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JUN 13 2001

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RECEIVED  
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EDMC

Dear Ms. Hedges:

TRANSMITTAL OF THE "SAMPLING AND ANALYSIS PLAN (SAP) FOR DEVELOPMENT OF A CONCEPTUAL GEOCHEMICAL MODEL FOR URANIUM TRANSPORT IN THE UNSATURATED AND SATURATED SEDIMENTS AT THE 200-WEST AREA OF THE DEPARTMENT OF ENERGY HANFORD SITE, WASHINGTON," MSE TECHNOLOGY APPLICATIONS, INC.

Attached is the subject SAP for your information. This document presents the rationale and strategy for the sampling and analysis activities to be performed in support of the uranium mobility study in the 200-PW-2 and 200-UP-1 Operable Units. The draft version of the SAP was previously reviewed by the State of Washington Department of Ecology.

Please provide concurrence on this document. If you have any questions, please contact me at (509) 373-9631.

Sincerely,

Arlene C. Tortoso, Project Manager  
Environmental Restoration Division

ERD:ACT

Attachment

cc: See page 2

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Zelma Maine  
State of Washington Department of Ecology

---

Date

Ms. Jane A. Hedges  
01-ERD-089

-2-

JUN 13 2001

cc w/attach:

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**SAMPLING AND ANALYSIS PLAN**

**FOR**

**DEVELOPMENT OF A CONCEPTUAL GEOCHEMICAL MODEL FOR  
URANIUM TRANSPORT IN THE UNSATURATED AND SATURATED  
SEDIMENTS AT THE 200-WEST AREA OF THE DEPARTMENT OF  
ENERGY HANFORD SITE, WASHINGTON**

**PREPARED BY:  
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**JUNE 7, 2001**

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## LIST OF ACRONYMS

ARA	Applied Research Associates, Inc.
BHI	Bechtel Hanford, Inc.
CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification
CFR	Code of Federal Regulations
COCs	Contaminants of Concern
CO <sub>2</sub>	Carbon Dioxide
CPT	Cone Penetrometer Test
DI/DS	Deionized/Distilled
DOE	Department of Energy
DOE-RL	DOE-Richland
DOW	Description of Work
DQO	Data Quality Objective
ERC	Environmental Restoration Contractor
ETF	Effluent Treatment Facility
HGET	Hanford General Employee Training
ICB	Initial Calibration Blank
ICP	Inductively Coupled Plasma Spectrometer
ICV	Initial Calibration Verification
LCS	Laboratory Control Sample
MCL	Maximum Contaminant Level
MSE	MSE-Technology Applications
MTCA	Model Toxics Control Act
OD	Outside Diameter
ppm	parts per million
PQL	Practical Quantitation Limits
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
ROD	Record of Decision
RAO	Remedial Action Objective
RPD	Relative Percent Difference
SAP	Sampling and Analysis Plan
SCFA	Subsurface Containment Focus Area
STCG	Science and Technology Coordination Group
STR	Subcontractor Technical Representative
USGS	U.S. Geological Survey
µg/L	micrograms per liter

# 1 INTRODUCTION

This sampling and analysis plan (SAP) presents the rationale and strategy for the sampling and analysis activities proposed in support of the uranium mobility study in the PW-2 and UP-1 Operable Units in the 200 West Area of the Hanford Site. The objective of the study is to develop a conceptual geochemical model that quantifies the mobility of uranium in the unsaturated and saturated soils associated with the 216-U1/U2 Cribs in the 200 West Area, producing an acceptable correlation between predicted and observed concentrations of uranium in the groundwater.

This section provides background information about the project, as well as a discussion of the previous investigations, a list of the contaminants of concern (COCs), and a summary of the data quality objective (DQO) process.

Data quality assurance is addressed in Section 2 of this document. Section 3 addresses the rationale for the sampling and analysis that will be completed as part of this project. Section 4 presents the analytical requirements and Section 5 discusses the sampling and field measurements.

## 1.1 BACKGROUND

MSE-Technology Applications (MSE) is funded by the Subsurface Containment Focus Area (SCFA) and the U.S. Department of Energy (DOE) under TTP #FT-01WE-21 "*Subsurface Contaminant and In Situ Remediation Projects, Subtask M*" to contribute to fulfilling needs identified by the Hanford Science and Technology Coordination Group (STCG). As a result, MSE was requested by the Hanford Environmental Restoration Contractor (ERC), Bechtel Hanford, Inc. (BHI) to focus the efforts of the work in the 200 West Area of the Hanford Site where a plume of uranium exists in the groundwater down gradient from the 216-U1/2 cribs.

Currently, a pump and treat system in place in the 200 West Area is designed to reduce contaminant mass within the plume and minimize migration of uranium and technetium-99 from the 200 West Area. Analytical data from monitoring wells located within and around the contaminated groundwater indicate the pump and treat system is effectively removing the technetium-99 from the groundwater, however, it is not removing enough uranium from the groundwater to meet the compliance requirements for the site.

### 1.1.1 Previous Investigations

Previous investigations at the site include:

1. U1/U2 Uranium Plume Characterization (WHC June 1, 1988)
2. 200 West Area Limited Field Investigation (BHI March 1995)
3. Waste Site Grouping for 200 Areas Soil Investigations (DOE/RL January 1, 1997)
4. 200 Areas Remedial Investigation/Feasibility Study (DOE/RL April 1, 1999)

## 1.1.2 Contaminants of Concern

The study will focus on uranium, the primary contaminant of concern for this study, and how it interacts with the soil in terms of adsorption to the soil matrix. Technetium-99, nitrate and carbon tetrachloride are also present within 200-UP-1 Operable Unit in concentrations above the maximum concentration limit (MCL) for drinking water under the *Safe Drinking Water Act*. These contaminants have been adequately addressed by the pump and treat system, or are being addressed by other remedial systems and are not of specific concern at this site. However, other contaminants that may be present at the site will be considered from the standpoint of the impact they may have on the mobility of the uranium.

### 1.1.2.1 Remedial Action Objectives

The remedial action objective (RAO) for uranium in the groundwater, as stated in the *Interim Action Record of Decision for the 200-UP-1 Operable Unit* (EPA, February 1997), at the site is 480 micrograms per liter ( $\mu\text{g/L}$ ). This value corresponds to 10 times the cleanup level for uranium under the Washington State Department of Ecology's *Model Toxics Control Act* (MTCA).

In FY99, the average uranium concentration in extraction well 299-W19-39 was 210  $\mu\text{g/L}$ . Uranium concentrations have ranged from 275  $\mu\text{g/L}$  in 1997 to 210  $\mu\text{g/L}$  at the end of FY99 in the extraction well. Downgradient, in well 299-W19-40, the uranium concentration was approximately 200  $\mu\text{g/L}$ .

## 1.1.3 Conceptual Site Model

The following description of the distribution of uranium contamination at the site is taken from the Interim Action Record of Decision (ROD) for the 200-UP-1 Operable Unit (EPA, February, 1997).

The 200 West Area is an operational area of approximately 5.1 square kilometers (1.97 square miles) where spent nuclear fuel was processed in four main facilities: U Plant (primarily uranium recovery); Z Plant (primarily plutonium separation and recovery); and S and T Plants (primarily uranium and plutonium separation from irradiated fuel rods).

Contamination in the 200-UP-1 Operable Unit resulted from historic discharges of process water from the UO3 Plant to five primary liquid waste disposal sites (cribs). The predominant contaminants were uranium and technetium-99. The major portion of discharge to the soil column was via two cribs (216-U-1 and 216-U-2) between 1951 and 1968, which transported the mobile constituents, particularly technetium-99, to the water table. However, most of the uranium discharged to the cribs was retained in the upper 20 meters (66 feet) of the soil column. During the final years of the cribs operation (1966 through 1968), small volumes of highly acidic decontamination wastes were discharged, which resulted in the dissolution of part of the previously deposited autunite (uranium phosphate) and transport of its small fraction. Low concentrations of uranium were seen in the groundwater monitoring wells near 216-U1/U2 during this period. The majority of dissolved uranium was distributed throughout the soil column beneath the crib with the largest concentration deposited above a caliche layer at about 50 meters (164 feet) depth. During 1984, large volumes of cooling water were discharged to the adjacent 216-U-16 crib, which reportedly resulted in transport of uranium to the groundwater. This history

and the contaminant flow path are captured in Figure 1 ~~Figure 1~~, generated by MSE to facilitate the understanding of the site.

During 1985 uranium concentrations in the groundwater abruptly increased from 166 to 72,000 pCi/L. Limited pump and treat activities were initiated in 1985 to recover the uranium from the groundwater using ion exchange. During the six months of pump and treat, about 687 kilograms (1,500 pounds) of uranium were recovered and the concentration in well 199-W19-3 was reduced to 1,700 pCi/L.

