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Sampling and Analysis Plan Addendum for the C-Area Groundwater (CAGW) Operable Unit (OU) (U)

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Revision 1.1

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SAVANNAH RIVER SITE • AIKEN, SOUTH CAROLINA

LIST OF ACRONYMS (*Continued*)

RCRA	Resource Conservation and Recovery Act
~~R&D~~	~~Research and Development~~
RFI	RCRA Facility Investigation
RI	Remedial Investigation
ROD	Record of Decision
RSL	Regional Screening Level(s)
SAP	Sampling and Analysis Plan
SB/PP	Statement of Basis / Proposed Plan
SCDHEC	South Carolina Department of Health and Environmental Control
SRNS	Savannah River Nuclear Solutions, LLC
SRS	Savannah River Site
TCE	Trichloroethylene
TCL	Target Compound List
TO	Technical Oversight
TPH-DRO	Total Petroleum Hydrocarbons Diesel Range Organics
µg	micrograms
USEPA	United States Environmental Protection Agency
USDOE	United States Department of Energy
UTRA	Upper Three Runs Aquifer
U&U	Unverified and Unvalidated
VOA	Volatile Organic Analyses
VOC	Volatile Organic Compound
V&V	Verified and Validated
WSRC	Washington Savannah River Company (2005 - 2008)
WSRC	Westinghouse Savannah River Company (1989 – 2005)

3.5 Develop the Analytical Approach

Samples will be analyzed by laboratories that have passed the USDOE Consolidated Audit Program (DOECAP) qualification audit and using USEPA SW846 methods, or approved equivalents, which have been certified by SCDHEC. The EPA methods for TPH (EPA8015), VOCs (EPA8260) and SVOCs (EPA8270) specify the required laboratory QC samples that must be included in every analytical batch. At a minimum, laboratory QC samples required to be analyzed with each batch of samples for VOC and SVOC analyses include a method blank, laboratory control sample (AKA standard), laboratory duplicate sample, matrix spiked sample, and the addition of surrogate compound(s) to each regular sample and QC sample. Radiological analyses will be performance based and evaluated by the USDOE Mixed Analyte Performance Evaluation Program. Laboratory developed radionuclide methods are typically based on USEPA or USDOE methods, and specify the laboratory quality control standards to be included in each analytical batch. Typical laboratory QC samples analyzed with each batch of samples for tritium analyses include a method blank, laboratory control sample (AKA standard), laboratory duplicate sample, and a matrix spiked sample.

MCLs will be the primary point of comparison for groundwater constituent concentrations according to the protocols established in the Federal Facility Agreement (FFA 1993). In the absence of an MCL for a constituent, the USEPA tap water RSLs will be the primary point of comparison for an Action Level. The RSLs specify a $1xE10^{-06}$ or an HQ of 1 human health risk-based threshold value for constituents.

The EPA RSLs have divided TPH into the following six categories: Total Petroleum Hydrocarbons (Aliphatic High); Total Petroleum Hydrocarbons (Aliphatic Medium); Total Petroleum Hydrocarbons (Aliphatic Low); Total Petroleum Hydrocarbons (Aromatic High); Total Petroleum Hydrocarbons (Aromatic Medium); and Total Petroleum Hydrocarbons (Aromatic Low). Indicator compounds for each EPA RSL TPH category are listed in Table 4 (USDHHS 1999). The high, medium and low aromatic compounds can be analyzed by EPA methods for VOCs (EPA 8260B) and SVOCs (EPA 8270D), but none of the commercial laboratories under contract to SRS are currently certified to perform analyses for ~~any of~~ the TPH aliphatic compounds in groundwater samples for Phase 1 of this SAP Addendum. SRS will use TPH-Diesel Range Organics as the surrogate for aliphatic compounds.~~SRS proposes to have the~~

