TRI-PARTY AGREEMENT

Change Notice Number TPA-CN- 1105	TPA CHANGE NOTICE FORM	Date: July 28, 2021
Document Number, Title, and Revision: DOE/RL-2019-76, *200-ZP-1 Operable Unit Optimization Study Sampling and Analysis Plan*, Revision 0		Date Document Last Issued: January 12, 2020
Approved Change Notices Against this Document: N/A		
Originator Mark E. Byrnes		Phone: 509 373-3996

Description of Change:
DOE/RL-2019-76 is being revised to remove oxidation-reduction potential as a required field parameter measurement for routine groundwater sampling. Groundwater purging/sampling rates were revised.

M.W. Cline (**DOE**) and E. Laija (**Lead Regulatory Agency**) agree that the proposed change modifies an approved workplan/document and will be processed in accordance with the Tri-Party Agreement Action Plan, Section 9.0, *Documentation and Records,* and not Chapter 12.0, *Changes to the Agreement*.

Requirement to measure oxidation-reduction potential (ORP) was removed from the document. This change affects Tables 1-6, 2-3, and 2-6. Reference to ORP measurements was removed from Section 3.3.

Groundwater purging and sampling requirements in Sections 2.1.5 and 3.3 were revised.

Additions are shown using double underline. Deletions are shown using ~~strikeout~~.

Note: Include affected page number(s): 1-26, 2-10, 2-12, 2-18, and 3-5

Justification and Impacts of Change:

Oxidation-reduction potential (ORP) is being removed from the suite of field parameters monitored at the wells included in this SAP. ORP field measurements collected during routine groundwater sampling have been assessed and shown to be unreliable, inconsistent, and consistently qualified as unusable during data review. Dissolved oxygen (DO) is also measured as a part of the field parameters and is a more reliable indicator of oxidation conditions in the aquifer. DO measurements will replace ORP for this use. Technical Memorandum - CHPRC-04653 contains information supporting this change.

The groundwater purging and sampling requirements in Sections 2.1.5 and 3.3 were revised to specify pumping rates instead of casing volumes. This change is in line with reducing unnecessary purge volumes and high sampling rates.

Approvals:

Michael W. Cline — Digitally signed by Michael W. Cline Date: 2021.07.29 11:13:07 -07'00'		[X] Approved [ ] Disapproved
DOE Project Manager	Date	
EMERALD LAIJA — Digitally signed by EMERALD LAIJA Date: 2021.07.30 11:31:30 -04'00'		[X] Approved [ ] Disapproved
EPA Project Manager	Date	
N/A		[ ] Approved [ ] Disapproved
Ecology Project Manager	Date	

Table 1-6. Analytes for 200-ZP-1 OU Optimization Study Long-Term Groundwater Monitoring

COC	CAS Number	Purpose
COCs		
Carbon tetrachloride	56-23-5	Delineate carbon tetrachloride plume; optimization study monitoring
Nitrate-N	14797-55-8	Delineate nitrate plume; optimization study monitoring
Other Constituents		
Chloride	16887-00-6	Evaluate chlorinated solvent natural attenuation; optimization study monitoring
Manganese[a]	7436-96-5	Evaluate natural attenuation; optimization study monitoring
Nickel[a]	7440-02-0	Evaluate stainless-steel corrosion; optimization study monitoring
Nitrite-N	14797-65-0	Evaluate nitrate natural attenuation; optimization study monitoring
Sulfate	14808-79-8	Evaluate natural attenuation; optimization study monitoring
Total organic carbon	TOC	Evaluate natural attenuation; optimization study monitoring
Field Screening Parameters[b]		
Dissolved oxygen	N/A	Evaluate natural attenuation and well purge for sampling
~~Oxidation-reduction potential~~	~~N/A~~	~~Evaluate natural attenuation~~
pH	N/A	Evaluate well purge for sampling
Specific conductance	N/A	Evaluate well purge for sampling
Temperature	N/A	Evaluate well purge for sampling
Turbidity	N/A	Evaluate well purge for sampling

a. Collect filtered and unfiltered samples for metals.

b. Field screening parameters to be collected in accordance with DOE/RL-96-68, *Hanford Analytical Services Quality Assurance Requirements Document*, *Vol. 3, Field Analytical Technical Requirements*.

CAS = Chemical Abstracts Service
COC = contaminant of concern
N/A = not applicable
TOC = total organic carbon

1.5 Project Schedule

The optimization study groundwater monitoring requirements have been divided into two phases: near-term and long-term. The near-term groundwater sampling and analysis requirements were implemented through TPA-CN-0875 for FY 2020 and are not included in this SAP. The long-term groundwater monitoring for the 200-ZP-1 OU optimization study covered under this SAP is currently expected to be completed over a period of 4 years (FY 2021 through FY 2024). However, as discussed in Section 4.1.3 of the 200-ZP-1 OU OSP (DOE/RL-2019-38), additional time may be needed to collect sufficient data to meet study objectives, which could result in the optimization study continuing for an additional 2 years (through FY 2026).