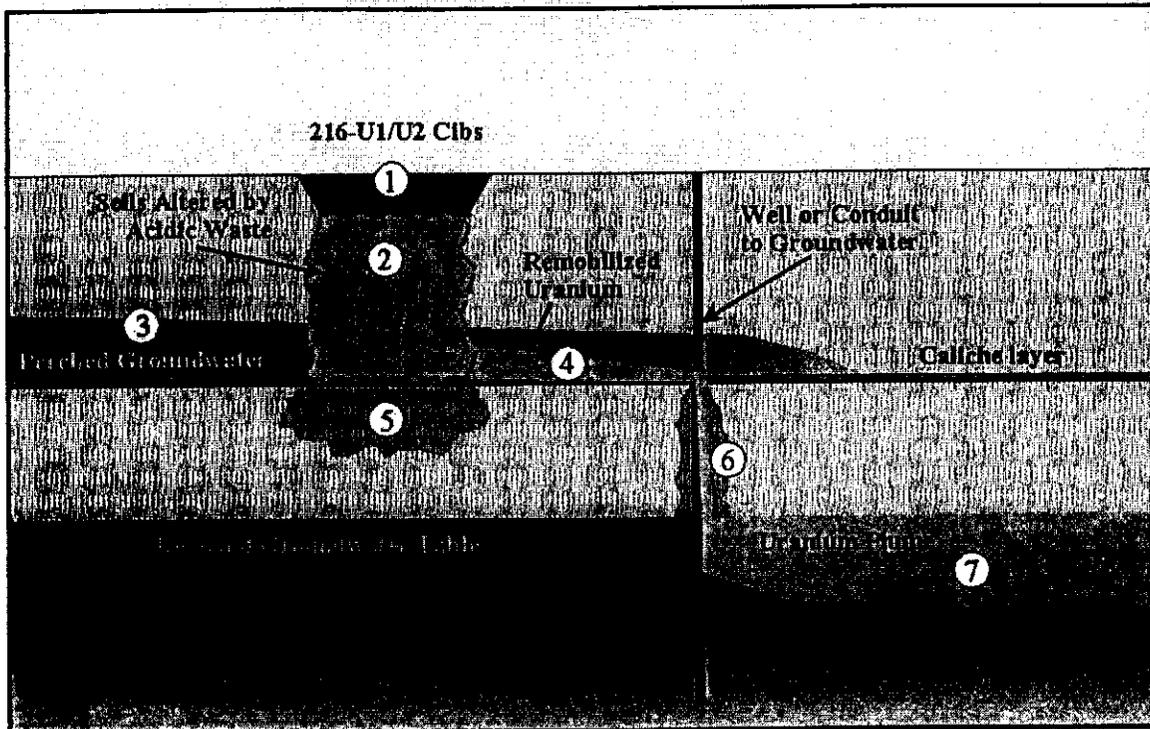
From September 1995 to February 1997, the Phase I pump-and-treat injection operations operated using a single extraction well and a single injection well. Operations were halted from February 8, 1997 to March 30, 1997.

On February 25, 1997, an interim action ROD was issued for the 200-UP-1 pump-and-treat operations. The selected remedy consisted of pumping and treating the highest concentration zone of the uranium and technetium-99 plumes. Before the interim action ROD, groundwater was treated onsite using ion-exchange technology and granular activated carbon. Since starting Phase II of the operations in March 1997, groundwater is transported to the Effluent Treatment Facility (ETF). Once treated, the groundwater is discharged to the state-approved land disposal site north of the 200 West Area.

In addition to the uranium and technetium-99 plumes, nitrate and carbon tetrachloride are also present within 200-UP-1 Operable Unit in concentrations above the MCL for drinking water. Nitrate contamination resulted from discharges of neutralized nitric acid to various cribs located in the U Plant and S Plant areas. The source for the carbon tetrachloride is believed to be upgradient and outside the 200-UP-1 Operable Unit, and associated with the Z Plant disposal sites. The extent of carbon tetrachloride and nitrate contaminant plumes are much larger compared to uranium and technetium-99 plumes. Carbon tetrachloride contamination in the groundwater is found throughout the entire 200 West Area. The nitrate plume extends from west of the 200 Area to the Columbia River. A small portion of carbon tetrachloride was used as a degreasing agent in the 200 Area. Therefore, the carbon tetrachloride plume was reported and designated as a listed waste. The nitrate plume is much larger and coalesces with other nitrate contaminant plumes from a number of 200 West Area facilities.

The leading edge of the uranium plume has migrated beyond the 200 West Area boundaries. The combined uranium and technetium-99 plume covers an area of approximately 0.5 square kilometers (0.2 square miles).

**Conceptual Model for Uranium Transport to the  
Groundwater from the 216-U1/U2 Cribs  
200 West Area, Hanford Site**



- ① Dilute acidic liquid waste containing uranium was disposed to the ground through the 216-U1/U2 cribs from 1957 until 1968. The uranium was immobilized in the soil by the formation of an insoluble carbonate-phosphate compound.
- ② From 1966 through 1968, the pH of the waste stream decreased and the uranium was re-mobilized and deposited deeper into the soils, possibly to a caliche layer. The more acidic waste stream may have also altered the soils directly below the cribs.
- ③ In the early 1980's, cooling water was discharged to a crib (216-U16) located south of the 216-U1/U2 cribs, creating a perched water table on the caliche layer.
- ④ This perched water may have been responsible for transporting the more mobile uranium to a vertical conduit, such as a well or thin spot in the caliche layer.
- ⑤ Some of the uranium may have permeated to the soil below the caliche layer beneath the 216-U1/U2 cribs.
- ⑥ The mobile uranium traveled down the vertical conduit to the regional groundwater table. As it traveled, the uranium may have permeated into the soils surrounding the conduit.
- ⑦ Upon reaching the water table, the uranium spread out and formed the uranium plume found at the site.

**Figure 1. Conceptual model of 216-U1/U2 cribs uranium distribution.**

## 1.2 DATA QUALITY OBJECTIVES

The results of the data quality objectives (DQO) process for the project are summarized in Table 1. The results of the DQO process for the project are documented in the Project DQO Summary Report (MSE 2001). This sampling and analysis plan expands on the inputs to the decision as stated in Step 3 of the DQO process. The experimental design and rationale for the sampling are described in Section 3 of this document. The analytical requirements are described in Section 4 of this document.

**Table 1. DQO Summary**

DQO Process Step	DQO Process Output
<b>Step 1</b> <i>Statement of Problem</i>	The limited success of the pump-and-treat system on remediating the uranium plume to the RAO of 480 µg/L indicates that the mobility of uranium in the unsaturated and saturated zones of the PW-2 and UP-1 Operable Units in the 200 West Area of the Hanford site is not well understood.
<b>Step 2</b> <i>Principle Study Question</i>	How do the geological and geochemical properties of the soil column affect the mobility of uranium in the unsaturated and saturated zones of the PW-2 and UP-1 Operable Units in the 200 West Area?
<b>Step 2</b> <i>Alternative Actions</i>	Uranium mobility in the unsaturated and saturated zones of the PW-2 and UP-1 Operable Units can be better characterized through the development of a detailed geochemical model. The geochemical model will define a partitioning relationship for the uranium between the soil matrix and porewater and can be developed using several approaches. The simplest approach, which will not be used for this project, is an empirical method often using the linear or non-linear distribution coefficient, or $K_d$ , model. A more comprehensive approach, the surface complexation method will be used for this project. This approach uses the principles of chemistry and physics to describe the processes of adsorption and desorption of contaminants to the soil matrix in the unsaturated and saturated zones.

DQO Process Step	DQO Process Output
<b>Step 2 <i>Decision Statement</i></b>	Determine whether the current pump-and-treat system is the most effective remedial option for removing uranium from the contaminated groundwater and should continue to be used; or should the current pump-and-treat system be optimized or replaced with a new remedial technology.
<b>Step 3 <i>Identify Inputs to Decision</i></b>	<p>The primary information required to develop a detailed geochemical model include:</p> <ol style="list-style-type: none"> <li>1. Soil samples from the distinct lithologic horizons present in the unsaturated and saturated zones of the PW-2 and UP-1 Operable Units. Samples should be obtained in the unsaturated and saturated zones during the installation of a well in FY01 and if possible from existing cores.</li> <li>2. Sampling the concentration of carbon dioxide (CO<sub>2</sub>) in the unsaturated zone of the soil column.</li> <li>3. Detailed analysis of the unsaturated and saturated zone soil samples to determine the physical and chemical properties of the soil and the porewater chemistry.</li> </ol>