~~Savannah River National Laboratory (SRNL) develop screening level research and development (R&D) methods using gas chromatography - mass spectrometry (GC-MS) instrumentation and analyze for the following low and medium aliphatic compounds: heptane, nonane, decane, undecane, dodecane. The development effort occurred in 2017. SRNL cannot currently develop a method to analyze for the aliphatic high category compounds, but the compounds in this category have the lowest solubility, so they are unlikely to migrate into the groundwater, and these compounds have the lowest associated health risks (USDHHS 1999). The MDLs and SQLs for the low and medium aliphatic compounds will not be known until the methods have been developed by SRNL, but SRS anticipates MDLs of approximately 1,000 µg/L. The EPA RSLs for the TPH low and medium aliphatic compound categories are 1,300 µg/L and 100 µg/L. Also the solubility of the aliphatic compounds is much lower than that of the aromatic compounds, making them less likely to migrate into the groundwater, but requiring lower MDLs to detect their presence in groundwater (USDHHS 1999). A method blank, laboratory control standard, and a laboratory duplicate sample will be run with each batch of samples. If the analytical development method is unsuccessful, and/or these data are not deemed of reliable quality and reproducibility, then these data will not be used or reported as part of this project, and monitoring options will be discussed with the core team.~~

3.6 Specify Performance or Acceptance Criteria

The USEPA guidance (USEPA 2006) states "The U.S. Environmental Protection Agency (EPA) has developed the Data Quality Objectives (DQO) Process as the Agency's recommended planning process when environmental data are used to select between two alternatives or derive an estimate of contamination. The DQO Process is used to develop performance and acceptance criteria (or data quality objectives) that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions."

USEPA SW-846 methods are analytical specifications for the Target Compound List (TCL) VOC and SVOC constituents (Tables 5 and 6), while tritium methods are generally modified EPA/DOE methods or performance based methods by each laboratory (Tables 5 and 6). Additional analytical details are presented in the Analytical Plan, Section 5. Table 7 is the DQO worksheet developed for the CAGW OU Groundwater Subunit and Surface Water Subunit, which specifies the quantity, type, and quality of data. None of the SRS contracted laboratories are certified to analyze for the aliphatic compounds. ~~Instead, screening level analyses will be performed by to determine if these aliphatic compounds are present. The analysis does not quantify the concentrations, so only estimated values will be reported.~~

Total study error is the additive impact of sampling error and measurement error. Sampling error is responsible for the vast majority of the total error. "As much as 90% or more of the uncertainty in environmental data sets is due to sampling variability as a direct consequence of the heterogeneity of the environmental matrices" as stated by Deana M. Crumbling, USEPA (Crumbling 2001), and the method best suited to reduce sampling error is to gather representative samples.

It is incorrect to assume that randomly collected, non-representative samples, plus perfect analytical chemistry will always lead risk managers to correct risk management decisions. In order to avoid incorrect risk management decisions, it is more important to develop Decision Quality Data (DQD). DQD is defined as data of known quality that can logically be demonstrated to be effective for making the specified decision because both the sampling and analytical uncertainties are managed to the degree necessary to meet clearly defined and stated data needs (Crumbling 2001). Therefore, it is more important for the risk managers to use decision quality data, emphasizing representative sampling with a specified percentage of definitive data, in order to make a correct decision and should not be confused by emphasizing data quality which does not necessarily equate to a correct risk management decision.

Because the SRS possesses significant process and historical knowledge of C-Area, this sampling plan will largely control sampling error (the cause of greatest total error) and set tolerable limits on decision errors by gathering data using proven procedures for obtaining representative groundwater and surface water samples to generate decision quality data. Judgmental sampling will be used to control decision errors, since sample collection will be focused on known source areas of contamination and areas of groundwater discharge, rather than using a sampling design intended to search for contamination. This approach is a very conservative sampling strategy, and in conjunction with using methods to ensure representative sampling, it will yield a high bias for detecting maximum contaminant concentrations. Specific performance objectives include the following:

samples will be analyzed for VOCs, semi-VOCs and~~,~~ TPH-DRO~~, and R&D analyses for TPH aliphatic compounds~~.

Phase 2 will include 5 DPT soil sampling locations in the UAZ to better define the area of elevated TCE in groundwater near the C Reactor (Figure 19). Soil plugs will be collected at 3-m (10 ft) intervals for VOCs from the water table to the lower clay of the tan clay, a vertical depth of about 18.3 m (60 ft) in the UAZ. Phase 2 will also include the installation of 10 DPTs for groundwater sampling and two new monitoring wells in order to better define tritium and TCE plume concentrations discharging into an unnamed tributary of Castor Creek (Table 3 and Figure 20). These data will support the scope of a remediation alternative to address the TCE contamination prior to its discharge into the unnamed tributary. The DPT groundwater samples and new well samples upgradient of the unnamed tributary will be analyzed for tritium and VOCs.