Regarding minor field changes, the OU technical lead (in coordination with the Soil and Groundwater Remediation Project [S&GRP] subject matter expert) will approve deviations from the SAP that do not have an adverse effect on the technical integrity or adequacy of the sampling activity. Examples of minor field changes are as follows:

- During groundwater sampling, most groundwater samples will be pumped, although use of another method may be authorized by the OU technical lead.
- The sample depths provided in this SAP are estimated based on known characterization data and geology collected from nearby wells. For this reason, adjustments to the sample depths are anticipated. The sample depths may be altered during drilling in consultation with the OU technical lead.
- During split-spoon sampling, if insufficient material is recovered or the split spoon is overdriven, then (when feasible) a second split spoon will be collected prior to advancing the borehole. If there is not enough sample volume recovered during split-spoon sampling, laboratory-approved minimum sample volumes will be used to run all required sample analyses. If it is not possible to collect sufficient sample volume and perform all analyses, then DOE-RL will be consulted to concur on the path forward.
- Groundwater samples ~~may~~should not be collected before ~~a minimum of three well casing volumes have been purged and~~ water chemistry (e.g., temperature, pH, and conductivity) has stabilized within 10% variance over three consecutive measurements unless approved by the OU technical lead. ~~Note that one borehole volume is acceptable if water chemistry (e.g., temperature, pH, and conductivity) has stabilized within 10% variance over three consecutive measurements for the depth-discrete groundwater samples collected during drilling.~~

Regarding minor changes, the OU technical lead (in coordination with the S&GRP subject matter expert) will consult with DOE-RL and the lead regulatory agency when deviations from the SAP do not affect the overall intent of the plan. Examples of minor changes include the following:

- Changing the type of sample being collected. For example, collecting continuous grab samples instead of continuous cores.
- Selecting a different well construction material and/or well design.
- Changing to a different drilling method.

The OU technical lead (in coordination with the S&GRP subject matter expert) will inform DOE-RL and EPA of deviations from the SAP that affect the overall intent and schedule may require revision to the approved plan.

Logbooks are required to document field sampling activities. The logbook must be identified with a unique project name and number. Only authorized individuals may make entries into the logbooks. Logbooks will be controlled in accordance with internal work requirements and processes. Data forms are also required for field activities and will be controlled in accordance with internal work requirements and processes.

The FWS and SMR are responsible for ensuring that the field instructions are maintained and aligned with revisions or approved changes to the SAP. SMR will ensure that deviations from the SAP (i.e., minor field changes, as documented in Table 2-2) are reflected in revised field sampling documents for the samplers and the analytical laboratory. All other changes need to be documented by the

2.2 Data Generation and Acquisition

This section addresses data generation and acquisition to ensure that the project's methods for sampling measurement and analysis, data collection or generation, data handling, and QC activities are appropriate and documented. Requirements for instrument calibration and maintenance, supply inspections, and data management are also addressed.

2.2.1 Analytical Methods Requirements

Table 2-3 provides information regarding analytical method requirements for samples collected. Updated EPA methods and nationally recognized standard methods may be substituted for the analytical methods identified in Table 2-3 in order to follow any changed requirements in method updates. The new method must achieve project DQOs as well as or better than the replaced method.

Table 2-3. Performance Requirements for Groundwater Sample Analysis

Constituent	CAS Number[a]	MCL or WAC Requirement (µg/L)[b]	Analytical Method[c]	PQL (µg/L)[e]
General Chemical Parameters				
Total organic carbon	TOC	--	9060	1,050
Chloride	16887-00-6	250,000	9056, 300.0	400
Nitrate	14797-55-8	10,000	9056, 300.0	~~250~~525
Nitrite	14797-65-0	1,000	9056, 300.0	~~250~~525
Sulfate	14808-79-8	250,000	9056, 300.0	1,050
Inorganics – Metals				
Manganese[d]	7439-96-5	50	6020	~~5.25~~10.5
Nickel[d]	7440-02-0	320	6020	21
Volatile Organics				
Carbon tetrachloride	56-23-5	3.4	8260	3
Field Measurements				
Dissolved oxygen	N/A	N/A	--	N/A
~~Oxidation reduction potential~~	~~N/A~~	~~N/A~~	~~--~~	~~N/A~~
pH	N/A	N/A	--	N/A
Specific conductance	N/A	N/A	--	N/A
Temperature	N/A	N/A	--	N/A
Turbidity	N/A	N/A	--	N/A

a. The Hanford Environmental Information System database constituent identification number is used.

b. WAC 173-340-720, "Model Toxics Control Act—Cleanup," "Groundwater Cleanup Standards," Method B. The values listed are equivalent to the action levels listed in Appendix B, Table B-9 of the 200-ZP-1 OU PMP (DOE/RL-2009-115, *Performance Monitoring Plan for the 200-ZP-1 Groundwater Operable Unit Remedial Action*).