DQO Process Step	DQO Process Output
<p><b>Step 4 <i>Define Study Boundaries</i></b></p>	<p>The decisions that may be supported by this work will apply to the uranium from the 216-U1/U2 cribs including the uranium in sediments below cribs (200-PW-2 operable unit) and the uranium plume in the 200-UP-1 Groundwater Operable Unit.</p> <p>The geographical boundaries for the study include areas influenced by the contamination from U1/U2 cribs and encompass the uranium groundwater plume and contaminated portion of the vadose zone.</p> <p>The administrative temporal boundaries that constrain the study include the need to have additional information on the uranium mobility for the next 5-year review (2005), and for the completion of the final ROD for the site.</p> <p>Technical temporal boundaries for the project include the schedule for the well installation that will be used to obtain samples and the need to have an analytical laboratory scheduled to receive the samples prior to start of drilling.</p>
<p><b>Step 5 <i>Develop Decision Rule</i></b></p>	<p>The recommended remedial action will be based on the outputs of the study. The output will not be a statistical parameter that can be used to make a decision, but rather a description of a process that may be used by the decision makers to arrive at a final remedial action. Therefore, a decision rule is not defined for this project.</p>
<p><b>Step 6 <i>Specify Tolerable Limits on Decision Errors</i></b></p>	<p>Since the samples for this investigation are proposed to be collected from judgmental locations, Step 6 of the DQO process does not apply.</p> <p>As stated in Step 5, the output of this study is not a statistical parameter, but rather a description of a process. The process description will be evaluated in terms of the accuracy that it reflects the true state of the uranium mobility in the subsurface. This information will be considered in the decision making process.</p>

DQO Process Step	DQO Process Output
<b>Step 7 <i>Optimize the Design</i></b>	The result of the design optimization step was to use the surface complexation approach to determining the partitioning of uranium between the soil and porewater, resulting in a conceptual geochemical model that can be used to investigate transport scenarios for the current site conditions and adapted to investigate remedial options for the site.

## 2 QUALITY ASSURANCE PROJECT PLAN

This section provides the quality assurance project plan (QAPP) for the sampling and analysis activities proposed in support of the uranium mobility study in the PW-2 and UP-1 Operable Units in the 200 West Area of the Hanford Site. The purpose of the QAPP is to integrate the technical aspects with the quality aspects of the project to ensure that the results are good quality. The quality assurance/quality control (QA/QC) requirements presented in this QAPP implement a graded approach based on EPA QA-R-5, *EPA Requirements for Quality Assurance Project Plans* (EPA 1999). Consequently, the level of detail described for each of the tasks varies based on the nature of the sampling and testing being performed.

### 2.1 PROJECT MANAGEMENT

This section addresses project management, including project objectives and roles and responsibilities of the participants. The project team includes participants from the following organizations:

- DOE-Richland (DOE-RL);
- Bechtel Hanford Incorporated (BHI);
- Washington Department of Ecology; and
- MSE Technology Applications, Inc. (MSE).

#### 2.1.1 Project/Task Organization

The project team organizations, their responsibilities and tasks, and the key individuals for the project team in planning and implementing the project tasks have been identified in the *Multi-Year Implementation and Project Management Plan*, Section 2.1 (MSE 2001).

#### 2.1.2 Problem Definition/Background

Currently, a pump and treat system is in place in the 200 West Area of the Hanford Site and is designed to reduce contaminant mass within the plume and minimize migration of uranium and technetium-99 from the 200 West Area. Specifically, the remedial action objectives for the pump and treat system are to:

- Reduce contamination in the area(s) of highest concentrations to below 10 times the cleanup level under the MTCA for uranium and 10 times the MCL for technetium-99.
- Reduce potential adverse human health risks through reduction of contaminant mass.
- Prevent further movement of these contaminants from the highest concentration area.
- Provide information that will lead to development and implementation of a final remedial action that will be protective of human health and the environment.

The problem that is driving this study is:

“Analytical data from monitoring wells located within and around the contaminated groundwater indicate the pump-and-treat system has had limited success in remediating the uranium plume to the remedial action objective (RAO) of 480 µg/L.”

### **2.1.3 Project/Task Description**

Project tasks, combined efforts of BHI and MSE, are geared toward accomplishing the project goals and objectives. The project tasks for all project team members, MSE, and BHI have been described in the *Multi-Year Implementation and Project Management Plan*, Section 2.4.2 (MSE 2001).

### **2.1.4 Quality Assurance Objectives and Criteria for Measurement Data**

The quality assurance objectives are the specifications that the critical measurements must meet to ensure that the data used to develop the conceptual geochemical model is of good quality.

#### **2.1.4.1 Quantitative Quality Assurance Objectives**

The quantitative QA objectives for the critical measurements are practical quantitation limits (PQL), precision, accuracy, and completeness. The quantitative QA objectives are presented in Table 2. The precision, accuracy, and completeness goals are based on best laboratory practices and well within the analytical capabilities of the specified methods. After the analytical laboratory has been selected, the appropriate PQLs will be reviewed. If the laboratory's current PQLs are not appropriate, other methods of analysis may be necessary.

#### **2.1.4.2 Qualitative Quality Assurance Objectives**

Comparability is a qualitative parameter that expresses the degree of confidence that data are comparable for a specific parameter or group of parameters for samples taken from various locations. Comparability will be achieved in this project by adhering to standardized sampling procedures described in Section 2.2.2 and analytical methodologies provided in Section 4.1, Tables 5 and 6.

Representativeness expresses the degree to which sample data accurately represents a characteristic of population, parameter variations at a sampling point, or an environmental condition. Representativeness is a qualitative parameter based on professional judgment that reflects the design of the sampling program and standard operating procedures, including whether sampling locations are selected properly and whether a sufficient number of samples are collected. For this project, representativeness is maintained by taking soil samples from each distinct lithologic horizon or every thirty feet of drilling if no change in the lithology is observed (See Section 5.1.1).

**Table 23 . Quality Assurance Objectives and Criteria for Measurement Data**

Parameter	Matrix	Measurement Method	Precision <sup>a</sup>	Accuracy <sup>b</sup>	Completeness <sup>c</sup>
Sediment Mineralogy, to include grain coatings and precipitates	Soil	Optical Mineralogical Analysis	≤20%	N/A	N/A
		X-ray Analysis	≤35%	70-130%	90%
Shape Factor of Soil Particles	Soil	Optical Mineralogical Analysis	≤20%	N/A	N/A
Grain Size Distribution	Soil	Sieve Analysis	≤20%	70-130%	90%
Surface Area	Soil	BET Analysis	≤20%	70-130%	90%
Soil Organic Matter	Soil	Combustion	≤35%	70-130%	90%
Specific Density	Soil	Pycnometer Method	≤35%	70-130%	90%
Bulk Density	Soil	Core Method	≤35%	70-130%	90%
Speciation of Uranium bound to Soil Matrix	Soil	Dissolution of Metals	≤20%	75-125%	90%
Identifying the Main Sorbent(s) of Uranium	Soil	Optical Mineralogical Analysis	≤20%	N/A	N/A
		Electron Microscope	≤20%	N/A	N/A
Surface Charge Density of the Main Sorbent(s) of Uranium.	Soil	Literature Values	N/A	N/A	N/A
Percent Soil Moisture (Field)	Soil	"Speedy" Soil Moisture	≤10%	70-130%	90%
Percent Soil Moisture (Lab)	Soil	Laboratory Measurement	≤20%	70-130%	90%
Percent Soil Moisture (Borehole)	Soil	Neutron Moisture Log	≤10%	75-125%	90%
Major Anions (SO <sub>4</sub> , Cl)	Aqueous	Laboratory Analysis by Ion Chromatography	≤20%	75-125%	90%
Total Recoverable Metals (Ca, Mg, Na, K)	Aqueous	Laboratory Analysis by Inductively Coupled Plasma Spectrometer	≤20%	75-125%	90%
Iron Speciation	Aqueous	Laboratory Analysis by Colorimetric	≤20%	80-120% of LCS	90%
Uranium	Aqueous	Laboratory Specific Analysis	≤20%	75-125%%	90%
pH of Porewater-Vadose Zone	Aqueous	Computed from Alkalinity and Soil Gas CO <sub>2</sub> pressure	±0.2 pH units	±0.2 pH units	90%
pH of Porewater-Saturated Zone	Aqueous	Electrometric Method	±0.2 pH units	±0.2 pH units	90%

Parameter	Matrix	Measurement Method	Precision <sup>a</sup>	Accuracy <sup>b</sup>	Completeness <sup>c</sup>
Alkalinity (Forms) of Porewater	Aqueous	Titration	≤20%	75-125%	90%
Dissolved CO <sub>2</sub> - Vadose Zone	Gas	CO <sub>2</sub> Analyzer.	≤20%	70-130%	90%
Dissolved CO <sub>2</sub> - Saturated Zone	Gas	Calculated from pH and Alkalinity	N/A	N/A	N/A
Carbon Isotopes	Gas	Gas Chromatograph /Mass Spectrometer (GC/MS)	≤20%	75-125%	90%
<sup>a</sup> Precision will be determined by the relative percent difference (RPD) of duplicates, unless otherwise indicated. <sup>b</sup> Accuracy will be determined by the percent recovery of matrix spikes, unless otherwise indicated. <sup>c</sup> Completeness will be determined by the number of valid measurements compared to the total number of samples.					