A monitoring network of 74 existing wells, seepline stations, and surface water stations currently provide data for the annual CAGW OU groundwater data reports (Table 2). In addition, pertinent groundwater and surface water data collected for the C-Area Burning Rubble Pit (CBRP) OU are evaluated with the CAGW OU groundwater data for an overall understanding of groundwater conditions. Likewise, selected F- and H-Areas surface water data are evaluated with the CAGW OU surface water data for an overall understanding of surface water conditions. F- and H-Area groundwater plumes contribute the majority of tritium to FMB. Both practices will continue for a better overall understanding of groundwater and surface water conditions of the CAGW OU.

The Fuel Unloading Facilities Power (108-3C) well installed as part of Phase 1 of this SAP Addendum will be included with the CAGW OU wells monitoring the TCE and tritium source zone areas near the C-Reactor Building (105-C) and it will be sampled semi-annually. The new seepline locations installed in Phase 1 of this SAP Addendum and the distal new well(s) installed in Phase 2 of this SAP Addendum will be included with the other CAGW OU seepline and surface water stations and they will be sampled semi-annually. Two surface water stations (CCT-02 and CCT-03) will also be added for semi-annual sampling and analyses (VOCs and tritium) as part of Phase 1 of this SAP Addendum. No changes are planned for the mid-plume wells so they will continue to be sampled annually (Table 2). Samples will be collected per procedures in the Savannah River Nuclear Solutions (SRNS), LLC 3Q1 Manual, Section 9000, *Hydrogeologic Data Collection Procedures and Specifications (*SRNS 2010c*)*. Samples will be analyzed for VOCs and tritium using standard USEPA methods, or approved equivalents, at SCDHEC certified laboratories, which have also been approved through the DOECAP audit process. ~~The exception will be for the R&D analyses on the TPH aliphatic compounds.~~ Method Detection Limits (MDLs) and Sample Quantitation Limits (SQLs) will be less than the MCLs for TCE (5 µg/L) and tritium (20 pCi/mL).

Data will be received electronically from the labs, loaded into, and managed with the Environmental Restoration Data Management System (ERDMS).

5.0 DATA VALIDATION

The data quality level for the permanent well and seepline stations will be Verified and Validated (V&V) data level (SRNS 2010a and SRNS 2010b)~~, except the TPH aliphatic compounds, which will be Unverified and Unvalidated (U&U) data quality level~~. The data quality level for the DPT station samples will be Verified and Unvalidated (V&U) data level (SRNS 2010a and SRNS 2010b)~~, again except for the TPH aliphatic compounds, which will be Unverified and Unvalidated (U&U) data quality level~~. Water samples may be analyzed using USEPA approved methods for constituent analysis or screening methods to determine field results (i.e., dissolved oxygen, pH, turbidity, etc.), except for the TPH aliphatic compounds which will be R&D methods. Data will be qualified by the SRNS auto-validation software module for the following aspects of USEPA Functional Guideline Criteria to achieve the V&V quality level: Quantitation Limits, surrogate or tracer recoveries, blanks (method/lab/prep, trip, field, rinsate), lab control sample recoveries, matrix spike recoveries/duplicates, lab replicates, field duplicates, cooler temperatures, chemical preservation, holding times. The laboratory will provide an electronic data deliverable and case narrative, and respond to inquiries about the analytical data package in order for SRNS to run the auto-validation software. All fatal errors, data errors, and warnings will be fixed during the verification process, and the data set will be reviewed for completeness.