Table 2-6. Holding-Time Guidelines for Laboratory Analytes

Constituent/ ~~Parameter~~Method	Preservation*	Holding Time
General Chemistry Parameters		
pH	None	Analyze immediately
Total organic carbon	Store ≤6°C, adjust pH to <2 with H_2SO_4 or HCl	28 days
Inorganics – Anions		
Nitrate, nitrite	Store ≤6°C	48 hours
Chloride, sulfate	Store ≤6°C	28 days
Inorganics – Metals		
ICP/MS	Adjust pH to <2 with HNO_3	6 months
Volatile Organics		
GC/MS	Store ≤6°C; adjust pH to <2 with HCl or H_2SO_4 (optional)	7 days preserved/ 14 days unpreserved

Notes:

Holding times and preservation methods are dependent on the constituent and are consistent with U.S. Environmental Protection Agency guidance and approved analytical methods.

Container types and volumes will be identified on the chain-of-custody form.

This table only applies to laboratory analyses. Depth to water, dissolved oxygen, ~~oxidation-reduction potential,~~ pH, specific conductance, temperature, and turbidity are not listed because they are measured in the field.

*For preservation identified as stored at <6°C, the sample should be protected against freezing unless it is known that freezing will not impact the sample integrity.

GC/MS = gas chromatography/mass spectrometry

ICP/MS = inductively coupled plasma/mass spectrometry

2.2.4 Measurement Equipment

Each measuring equipment user is responsible for ensuring that equipment is functioning as expected, properly handled, and properly calibrated at required frequencies per methods governing control of the equipment. Onsite environmental instrument testing, inspection, calibration, and maintenance will be recorded in accordance with approved methods. Field screening instruments will be used, maintained, and calibrated in accordance with manufacturers' specifications and other approved methods.

2.2.5 Instrument and Equipment Testing, Inspection, and Maintenance

Collection, measurement, and testing equipment should meet applicable standards (e.g., ASTM International [formerly the American Society for Testing and Materials]) or have been evaluated as acceptable and valid in accordance with instrument-specific methods, requirements, and specifications. Software applications will be acceptance tested prior to use in the field.

Measurement and testing equipment used in the field or laboratory will be subjected to preventive maintenance measures to minimize downtime. Laboratories must maintain and calibrate their equipment. Maintenance requirements (e.g., documentation of routine maintenance) will be included in the individual laboratory and onsite organization's QA plan or operating protocols, as appropriate. Maintenance of laboratory instruments will be performed in a manner consistent with applicable HASQARD requirements (DOE/RL-96-68).

3.3 Sampling Methods

Sampling may include, but is not limited to, the following methods:

- Field screening measurements
- Radiological screening
- Borehole sampling
- Groundwater sampling
- Water-level measurements

Groundwater samples will be collected post-well purging in accordance with the current revision of applicable operating methods~~, as described in general in the following discussion~~. Prior to sample collection, purging of the sampling interval will be performed at flow rates of <38 L/min (10 gal/min) until field parameters stabilize as indicated below. Samples will be collected from the aquifer at flow rates of <3.8 L/min (1 gal/min). Groundwater samples are collected after field measurements of purged groundwater have stabilized:

- **pH:** Two consecutive measurements agree within 0.2 pH units,
- **Temperature:** Two consecutive measurements agree within 0.2°C (32.3°F).
- **Conductivity:** Two consecutive measurements agree within 10% of each other.
- **Turbidity:** Less than 5 nephelometric turbidity units (NTUs) prior to sampling (or upon recommendation of the OU technical lead).

Dissolved oxygen ~~and oxidation-reduction potential also~~ will be measured in the field under this SAP. Dissolved oxygen ~~and oxidation-reduction potential~~ measurements are not required to be stable prior to sample collection.

Unless special requirements are requested from the OU technical lead, wells are typically purged using the equivalent volume as that of three borehole diameters multiplied by the length of the saturated portion of the well screen. Stable field readings are also required, as specified above. The default pumping rate is 7.6 to 45.4 L/min (2 to 12 gal/min) depending on the pump, although this is not practical at every well. On occasions when the purge volume is extraordinarily large, wells are purged for a minimum of one hour and then sampled once stable field readings are obtained.

Field measurements (except for turbidity) are obtained using a flow-through cell. Groundwater is pumped directly from the well to the flow-through cell. At the beginning of the sampling event, field crews attach a clean, stainless-steel sampling manifold to the riser discharge. The manifold has two valves and two ports: one port is used only for purge water, and the other port is used to supply water to the flow-through cell. Probes are inserted into the flow-through cell to measure pH, temperature, conductivity, and dissolved oxygen~~, and oxidation-reduction potential~~. Turbidity is measured by inserting a sample vial into a turbidimeter. The purge water is discharged to the purge water truck.

Once field measurements have stabilized, the hose supplying water to the flow-through cell is disconnected and a clean, stainless-steel drop leg is attached for sampling. The flow rate is reduced during sampling to minimize loss of volatiles (if any) and prevent overfilling the bottles. Sample bottles are filled in a sequence designed to minimize loss of volatiles (if any). Filtered samples are collected after collection of the unfiltered samples. For some constituents (e.g., metals), both filtered and unfiltered samples are collected. If additional samples require filtration (e.g., at turbidity >5 NTUs), an inline, disposable 0.45 μm filter is used.