### 2.1.5 Special Training/Certification Requirements

Training/certification requirements for personnel supporting field activities to collect samples are described in BHI-HR-02, *ERC Training Procedures*. Prior to the start of field activities, site workers will have completed the minimum training requirements as outlined in Table 3.

**Table 34. Minimum Training Requirements**

Training Elements	Applicability
Occupational Safety and Health Administration 40-Hour Hazardous Waste Worker Training	All site workers
Radiation Worker II Training	All site workers
Hanford General Employee Training (HGET)	All site workers
BHI-QA-03, <i>ERC Quality Assurance Program Plans</i> , Plan 5.1, "Field Sampling Quality Assurance Program Plan"	Samplers
BHI-QA-03, <i>ERC Quality Assurance Program Plans</i> , Plan 5.3, "Environmental Radiological Measurements Quality Assurance"	Radiological control technicians
U.S. Department of Transportation shippers training as required by 49 CFR 700	Personnel transporting samples from the collection site to the laboratory.
CFR = Code of Federal Regulations	

### 2.1.6 Documentation and Records

Sample collection (BHI's responsibility) and analytical work (analytical work) will follow procedures outlined in BHI-EE-01, *Environmental Investigation Procedures*, Procedure 2.0, "Sample Event Coordination." The sample authorization form information generated through the sample event coordination process will specify the media (container type, size, and preservatives)

laboratories; turnaround times, and data deliverable requirements. Field documentation of sample collection will be maintained in accordance with BHI-EE-01, *Environmental Investigation Procedures*, including the following procedures:

- Procedure 1.5, "Field Logbooks"
- Procedure 1.13, "Environmental Site Identification and Information Reporting"
- Procedure 3.0, "Chain of Custody"
- Procedure 3.1, "Sample Packaging and Shipping."

Annual status reports will be prepared after an annual status report outline has been reviewed by the project team to ensure the content of the report will meet the project needs. The report will cover the activities completed during the past year, major findings from the activities, projected work for the following year, and any recommendations for additional work related to the project.

The final report for the project will include:

- a description of the fate and transport of uranium in the unsaturated and saturated zones as best understood at the completion of the project,
- a discussion of how the fate and transport should be modeled using groundwater flow and contaminant fate and transport model,
- recommendation for groundwater flow and contaminant fate and transport models that can be used to model the uranium fate and transport,
- recommendations for additional characterization data if any, and
- recommendations for remedial options to investigate for the site.

## **2.2 MEASUREMENT/DATA ACQUISITION**

This section addresses all aspects of data generation and acquisition to ensure that the appropriate methods for sampling, measurement and analysis, data collection or generation, data handling, and QC activities are employed and documented.

### **2.2.1 Sampling Process Design**

The sampling process design is provided in Sections 4 and 5.

### **2.2.2 Sample Collection, Handling, Shipping, and Custody Requirements**

Sample collection, handling, shipping, and custody requirements are outlined in Section 4.2, Table 7 and will be performed in accordance with BHI-EE-01, *Environmental Investigation Procedures*, including the following procedures:

- Procedure 3.1, "Sampling, Packaging, and Shipping"
- Procedure 3.0, "Chain of Custody"
- Procedure 4.0, "Soil and Sediment Sampling"

### **2.2.3 Analytical Methods Requirements**

Analytical methods and performance requirements are outlined in Table 2 and Section 4.1, Tables 5 and 6.

### **2.2.4 Quality Control Requirements**

Quality control procedures shall be implemented in the field and the laboratory to ensure that reliable data are obtained.

#### **2.2.4.1 Sample Collection**

Samples shall be collected in accordance with the quality requirements presented in BHI-QA-03, *ERC Quality Assurance Program Plans*, Plan 5.1, "Field Sampling Quality Assurance Program Plan." When performing field sampling, care will be taken to prevent the cross-contamination of sampling equipment, sample containers, and other equipment that could compromise sample integrity.

##### ***2.2.4.1.1 Types of Quality Control Checks***

The following QC checks shall be implemented in the field by the individual collecting samples. The type and frequency of QC checks are listed below.

***Primary Sample***—A single field sample.

***Field Duplicate***—Consists of one sample collected at the same location as the primary sample and placed in a separate container for separate analysis. Field duplicates will be collected every tenth sample. Due to the possible limitation of porewater in the vadose zone, the laboratory shall insure primary porewater sample is extracted from the soil sample. If enough porewater remains, a laboratory duplicate sample will be collected every tenth sample.

***Field Blank***—Prepared at the test site by the same protocols as a non-QC sample, but it is not exposed to any sampling equipment. The sample is prepared by filling a sample bottle with filtered or non-filtered deionized/distilled (DI/DS) water at the sampling site and then placing the sample in the transport container. Field blanks for the core samples are not appropriate, but sample blanks for the porewater will be collected each day of sampling.

#### **2.2.4.2 Analytical Laboratory Measurements**

Quality control associated with the analyses conducted at the laboratory will be consistent with the quality objectives presented in Table 2, the chosen analytical methods, and the internal quality control checks defined in the following sections. Method specific QC will conform to the requirements of the procedures as referenced in the EPA SW-846 guidelines. Control limits and frequency shall match or exceed the referenced protocols or as established in Table 4.

##### ***2.2.4.2.1 Types of Quality Control Checks***

Internal QC checks shall be implemented by the analytical laboratory. The types and frequency of internal QC are listed below.

***Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)***—Prepared with a known concentration of the analyte(s) being measured and in the same matrix as the samples to be analyzed, used to verify the calibration of instruments and equipment and to verify the calibration curve for a particular method. The ICV is of a different origin than the calibration standards and the CCV.

***Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)***—The objectives of the two blanks are to determine the existence and magnitude of contamination problems caused by instrument carryover (memory).

***Preparation/Extraction Blanks***—Prepared for methods that require preparation/extraction prior to analysis. A sample of DI/DS water is treated identically to the other samples being analyzed in the batch, including the addition of reagents. This blank will indicate contamination introduced in the laboratory by reagents and/or careless preparation techniques.

***Laboratory Control Sample (LCS)***—Prepared for methods that require preparation before analysis to verify the use of proper sample preparation techniques. A sample with a known concentration of the analyte(s) being measured is prepared and treated identically to the samples being analyzed.

***Pre-Digestion/Extraction Spikes***—The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. A known addition of the analyte(s) being measured is added to a split of one of the primary samples in the batch, and is otherwise treated identically to other samples in the batch. The recovery of matrix spike samples is used to calculate the accuracy of the measurement. The spiking solution will be fresh standard stock solutions. Appropriate spiking levels will be used depending on the indigenous concentrations in the feed water.

***Post-Digestion/Spikes***—Prepared following digestion/speciation and performed at the instrument (ICP) by adding a known quantity of the analyte to an aliquot of the digested or speciated sample. The analytical spike is run directly after the original sample.

***Analytical Duplicate Samples***—Used to determine the precision of the analytical method. These samples are created in the laboratory by duplicating all steps of an analytical procedure on a sample split from one of the primary samples in the batch. Precision will be calculated using the relative percent difference of the analytical duplicate samples.

#### ***2.2.4.2.2 Internal Quality Control Procedures***

The general practices required of the laboratory include the use of reagents that are of reagent-grade or higher quality. Samples produced during the testing will be placed in an acid matrix consistent with the digestion methods before analysis. Table 4 summarizes the internal quality control procedures for the critical analyses.

**Table 45. Internal Quality Control Procedures**

Analysis, Method	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
Sediment Mineralogy, Optical Mineralogical Analysis	Duplicate Sample	Every 20 samples or each batch, whichever is more frequent	≤20% RPD	Reanalyze, flag results, analyze for usability
Sediment Mineralogy, X-Ray Analysis	Internal Standard	Every sample	Identification of SRM from Spectra	Repreparation and reanalysis of sample
	Standard Reference Material	Monthly	Delta 2θ ≤ 0.1 degrees	Terminate analysis, correct problem, rerun SRM
Shape Factor of Soil Particles, Optical Mineralogical Analysis	Duplicate Sample	Every 20 samples or each batch, whichever is more frequent	≤20% RPD	Reanalyze, flag results, analyze for usability
Grain Size Distribution, Sieve Analysis	Duplicate Sample	Every 20 samples or each batch, whichever is more frequent	≤20% RPD per fraction	Reanalyze, flag results, analyze for usability
Surface Area, BET Analysis	Duplicate Sample	Every 20 samples or each batch, whichever is more frequent	≤20% RPD	Reanalyze, flag results, analyze for usability
Soil Organic Matter, Combustion	According to manufacturer's recommendations	Before each new analytical run, every 15 samples	Follow manufacturer's recommendations	Investigate, correct if necessary, recalibrate as required.
Specific Density, Pycnometer Method	According to manufacturer's recommendations	Before each new analytical run, every 10 samples	Follow manufacturer's recommendations	Investigate, correct if necessary, recalibrate as required.
Bulk Density, Core Method	Duplicate Sample	Every 10 samples	Identification of SRM from Spectra	Repreparation and reanalysis of sample
Speciation of Uranium, Dissolution of Metals	Extraction Blank	Batch, every 20 samples, whichever is more frequent	No significant contamination <sup>1</sup>	Repreparation, Reanalysis of samples
	Extraction Duplicate	Batch, every 20 samples, whichever is more frequent	≤20% RPD	Flag results, evaluate for usability
	Extraction Spike	Batch, every 20 samples, whichever is more frequent	75-125% recovery	Flag results, evaluate for usability