The auto-validation routines will be conducted and the data qualified accordingly. Data usability will be assessed using the following PARCC parameters:

Table 3. C-Area Proposed New Stations

STATION	UTM EAST	UTM NORTH	STATION TYPE	MONITORING QUARTERS	Phase	ANALYTES
1083C-06	437009.18	3678749.17	DPT	One Time Only	Phase 1	SVOC, VOC, ~~Aliphatics~~TPH-DRO
1083C-07	437006.10	3678755.56	DPT	One Time Only	Phase 1	SVOC, VOC, ~~Aliphatics~~TPH-DRO
1083C-08	437009.97	3678762.08	DPT	One Time Only	Phase 1	SVOC, VOC, ~~Aliphatics~~TPH-DRO
CRW022D	437003.60	3678757.19	Monitoring Well	1Q, 2Q & 4Q	Phase 1	SVOC, VOC, ~~Aliphatics~~TPH-DRO
CCSL-21R	435792.50	3677183.70	Seepline	1Q, 2Q & 4Q	Phase 1	H-3, VOC, MNA
CCSL-22R	435917.33	3677208.45	Seepline	1Q, 2Q & 4Q	Phase 1	H-3, VOC, MNA
CCSL-23R	436027.69	3677332.09	Seepline	1Q, 2Q & 4Q	Phase 1	H-3, VOC, MNA
CAGW-01	436126.63	3677702.54	DPT	One Time Only	Phase 2	H-3, VOC
CAGW-02	436090.88	3677693.76	DPT	One Time Only	Phase 2	H-3, VOC
CAGW-03	436054.25	3677682.98	DPT	One Time Only	Phase 2	H-3, VOC
CAGW-04	436019.87	3677674.51	DPT	One Time Only	Phase 2	H-3, VOC
CAGW-05	436118.75	3677530.45	DPT	One Time Only	Phase 2	H-3, VOC
CAGW-06	436103.29	3677530.37	DPT	One Time Only	Phase 2	H-3, VOC
CAGW-07	436087.28	3677530.57	DPT	One Time Only	Phase 2	H-3, VOC
CAGW-08	436078.36	3677519.88	DPT	One Time Only	Phase 2	H-3, VOC
CAGW-09	436066.17	3677513.95	DPT	One Time Only	Phase 2	H-3, VOC
CAGW-10	436052.18	3677508.85	DPT	One Time Only	Phase 2	H-3, VOC
CRW023C	436070.93	3677520.22	Monitoring Well	2Q & 4Q	Phase 2	H-3, VOC
CRW024C	436074.31	3677688.54	Monitoring Well	2Q & 4Q	Phase 2	H-3, VOC
CRGW-24	436924.04	3678853.66	DPT	One Time Only	Phase 2	VOCs
CRGW-25	436873.19	3678832.45	DPT	One Time Only	Phase 2	VOCs
CRGW-26	436856.75	3678854.90	DPT	One Time Only	Phase 2	VOCs
CRGW-27	436838.86	3678879.48	DPT	One Time Only	Phase 2	VOCs
CRGW-28	436821.21	3678903.79	DPT	One Time Only	Phase 2	VOCs

Table 5. CRDLs Compared to RSLs for Surface Water and Groundwater *(Continued/end)*

