americium-241	10-05-2017	MB	TRG	-2.33	U	6.38								
	Antimony-125	10-05-2017	MB	TRG	0.13	U	5.09								
	Cerium-144	10-05-2017	MB	TRG	-7.93	U	14.1								
	Cesium-134	10-05-2017	MB	TRG	-1.58	U	2.23								
	Cesium-137	10-05-2017	LCS	SC	39400.00		4640	105.00		85	115				
	Cesium-137	10-05-2017	MB	TRG	-2.45	U	2.05								
	Cobalt-60	10-05-2017	LCS	SC	39900.00		4680	101.00		85	115				
	Cobalt-60	10-05-2017	MB	TRG	-1.52	U	2.45								
	Europium-152	10-05-2017	MB	TRG	-0.34	U	11.8								
	Europium-154	10-05-2017	MB	TRG	-11.70	U	13.4								
	Europium-155	10-05-2017	MB	TRG	-1.53	U	3.89								
	Gross Alpha	10-10-2017	MB	TRG	-0.16	U	0.41								
	Gross Alpha	10-11-2017	LCS	SC	255.00		46.5	113.00		75	125				
	Gross Beta	10-10-2017	MB	TRG	-0.22	U	0.616								
	Gross Beta	10-11-2017	LCS	SC	186.00		32.4	96.50		75	125				
	Lead-212	10-05-2017	MB	TRG	2.00	U	6.16								
	Potassium-40	10-05-2017	MB	TRG	42.90	U	69.3								
	Promethium-144	10-05-2017	MB	TRG	-3.25	U	6.52								
	Promethium-146	10-05-2017	MB	TRG	-2.88	U	2.28								

QC Types: LCS: Laboratory Control Sample LCS/D: Laboratory Control Sample Duplicate MB: Method Blank MS: Matrix Spike MSD: Matrix Spike Duplicate R: Replicate

Result Types: IS: Internal Standard SC: Spike Analyte TRG: Target analyte

QC Checks: RPD: Relative Percent Difference RER: Relative Error Ratio TPU: Total Propagated Uncertainty

Radiochemistry Data Validation Worksheet

Page 2 of 3

30-Nov-2017

Project: Rulison Produced Water

Task Code: RUL01-02.1709001

Lab Code: PAR

Sample ID	Analyte	Analysis Date	QC Type	Result Type	Result	Flag	TPU	Spike Recovery	Spike Dup Recovery	Lower Limit	Upper Limit	RPD	RPD Limit	RER	Comments
	Ruthenium-106	10-05-2017	MB	TRG	-12.10	U	20								
	Thorium-234	10-05-2017	MB	TRG	-5.47	U	43.6								
	Tritium	10-12-2017	LCS	SC	16800.00		2590	94.40		85	115				
	Tritium	10-12-2017	MB	TRG	74.80	U	195								
	Uranium-235	10-05-2017	MB	TRG	7.74	U	15.6								
	Yttrium-88	10-05-2017	MB	TRG	1.95	U	2.47								
RUL01-02.1709001-007	Gross Alpha	10-10-2017	R	TRG	243.00		53							0.92	
RUL01-02.1709001-007	Gross Alpha	10-11-2017	MS	SC	7630.00		1530	81.30		60	140				
RUL01-02.1709001-007	Gross Beta	10-10-2017	R	TRG	182.00		40.7							0.533	
RUL01-02.1709001-007	Gross Beta	10-11-2017	MS	SC	7170.00		1250	90.90		60	140				
RUL01-02.1709001-008	Actinium-228	10-05-2017	R	TRG	36.40		14.8							1	
RUL01-02.1709001-008	Americium-241	10-05-2017	R	TRG	3.55	U	74.5							0.0412	
RUL01-02.1709001-008	Antimony-125	10-05-2017	R	TRG	3.64	U	6.34							0.722	
RUL01-02.1709001-008	Cerium-144	10-05-2017	R	TRG	-10.00	U	16.5							0.999	
RUL01-02.1709001-008	Cesium-134	10-05-2017	R	TRG	2.27	U	1.62							0.657	
RUL01-02.1709001-008	Cesium-137	10-05-2017	R	TRG	-1.38	U	2.74							0.698	
RUL01-02.1709001-008	Cobalt-60	10-05-2017	R	TRG	0.83	U	2.8							1.09	
RUL01-02.1709001-008	Europium-152	10-05-2017	R	TRG	5.63	U	13.8							0.816	
RUL01-02.1709001-008	Europium-154	10-05-2017	R	TRG	-3.51	U	14.7							0.517	

QC Types: LCS: Laboratory Control Sample LCSD: Laboratory Control Sample Duplicate MB: Method Blank MS: Matrix Spike MSD: Matrix Spike Duplicate R: Replicate

Result Types: IS: Internal Standard SC: Spike Analyte TRG: Target analyte

QC Checks: RPD: Relative Percent Difference RER: Relative Error Ratio TPU: Total Propagated Uncertainty

Radiochemistry Data Validation Worksheet

Page 3 of 3

30-Nov-2017

Project: Rulison Produced Water

Task Code: RUL01-02.1709001

Lab Code: PAR

Sample ID	Analyte	Analysis Date	QC Type	Result Type	Result	Flag	TPU	Spike Recovery	Spike Dup Recovery	Lower Limit	Upper Limit	RPD	RPD Limit	RER	Comments
RUL01-02.1709001-008	Europium-155	10-05-2017	R	TRG	9.82	U	10.7							1.4	
RUL01-02.1709001-008	Lead-212	10-05-2017	R	TRG	4.51	U	9.63							0.722	
RUL01-02.1709001-008	Potassium-40	10-05-2017	R	TRG	122.00	U	77.4							1.45	
RUL01-02.1709001-008	Promethium-144	10-05-2017	R	TRG	-0.06	U	2.67							0.77	
RUL01-02.1709001-008	Promethium-146	10-05-2017	R	TRG	-0.60	U	3.03							0.744	
RUL01-02.1709001-008	Ruthenium-106	10-05-2017	R	TRG	-36.80	U	25.7							1.1	
RUL01-02.1709001-008	Thorium-234	10-05-2017	R	TRG	-19.50	U	131							0.708	
RUL01-02.1709001-008	Uranium-235	10-05-2017	R	TRG	8.18	U	16							0.237	
RUL01-02.1709001-008	Yttrium-88	10-05-2017	R	TRG	3.97	U	3.12							0.494	
RUL01-02.1709001-011	Tritium	10-12-2017	MS	SC	18000.00		2780	101.00		85	115				
RUL01-02.1709001-011	Tritium	10-12-2017	R	TRG	37.50	U	197							0.225	

QC Types: LCS: Laboratory Control Sample LCSD: Laboratory Control Sample Duplicate MB: Method Blank MS: Matrix Spike MSD: Matrix Spike Duplicate R: Replicate

Result Types: IS: Internal Standard SC: Spike Analyte TRG: Target analyte

QC Checks: RPD: Relative Percent Difference RER: Relative Error Ratio TPU: Total Propagated Uncertainty

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