Analysis, Method	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
Main Sorbent(s) of Uranium, Optical Mineralogical Analysis	Duplicate Sample	Every 20 samples or each batch, whichever is more frequent	$\leq 20\%$ RPD	Reanalyze, flag results, analyze for usability
Main Sorbent(s) of Uranium, Electron Microscope	Duplicate Sample	Every 20 samples or each batch, whichever is more frequent	$\leq 20\%$ RPD	Reanalyze, flag results, analyze for usability
Percent Soil Moisture, "Speedy" Soil Moisture	Duplicate Sample	Every 10 samples	$\leq 10\%$ RPD	Repreparation and reanalysis of sample
Percent Soil Moisture, ASTM D 4959-89	Duplicate Sample	Every 20 samples or each batch, whichever is more frequent	$\leq 20\%$ RPD	Reanalyze sample
Percent Soil Moisture, Neutron Moisture Log	Calibration	Daily	Follow manufacturer's recommendations	Investigate, correct if necessary, recalibrate as required.
	Duplicate	Every well	$\leq 10\%$ RPD	Re-log well
Major Anions, Ion Chromatography	Calibration of the instrument	Each time instrument is set up	$r \geq 0.995$	Terminate analysis, correct problem and recalibrate instrument
	Initial Calibration Verification	Following calibration of instrument	90-110% recovery of true value	Recalibrate instrument
	Initial Calibration Blank	Following ICV	$\leq 2$ times the IDL	Recalibrate instrument
	Continuing Calibration Verification	Following ICB, every 10 samples, end of run	90-110% recovery of true value	Recalibrate instrument, rerun affected samples
	Continuing Calibration Blank	Following ICB, every 10 samples, end of run	$\leq 2$ times the IDL	Recalibrate instrument, rerun affected samples
	Blank	Batch, every 20 samples, whichever greater	No significant contamination <sup>1</sup>	Repreparation, Reanalysis of samples
	Analytical Duplicate	Batch, every 20 samples, whichever greater	$\leq 20\%$ RPD	Flag results, evaluate for usability

Analysis, Method	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
	Laboratory Control Sample	Batch, every 20 samples, whichever greater	80-120 % Recovery	Repreparation, Reanalysis of samples
	Spike	Batch, every 20 samples, whichever greater	75-125% Recovery	Flag results, evaluate for usability
Total Recoverable Metals, Inductively Coupled Plasma Furnace	Calibration	Daily, 1 std + blank	$r \geq 0.995$	Recalibrate the instrument
	Calibration Verification	Beginning of run, every 10 samples, end of run	90-110% recovery of true value	Recalibrate, reanalyze associated samples
	Calibration Blank	Following calibration verification	No significant contamination <sup>1</sup>	Recalibrate, reanalyze associated samples
	Preparation blank	Batch, every 20 samples, whichever greater	No significant contamination <sup>1</sup>	Repreparation, Reanalysis of samples
	Analytical Duplicate	Batch, every 20 samples, whichever greater	$\leq 20\%$ RPD	Flag results, evaluate for usability
	Pre-Digestion Spike	Batch, every 20 samples, whichever greater	75-125% Recovery	Flag results, evaluate for usability
	Laboratory Control Sample	Batch, every 20 samples, whichever greater	80-120 % Recovery	Repreparation, Reanalysis of samples
	Post-Digestion Spike	When matrix spike fails, or new matrix	85-115% Recovery	Perform MSA if appropriate or flag samples
Iron Speciation, Colorimetric	Calibration	Every time instrument is set up, 3 stds + blank	$r \geq 0.995$	Recalibrate the instrument
	Preparation blank	Batch, every 20 samples, whichever greater	No significant contamination <sup>1</sup>	Repreparation, Reanalysis of samples
	Analytical Duplicate	Batch, every 20 samples, whichever greater	$\leq 20\%$ RPD	Flag results, evaluate for usability
	Laboratory Control Sample	Batch, every 20 samples, whichever greater	80-120 % Recovery	Repreparation, Reanalysis of samples
Uranium, Laboratory Specific Analysis	Calibration	Every time instrument is set up, 3 stds + blank	$r \geq 0.995$	Recalibrate the instrument
	Preparation blank	Batch, every 20 samples, whichever greater	No significant contamination <sup>1</sup>	Repreparation, Reanalysis of samples

Analysis, Method	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
	Analytical Duplicate	Batch, every 20 samples, whichever greater	≤ 20% RPD	Flag results, evaluate for usability
	Matrix Spike	Batch, every 20 samples, whichever greater	75-125% Recovery	Flag results, evaluate for usability
	Laboratory Control Sample	Batch, every 20 samples, whichever greater	80-120 % Recovery	Repreparation, Reanalysis of samples
pH of porewater, electrometric method	Calibration	Every time instrument is set up	≤ 0.05 pH units of true value	Investigate, correct, recalibrate instrument
	Calibration Verification	Following calibration, every 10 samples, end of run	≤ 0.1 pH units of true value	Recalibrate, reanalyze affected samples
	Analytical Duplicate	Batch, every 20 samples, whichever greater	≤ 20% RPD	Flag results, evaluate for usability
Alkalinity of porewater, EPA Standard Method 2320B	Spike	Batch, every 20 samples, whichever greater	75-125% Recovery	Flag results, evaluate for usability
	Calibration Verification	Following calibration, every 10 samples, end of run	≤ 10% of true value	Recalibrate, reanalyze affected samples
	Standard Reference Material	Monthly	Follow manufacturer's recommendations	Follow manufacturer's recommendations
	Analytical Duplicate	Batch, every 20 samples, whichever greater	≤ 20% RPD	Flag results, evaluate for usability
	Spike	Batch, every 20 samples, whichever greater	75-125% Recovery	Flag results, evaluate for usability
	Blank	Batch, every 20 samples, whichever greater	No significant contamination <sup>1</sup>	Repreparation, Reanalysis of samples
Dissolved CO <sub>2</sub> -Vadose Zone, CO <sub>2</sub> Analyzer	Calibration	Every time instrument is set up, 3 stds + blank	r≥ 0.995	Recalibrate the instrument
	Preparation blank	Batch, every 20 samples, whichever greater	No significant contamination <sup>1</sup>	Repreparation, Reanalysis of samples
	Analytical Duplicate	Batch, every 20 samples, whichever greater	≤ 20% RPD	Flag results, evaluate for usability

Analysis, Method	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
	Matrix Spike	Batch, every 20 samples, whichever greater	75-125% Recovery	Flag results, evaluate for usability
	Laboratory Control Sample	Batch, every 20 samples, whichever greater	80-120 % Recovery	Repreparation, Reanalysis of samples
Carbon Isotopes, GC/MS	Calibration	Laboratory Specific	Laboratory Specific	Laboratory Specific
	Preparation blank	Laboratory Specific	Laboratory Specific	Laboratory Specific
	Analytical Duplicate	Laboratory Specific	Laboratory Specific	Laboratory Specific
	Matrix Spike	Laboratory Specific	Laboratory Specific	Laboratory Specific
1/2 to 4 times the IDL.				

### 2.2.5 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

All field instruments will be tested, inspected, and maintained in accordance with BHI-QA-03, *ERC Quality Assurance Program Plans*, Plan 5.3, "Environmental Radiological Measurements Quality Assurance." The results from all testing, inspection, and maintenance activities will be recorded in the field logbook in accordance with BHI-EE-01, *Environmental Investigation Procedures*, Procedure 1.5, "Field Logbooks." Testing, inspection, and maintenance of instruments used in the analytical laboratory will be consistent with the requirements specified in the laboratory's quality assurance program.

### 2.2.6 Instrument Calibration and Frequency

All field instruments will be calibrated in accordance with BHI-QA-03, *ERC Quality Assurance Program Plans*, Plan 5.3, "Environmental Radiological Measurements Quality Assurance." The results from all instrument calibration activities will be recorded in the field logbook in accordance with BHI-EE-01, *Environmental Investigation Procedures*, Procedure 1.5, "Field Logbooks." Tags will be attached to all field screening and onsite analytical instruments, noting the date when the instrument was last calibrated and the calibration expiration date. Calibration of instruments used in the analytical laboratory will be consistent with the requirements specified in the laboratory's quality assurance program.

### 2.2.7 Inspection/Acceptance Requirements for Supplies and Consumables

Procurement activities will be limited to requisitions provided to ERC Procurement in accordance with the requirements of applicable procurement procedures. Project personnel will review received items for conformance to specifications established in the associated requisition. Items that do not meet specifications will be dispositioned through the nonconformance system.