Analyte	CAS	Analysis	Tap Water RSL (µg/L)	MCL (µg/L)	CRDL (µg/L)	CRDL> MCL/RSL
PARATHION	56-38-2	SVOC	86	N/A	29	No
P-CHLORO-M-CRESOL	59-50-7	SVOC	1400	N/A	10	No
P-DIMETHYLAMINOAZOBENZENE	60-11-7	SVOC	0.005	N/A	10	>RSL
PENTACHLOROBENZENE	608-93-5	SVOC	3.2	N/A	10	>RSL
PENTACHLOROETHANE	76-01-7	SVOC	0.65	N/A	29	>RSL
PENTACHLORONITROBENZENE	82-68-8	SVOC	0.12	N/A	29	>RSL
PENTACHLOROPHENOL	87-86-5	SVOC	0.041	1	23	>RSL/MCL
PHENACETIN	62-44-2	SVOC	34	N/A	15	No
PHENANTHRENE	85-01-8	SVOC	N/A	N/A	4	No
PHENOL	108-95-2	SVOC	5800	N/A	10	No
PHORATE	298-02-2	SVOC	3	N/A	29	>RSL
P-NITROANILINE	100-01-6	SVOC	3.8	N/A	10	>RSL
P-PHENYLENEDIAMINE	106-50-3	SVOC	3800	N/A	299	No
PRONAMIDE	23950-58-5	SVOC	1200	N/A	15	No
PYRENE	129-00-0	SVOC	120	N/A	4	No
PYRIDINE	110-86-1	SVOC	20	N/A	16	No
SAFROLE	94-59-7	SVOC	0.096	N/A	15	>RSL
SULFOTEPP	3689-24-5	SVOC	7.1	N/A	34	>RSL
THIONAZIN	297-97-2	SVOC	N/A	N/A	29	No
~~N-Heptane[1]~~	~~142-82-5~~	~~GC-MS~~	~~1,300~~	~~N/A~~	~~TBD~~	~~TBD~~
~~N-Nonane~~	~~111-84-2~~	~~GC-MS~~	~~5.30~~	~~N/A~~	~~TBD~~	~~TBD~~
~~N-Decane[2]~~	~~124-18-5~~	~~GC-MS~~	~~100~~	~~N/A~~	~~TBD~~	~~TBD~~
~~N-Undecane[2]~~	~~1120-21-4~~	~~GC-MS~~	~~100~~	~~N/A~~	~~TBD~~	~~TBD~~
~~N-Dodecane[2]~~	~~112-40-3~~	~~GC-MS~~	~~100~~	~~N/A~~	~~TBD~~	~~TBD~~
TPH-DRO[1]	E1790674[2]	Organic	5,500	N/A	200.00	No
Tritium[3]	10028-17-8	Radio-logical	N/A	20 pCi/mL	15.00	No

Table 54 Notes:
C = Laboratories instructed to obtain lowest DL
N/A = Not Available
>RSL = CRDL is greater than the RSL
>MCL = CRDL is greater than the MCL
>RSL/MCL = CRDL is greater than both the RSL and MCL
TBD = To Be Decided
RSLs from May 2018~~6~~
~~1) TPH Aliphatic Low group RSL used for constituent.~~
~~2) TPH Aliphatic Medium group RSL used for constituent.~~
1) TPH (Aromatic Medium) has the lowest EPA Tapwater RSL (5,500 µg/L).
2) EPA number for TPH (Aromatic Medium) from Generic RSL Summary Table May 2018.
3)Tritium units are pCi/mL.

Table 6. Analytical Specifications for VOCs, SVOCs and Tritium in Water *(Continued/end)*

Analyte	**Analyte ID**	**Preparation [B] Method**	**Analytical [B] Method**	**CRDL [A] (µg/L)**
Semi-Volatiles (Continued)				
THIONAZIN	297-97-2	3510 and 3520	EPA8270D	29
TPH - DRO				
TPH by GC/FID Diesel Range Organics	TPHDRO	3510, 3535 and 3550	EPA8015C	200
~~N-Heptane~~	~~142-82-5~~	~~TBD~~	~~GC-MS~~	~~\~1,000~~
~~N-Nonane~~	~~111-84-2~~	~~TBD~~	~~GC-MS~~	~~\~1,000~~
~~N-Decane~~	~~124-18-5~~	~~TBD~~	~~GC-MS~~	~~\~1,000~~
~~N-Undecane~~	~~1120-21-4~~	~~TBD~~	~~GC-MS~~	~~\~1,000~~
~~N-Dodecane~~	~~112-40-3~~	~~TBD~~	~~GC-MS~~	~~\~1,000~~
Radionuclides				
Tritium	10028-17-8	EPA900.0MOD	EPA900.0MOD	15^{D}

Table 5 Notes:

A) CRDL is the Contract Required Detection Limit and is not always attainable.
B) Extraction and preparation methods differ depending upon media, concentration, instrument, laboratory, and analytical method. Preparation methods will also influence detection limits.
C) Laboratory instructed to obtain the lowest possible method detection limit.
D) Units for tritium are pCi/mL.