## **2.2.8 Data Management**

Samples and field data will be managed by BHI in accordance with BHI-EE-01, *Environmental Investigation Procedures*, Section 2, "Sample Management." Laboratory analytical results and field data will be maintained by MSE. The analytical laboratory shall provide a quality assurance report to MSE. MSE will submit the final project report to BHI, DOE/RL, and the Washington Department of Ecology. MSE will maintain an electronic copy and hard copies of the final report through Document Control.

## **2.2.9 Sample Preservation, Containers, and Holding Times**

The sample preservation, containers, and holding time requirements for the analyses to be performed are summarized in Section 4.2, Table 7.

## **2.2.10 Field Documentation**

Field documentation will be maintained in accordance with BHI-EE-01, *Environmental Investigation Procedures*, including the following procedures:

- Procedure 1.5, "Field Logbooks"
- Procedure 1.13, "Environmental Site Identification and Information Reporting"
- Procedure 3.0, "Chain of Custody"
- Procedure 3.1, "Sample Packaging and Shipping."

## **2.3 ASSESSMENT/OVERSIGHT**

This section addresses the activities for assessing the effectiveness of project implementation and associated QA and QC activities. The purpose of assessment is to ensure that the QAPP is implemented as prescribed.

### **2.3.1 Assessments and Response Actions**

Assessments will be conducted during the project to verify compliance with the requirements outlined in the SAP, project work packages, the BHI quality management plan, and BHI procedures and regulatory requirements. Assessments include, but are not limited to, surveillance, management systems reviews, readiness reviews, technical systems audits, performance evaluations, audits of data quality, and data quality assessments. Deficiencies identified by any of these assessments will be reported to project management. When appropriate, corrective actions will be implemented. Corrective actions will be documented in logbooks and management will be notified.

### **2.3.2 Reports to Management**

Assessment reports will be provided to project management. Management will be made aware of deficiencies identified by these assessments and the corrective actions implemented.

## **2.4 DATA VALIDATION AND USABILITY**

This section addresses the QA activities that occur after the data collection phase of the project is completed. These tasks determine whether or not the data conform to the quality assurance objectives and criteria defined in Section 2.1.4, thus satisfying the project objectives.

### **2.4.1 Data Review, Validation, and Verification Requirements**

Verification and validation are performed primarily to confirm that sampling and chain-of-custody documentation is complete, sample numbers can be tied to the specific sampling location, samples were packaged for shipment according to prescribed requirements, samples were analyzed within the required holding times, and analyses met the data quality requirements specified in the SAP. Verification activities will be performed in accordance with BHI-EE-01, *Environmental Investigation Procedures*, Section 2, "Sample Management."

### **2.4.2 Data Quality Assessment**

A data quality assessment will be performed in accordance with *EPA Guidance for Data Quality Assessment* (EPA 1996). The data quality assessment is a scientific and statistical evaluation to determine if the results are the right type, quality, and quantity to support the intended use. As appropriate, this evaluation shall include the following:

- Review the DQOs, including the objectives of the study and the sample design
- Review analytical data, including data packages and associated QC results
- Select and perform tests of the data
- Verify assumptions
- Determine corrective actions
- Draw conclusions
- Interpret and communicate the test results.

### **3 EXPERIMENTAL DESIGN**

The distribution of contaminants such as uranium in the soil profile depends on the physical properties of the waste stream, which provides the transport medium (i.e., water), and the chemical properties of the contaminant, which affect contaminant-soil interactions. Other characteristics affecting the contaminant soil interaction include the geologic and geochemical properties of the soil column and the composition of soil moisture and soil gases. Contaminant soil interaction is generally described in terms of the following processes:

1. Adsorption and desorption including ion exchange;
2. Precipitation and dissolution;
3. Filtration and remobilization of colloids and suspended particles; and
4. Diffusion into micro-pores within mineral grains.

Of these, adsorption and desorption of the contaminant to the soil matrix are probably the dominant processes for site conditions. As such, the project has been designed to understand controls on these processes. Precipitation and dissolution are also expected to influence uranium mobility, and will be investigated during the project. The other processes listed will be addressed to determine their relative importance. However, they are not expected to be important to the mobility of uranium at the site.

#### **3.1 THE GEOCHEMICAL AND CONCEPTUAL MODELS**

A geochemical model of the site will be developed to describe the mobility of uranium in unsaturated and saturated zones for the existing site conditions. To provide the best geochemical model, both the unsaturated and saturated zones must be characterized. The unsaturated zone is important because uranium is likely still bound in the soil. Consequently, the unsaturated zone is a potential continuing contaminant source. Likewise the saturated zone is important because it is the primary focus of the current remedial action (pump-and-treat).

The geochemical model will be used to enhance the current conceptual model of the site. The conceptual model is the basis for developing flow and transport models, which serve to evaluate potential remedial options for the site. It is imperative to study and understand the entire mobility system, including the contaminant source, vadose zone transport and adsorption processes, and the saturated zone transport and adsorption processes. Concentrating on one of these, could potentially lead to the implementation of a remedial action that will ultimately fail. By characterizing and understanding the entire process, future modeling of the uranium mobility will be significantly more detailed and as a result a more successful remedial system can be designed.

Developing the geochemical model will require going beyond empirical adsorption isotherm models, which cannot be extrapolated to conditions that differ from those considered in model parameterization. Surface complexation adsorption models can allow such extrapolation (Langmuir, 1997), and so may be used to predict uranium adsorption/desorption under conditions that might be encountered during various remediation scenarios outside those studied.

The use of surface complexation models requires an understanding of the chemical and physical properties of the soil, porewater (unsaturated zone), groundwater (saturated zone), and the waste stream. Surface complexation models take into account changes in adsorption as a function of pH, and concentrations of competing ions and complexed species, and therefore are well suited to

conditions of changing pH and soil/groundwater chemistry. Such variable conditions are expected at the site due to the variable nature of the waste stream. Additionally, remedial options for the site may also require consideration of the effects of changing soil/groundwater chemistry, including pH, on uranium mobility.

Once the geochemistry of the system is understood, both laboratory experiments and complexation modeling can be undertaken to describe the mobility of the uranium in the unsaturated and saturated sediments. This approach will allow a better understanding of the recharge of uranium from the vadose zone to the groundwater. Moreover, the mobility of uranium in the groundwater will be better understood. The detailed characterization of the unsaturated and saturated zones, with respect to uranium mobility, will permit a more precise evaluation of various remediation options for the site.

Results from the surface complexation models will be validated through additional laboratory analysis on the unsaturated and saturated zone soil samples acquired from the planned borehole. These analyses may include batch tests and column studies. The precise validation method will depend on the amount of sample material available and the sample characteristics (i.e., contaminated or uncontaminated).

### 3.1.1 Surface Complexation Parameters

The following discussion of surface complexation model parameters is from Langmuir (1997). There are several surface complexation modeling schemes. The three most common are the diffuse layer model, the constant capacitance model, and the triple layer model. All yield the same general solutions, however, the diffuse layer model requires the least number of parameters to execute. All of the models require the concentration of available sorbing sites in a given volume of the soil matrix, which is a function of the surface area of sorbents exposed to the porewater solution and the surface charge density of the sorbents. The concentration of available sorbing sites is typically expressed as the number of moles of sorbing sites in contact with a liter of solution. The concentration of sorbing sites is determined from the following relationship (Langmuir 1997).

$$\Gamma_{SOH} \text{ (mol} \cdot \text{sites / L)} = \frac{N_s \text{ (site / m}^2\text{)} \times S_A \text{ (m}^2 \text{ / g)} \times C_s \text{ (g / l)}}{N_A \text{ (sites / mole} \cdot \text{sites)}} \quad \text{Equation 1}$$

Where:

- $\Gamma_{SOH}$  is the concentration of sorbing surface sites, measured in moles of monovalent sites exposed to a liter of solution,
- $N_s$  is the surface site density,
- $S_A$  is the surface area per weight of sorbent,
- $C_s$  is the weight of sorbent in contact with a liter of solution, and
- $N_A$  is Avagadro's number of sorbent sites per moles of sites.

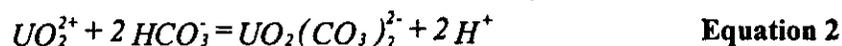
The primary sorbents of uranium are Fe(III) and Al oxyhydroxides<sup>1</sup>, clays, zeolites, phosphate minerals, and organic matter. The relative importance of sorbents can be determined through physical and optical examination including a particle size determination, and chemical and mineralogical analysis of the soils. The models also require equilibrium, so-called intrinsic constants that describe the adsorption and desorption of protons, and important cations, ligands and metal complexes. Measured and estimated intrinsic constants are available for a wide range of adsorption reactions on different mineral surfaces, as are other properties including mineral surface areas and surface charge densities (Dzombak and Morel, 1990; Langmuir, 1997). Many researchers have noted that any of the surface complexation models do equally well in general at modeling and predicting the adsorption behavior of uranium and other metals accurately (Turner, 1995). For this reason, and because the diffuse layer model is the simplest of these models to parameterize and apply, it has been chosen for this study.

### 3.1.2 Significance of Carbon Dioxide to Uranium Mobility in the Vadose Zone

Literature indicates that the concentration of CO<sub>2</sub> within the unsaturated zone may vary as much as one hundred fold of the CO<sub>2</sub> concentration in the atmosphere above grade, where it occurs at the level of approximately 330 parts per million (ppm). Concentration of CO<sub>2</sub> controls the uranium mobility because the uranyl [U(VI)] adsorption in soil is pH dependent, and the pH depends on concentration of CO<sub>2</sub>; the higher the CO<sub>2</sub> concentration, the lower the pH. Experiments show that uranyl adsorption by ferric oxides increases with pH up to pH 6 to 7, and then decreases with the uranium being desorbed, i.e., mobilized at higher pHs. In other words, uranyl is most mobile at low and high pHs and tends to be adsorbed if pH is close to neutral.

Although similar principles control the mobility of uranium in the saturated zone, the analytical approach to groundwater sampling is slightly different. Measurement of the groundwater pH is a routine procedure involving a direct measurement. However, for the unsaturated zone there is no cost-effective method to measure the pH of soil moisture at depth. Consequently, values of pH must be calculated from the measured values of CO<sub>2</sub>.

The mobility of hexavalent uranium [U(VI)] in unsaturated zone waters usually depends on its occurrence as carbonate complexes, which make uranium highly mobile. When U(VI) is in the form of a carbonate complex, it is poorly adsorbed and its minerals become orders of magnitude more soluble than if it occurs as an uncomplexed free uranyl ion (UO<sub>2</sub><sup>2+</sup>). Important carbonate complexes include UO<sub>2</sub>CO<sub>3</sub><sup>0</sup>, UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>, and UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup>. The carbonate complexes dominate the chemistry of U(VI) in most natural waters above pH 5-6. Their occurrence and abundance depends on both the pH and alkalinity of the water, as can be seen by the reaction forming the dicarbonate complex which may be written:



The equilibrium constant for this reaction is:

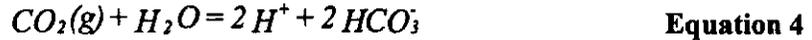
$$K_{eq} = \left[ \frac{(UO_2(CO_3)_2^{2-})(H^+)^2}{(UO_2^{2+})(HCO_3^-)^2} \right] \quad \text{Equation 3}$$

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<sup>1</sup> The Fe (III) oxyhydroxide mineral name is goethite and the Al oxyhydroxides mineral name is diaspore.

These expressions show that an increase in alkalinity or in pH favors formation of the complex.

It is possible to extract unsaturated zone moisture and analyze it to determine the alkalinity; but, there is no cost-effective way to measure the pH of soil moisture at depth. However, the pH of unsaturated zone waters depends on the CO<sub>2</sub> pressure in the unsaturated zone air, as is evident in the following reaction:



For which:

$$K_{eq} = \frac{(P_{CO_2})}{[H^+]^2 [HCO_3^-]^2} \quad \text{Equation 5}$$

The CO<sub>2</sub> pressure of unsaturated zone air cannot be assumed equal to its value of about 0.0003 bars found in atmospheric air. In fact, its pressure at depth is likely to be 10 to 100 times greater (cf. Langmuir, 1997, p. 158). Nevertheless, if the partial pressure of CO<sub>2</sub> gas in the unsaturated zone air and the alkalinity of the water are measured, the pH of soil moisture can be computed through Equation 5. The computed pH and measured alkalinity permit the calculation of concentrations of carbonate complexes through Equation 3, thereby making it possible to estimate the solubility of U(VI) and its tendency to be adsorbed. In other words, the measured alkalinity and CO<sub>2</sub> pressure permit estimating the mobility of uranium in the unsaturated zone, provided other geochemical information, e.g., sorption sites etc. is available.

MSE proposes to focus soil sampling activities in the Plio-Pleistocene unit, specifically the caliche layer often present in the unit. Sampling will be concentrated in this zone in an attempt to quantify the impact of the caliche layer on CO<sub>2</sub> concentration in the formation air.

### 3.2 EXPERIMENTAL APPROACH

The results of the diffuse layer model are typically expressed in terms of the concentration of sorbate in the porewater and the amount adsorbed to a given surface area of soil material. If the effective surface area of a weight of sorbent material is known, partitioning relationships can be derived from these results (Langmuir, 1997; Pabalan et al., 1998). The power of the surface complexation approach is that the partitioning relationships can be developed for various soil conditions that currently exist at the site, and for different conditions that might arise during remediation efforts. The result is a dynamic model for predicting uranium mobility at the site.

The majority of the data for developing the conceptual model will be obtained from analysis of soil and porewater samples acquired during the installation of a well planned for FY01 within the UP-1 Operable Unit. Other data sources may include soil samples as available from the core library and data obtained from a cone penetrometer test (CPT) conducted near the location of the borehole. In addition to acquiring subsurface data, the proposed CPT investigation is designed to optimize the sampling during the drilling program. The CPT investigation is described in detail in Section 5.1.2.

The sampling effort, to be accomplished at the Hanford Site, will be coordinated in conjunction with BHI, and site work requirements and protocols. BHI, as representative of the host site, has assumed responsibility for coordination of in-kind and direct sampling support for this effort, and is therefore providing the EM-40 cost sharing. The host site will provide support in the areas of

site interface and documentation requirements, as a minimum. The description of work will be developed in accordance with the Description of Work (DOW) format and the site requirements, i.e., review cycles, prior planning, and regulatory approvals.

The project will require the following:

1. Sampling of the soil and porewater for analysis of chemical and physical properties to develop a surface complexation model for the site. This will be used to determine the variation in the partitioning of the uranium between the soil and porewater for the site soil profile.
2. Using the surface complexation model, new partitioning relationships for potential contaminant transport paths at the site will be developed.
3. The new partitioning relationships will be used to simulate uranium transport for each potential transport path including its source.
4. The model providing the best fit of the simulated results with observed data will be considered the new and improved conceptual model of uranium transport at the site.

This new model may then be used to:

1. Target the remedial action to the most probable subsurface region that has been the main contributor to the groundwater plume.
2. Select an appropriate remedial action to disable or remove the contaminant source.
3. Evaluate options to meet the remedial action objectives for the uranium plume in the groundwater.

The experimental approach is primarily based on the assumption that the stratigraphy defined in nearby boreholes is locally consistent and representative of the project site. This assumes that the soils sampled during the well installation and samples taken from existing core(s) are representative of the condition of the soils below the cribs prior to the disposal of waste to the cribs.

Additionally, it is assumed that the waste stream history is sufficiently well known such that when combined with the geochemical conceptual model, the mass of uranium that is still being recharged to the groundwater from the soil column can be estimated.

### **3.3 SCHEDULE OF SAMPLING AND ANALYTICAL ACTIVITIES**

The project has been originally planned as a three-year effort beginning in FY01 and continuing through FY03.

The well installation is planned for the summer (June-July) of FY01. Other sampling activities not related to the well installation, such as the CPT investigation and obtaining representative soil samples from nearby "clean sites" may be started before the well installation. Geophysical data will be obtained from the borehole prior to completing the well.

The schedule for laboratory sample analysis, in support of the geochemical model development, will be dependent on the well installation schedule. If the planned well installation schedule of June-July (of FY01) is adhered to, then sample analysis will begin as soon as the samples are received by the contract laboratory (June-July of FY01) and continue through January 2002. This

schedule will allow the geochemical model to be developed by June 2002. Validation of the geochemical model is anticipated to be completed in 2002.

Precautions will be taken to ensure handling procedures do not adversely affect the acquired samples, in particular the loss of moisture. The soil moisture sample handling will follow the procedure discussed in the U.S. Geological Survey (USGS) Water-Resources Investigations Report 96-4048 (Yang et al 1996) or alike.

## 4 ANALYTICAL REQUIREMENTS

### 4.1 MEASUREMENTS

The parameters that control the mobility of uranium at the site will be quantified either through a prescribed measurement processes or from published values.

The parameters considered critical to the success of the project are discussed in the following sections. The parameters are grouped according to the source of sample material (i.e., soil, porewater, waste stream) and the measurement that will be used to quantify the parameter. Critical measurements require strict adherence to established quality assurance and quality control (QA/QC) plans and procedures to ensure that the data are usable to the project.

#### 4.1.1 Soil Chemical and Physical Properties

The analysis of the soil chemistry and physical properties will include identifying the major mineral composition; analysis of the grain coatings and precipitates present in the soil matrix; determination of the grain size distribution; and surface area of the sorbent phases identified in the analysis. This data will primarily come from soil samples obtained during the installation of the borehole scheduled for FY01 and the CPT investigation. The critical measurements for soil chemical and physical properties are listed in Table 5~~Table 6~~.