Table 7. Data Quality Objectives for CAGW OU Groundwater and Surface Water

Pathway (Media)	Probable Conditions	Exposure Pathway and/or Release Mechanisms	Data Needs and DQOs Including Engineering/ Physical Processes	Field Activities Including Removal and Characterization	Parameters	Potential Remedial Action Alternatives
Groundwater and surface water	TCE and Tritium exceeds MCLs in groundwater. TPH diesel range organics exceed 100 µg/L in the groundwater Tritium and TCE exceeds MCL in surface water.	Ingestion, inhalation, absorption, or direct exposure with water.	Collect data to support the CMS/FS. Determine the changing size and concentrations of the TCE and Tritium groundwater plumes discharging to Castor Creek and its tributary. Provide data to implement a removal action on the TCE plume discharging to the unnamed tributary of Castor Creek. Determine changes in the TCE plume near the C-Reactor Building (105-C) Establish a groundwater monitoring station downgradient of the Fuel Unloading Facilities Power (108-3C)	Collect ground-water and surface water samples at 69 locations with existing history throughout C-Area. Establish groundwater monitoring well at Fuel Unloading Facility (108-3C). Establish 3 Seepline stations along Castor Creek based on 2011 temporary seepline stations. Establish 1-2 monitoring well locations upgradient of the unnamed tributary to Castor Creek based on new DPT groundwater samples. Collect soil cores for VOC analyses in the UAZ downgradient of C-Reactor (105-C) to determine variations in the TCE plume near the former source area.	TCL-VOC and tritium for ground-water and surface samples. TCL VOC, TCL SVOC and- TPH-DRO~~R&D analyses for aliphatic compounds~~. All data validated to SRS electronic V&V level.	No Action. Monitored Natural Attenuation (MNA) with Land Use Controls. Phytoremediation (evapotranspiration) for TCE and tritium in groundwater. Anaerobic bioremediation of TCE

Table 8. Preservative, Holding Times, and Sample Containers[1] *(Continued/End)*

Parameter	Preservatives[2]		Holding Time		Containers[3]	
	Aqueous	**Solid**	**Aqueous**	**Solid**	**Aqueous**	**Solid**
~~**SRNL Aliphatic Compounds**~~						
~~Headspace analysis for Aliphatic organic compounds by gas chromatography/ mass spectrometry.~~	~~Aqueous samples with no residual chlorine present: Cool to 0 - 6 °C.~~	~~N/A~~	~~Samples extracted within 7 days and extracts analyzed within 40 days following extraction.~~	~~N/A~~	~~2 x 40 mL glass vial, PTFE septa cap~~	~~N/A~~

Table 8 NOTES:
1 – Additional standard method manuals may be applicable. Refer to individual methods employed for details.
2 – Reagents should be of appropriate grade or quality as identified within the analytical method.
3 – All containers must have PTFE (Teflon)-lined seals (Teflon-lined septa for volatile organic analytes [VOA] vials).
4 – VOC section is segregated based on prepatory procedures employed. Refer to SW-846 Method 5000 for details on determinative methods application to appropriate preparatory procedures.
5 – Refer to SW-846 Method 5035 for additional preservation options.
6 – Actual number of sample containers necessary for each location is based on project information.
7 – Samples must be derivatized and extracted within 3 days of collection and analyzed within 3 days of extraction.
8 – Refer to SW-846 Method 5021 for details on the matrix modifying solution needed.
9 – Extracts must be stored at -10ºC and in the dark until analysis.
10 – Extracts should be methylated within 48 hours of extraction and analyzed immediately thereafter.
11 – Extracts must be stored at 4ºC and in the dark until analysis
12 – The subset chemical parameters under Extractable Organics may be collected in the same container for soils.
13 – High-concentration waste samples does not need cooling.
14 – Metals and cyanide may be collected in the same container for soils.

Abbreviations used in Table 8:

- H_2SO_4 – Sulfuric acid
- HCL – Hydrochloric acid
- $NaHSO_4$ – Sodium bisulfate
- PTFE – Teflon lined seals
- $Na_2S_2O_3$ – Sodium Thiosulfate
- CWM – Clear Wide-Mouth Glass Jar with Teflon-lined Lid
- AG – Amber Glass Bottle with Teflon-lined Lid
- HNO_3 – Nitric acid
- HDPE – High-Density Polyethylene Bottle with Teflon-lined Lid
- BR – Boston Round bottle
- NA – Not Applicable