#### 4.1.2 Porewater Chemistry

The porewater analysis will include the determination of the major ions in solution, alkalinity, dissolved CO<sub>2</sub> in the unsaturated zone (via soil gas sampling), and pH in the saturated zone. The critical measurements for porewater analysis are listed in Table 6~~Table 8~~.

Dissolved CO<sub>2</sub> and alkalinity control the concentration of carbonate species, including uranyl carbonate complexes in the porewater, by affecting the pH of solution. Since it is not feasible to measure pH in the unsaturated zone porewater, dissolved CO<sub>2</sub> will be determined from measurements of the CO<sub>2</sub> concentration in the soil gas. The in situ CO<sub>2</sub> measurements are discussed further in Section 5.1.2 and in Section 5.2.1.

#### 4.1.3 Waste Stream pH and Chemistry

The waste stream discharged to the cribs must be characterized in terms of the major ions; heavy metals (especially those that may be competing with uranium); pH; and alkalinity. This data will come from site reports because the waste is no longer being discharged to the cribs. Data will be reviewed to determine if the quality of the data is consistent with the intended uses. Waste stream data that does not exist will be estimated, if necessary. Estimations will be based on in part on the existing waste stream data.

#### 4.1.4 Validation of Geochemical Model

The surface complexation geochemical model will be validated through additional laboratory analysis of soil samples from the unsaturated and saturated zones. Uranium

adsorption/desorption data will be compared to the data predicted using the surface complexation geochemical model. The validation method (i.e., batch tests and/or column tests) will be determined after the borehole sampling is completed and will depend on the amount of sample material available and the sample characteristics (i.e., contaminated or uncontaminated). A detailed analysis plan for the validation of the geochemical model will be prepared and submitted to BHI for approval prior to implementation.

**Table 56. Critical Measurements for Soil Chemical and Physical Properties**

Parameter	Measurement Method	Reference
Sediment Mineralogy, to include grain coatings and precipitates*	Optical Mineralogical Analysis	Methods of Soil Analysis, Part I, Chapter 8
	X-ray Analysis	Methods of Soil Analysis, Part I, Chapter 12
Shape Factor of Soil Particles*	Optical Mineralogical Analysis	Methods of Soil Analysis, Part I, Chapter 8
Grain Size Distribution	Sieve Analysis	Methods of Soil Analysis, Part I, Chapter 15
Surface Area*	BET Analysis	Methods of Soil Analysis, Part I, Chapter 16
Soil Organic Matter	Combustion	Methods of Soil Analysis, Part III, Chapter 34
Specific Density	Pycnometer Method	Methods of Soil Analysis, Part I, Chapter 14
Bulk Density	Core Method	Methods of Soil Analysis, Part I, Chapter 13
Speciation of Uranium bound to Soil Matrix*	Dissolution of Metals	Methods of Soil Analysis, Part III, Chapter 3
Identifying the Main Sorbent(s) of Uranium*	Optical Mineralogical Analysis	Methods of Soil Analysis, Part I, Chapter 8
	Electron Microscope	NA
Surface Charge Density of the Main Sorbent(s) of Uranium.	Literature Values	Langmuir, 1997
Percent Soil Moisture (Field)	"Speedy" Soil Moisture	ASTM D 4944-89
Percent Soil Moisture (Lab)	Laboratory Measurement	ASTM D 4959-89 (1994)
Percent Soil Moisture (Borehole)	Neutron Moisture Log	ASTM D 5220-92
*This test may also be completed on each fraction of a sample that has been gently sieved. If the data provide significant insight into the soil analysis, additional samples will be sieved and analyzed in the same manner.		

**Table 68. Critical Measurements for Porewater Chemistry**

Parameter	Measurement Method	Reference
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Parameter	Measurement Method	Reference
Major Anions (SO <sub>4</sub> , Cl)	Laboratory Analysis by Ion Chromatography	EPA SW-846, Method 9056
Total Recoverable Metals (Ca, Mg, Na, K)	Laboratory Analysis by Inductively Coupled Plasma Furnace	EPA SW-846, Preparation Method 3005A, ICP Method 6010B
Iron Speciation	Laboratory Analysis by Colorimetric	EPA Standard Methods 3500-Fe D
Speciation of Uranium	Laboratory Specific Analysis	NA
pH of Porewater-Vadose Zone	Computed from Alkalinity and Soil Gas CO <sub>2</sub> pressure	
pH of Porewater-Saturated Zone	Electrometric Method	EPA SW-846, Method 9040B
Alkalinity (Forms) of Porewater	Titration	EPA Standard Method 2320B
Dissolved CO <sub>2</sub> -Vadose Zone	Field Measurement of Partial Pressure of Soil Gasses.	
Dissolved CO <sub>2</sub> -Saturated Zone	Calculated from pH and Alkalinity	
Carbon Isotopic Compositions	Gas Chromatograph - Isotope Ratio Mass Spectrometry	

## 4.2 SAMPLING REQUIREMENTS FOR MEASUREMENTS

The sampling requirements for the measurements that will be made to support the project are summarized in Table 7~~Table 10~~, which includes the measurement, the sample matrix (i.e., pore water or soil), sample form (i.e., undisturbed, composite, etc.), any preservation steps required for the sample, the required quantity of sample, and any shipping and handling considerations for the sample.

**Table 7**~~10~~. Sampling Requirements

Parameter	Sample Matrix	Preservative	Holding Time	Sample Size and Container	Shipping/Handling Requirements
Optical Mineralogical Analysis	Soil	None	NA	5 g, HDPE or Glass*	NA
X-ray Analysis	Soil	None	NA	1 g, HDPE or Glass*	NA
Sieve Analysis	Soil	None	NA	200 g, HDPE or Glass*	NA
BET Analysis	Soil	None	NA	10 g, HDPE or Glass*	NA

Parameter	Sample Matrix	Preservative	Holding Time	Sample Size and Container	Shipping/Handling Requirements
Organic Content of Soil	Soil	None	NA	5 g, HDPE or Glass*	NA
Bulk Density	Soil	None	NA	10 cm of Core, HDPE or Glass*	NA
Specific Density	Soil	None	NA	20 g, HDPE or Glass*	NA
Speciation of Uranium Bound to Soil Matrix	Soil	None	NA	100 g, HDPE or Glass*	NA
Identifying the Main Sorbent(s) of Uranium	Soil	None	NA	5 g, HDPE or Glass*	NA
Percent Soil Moisture (Field)	Soil	None	Analyze immediately	Min. 20g	NA
Percent Soil Moisture (Lab)	Soil	None	Analyze immediately on arrival at laboratory	200g *	NA
Percent Soil Moisture (Borehole)	Soil	None	NA	NA	NA
Major Anions-Vadose Zone (SO <sub>4</sub> , Cl)	Aqueous**	≤4°C	28 days	As much as possible (25 ml should be sufficient)	On Ice
Total Recoverable Metals-Vadose Zone (Ca, Mg, Na, K)	Aqueous**	≤4°C, pH≤2, HNO <sub>3</sub>	6 Months	As much as possible (25 ml should be sufficient)	On Ice
Iron Speciation-Vadose Zone	Aqueous	Filter, ≤4°C, pH≤2, HCl	Analyze Immediately	As much as possible (25 ml should be sufficient)	On Ice
Speciation of Uranium in Porewater - Vadose Zone	Aqueous**	Laboratory Specific	Laboratory Specific	Laboratory Specific	Laboratory Specific
Alkalinity-Vadose Zone	Aqueous**	≤4°C	14 days	50 – 100 ml	On Ice
CO <sub>2</sub> -Vadose Zone	Gas	None	Real time	NA	NA
Major Anions-Saturated Zone (SO <sub>4</sub> , Cl)	Aqueous**	≤4°C	28 days	250 ml	On Ice

Parameter	Sample Matrix	Preservative	Holding Time	Sample Size and Container	Shipping/Handling Requirements
Total Recoverable Metals-Saturated Zone (Ca, Mg, Na, K)	Aqueous**	$\leq 4^{\circ}\text{C}$ , $\text{pH} \leq 2$ , $\text{HNO}_3$	6 Months	250 ml	On Ice
Iron Speciation-Saturated Zone	Aqueous	Filter, $\leq 4^{\circ}\text{C}$ , $\text{pH} \leq 2$ , $\text{HCl}$	Analyze Immediately	100 ml	On Ice
Speciation of Uranium in Groundwater - Saturated Zone	Aqueous**	Laboratory Specific	Laboratory Specific	Laboratory Specific	Laboratory Specific
Alkalinity-Saturated Zone	Aqueous**	$\leq 4^{\circ}\text{C}$	14 days	250 ml	On Ice
pH - Saturated Zone	Aqueous**	None	Analyze immediately in the field and/or on arrival at laboratory	250 ml	On Ice
Carbon Isotopic Compositions	Gas	None	14 days	500 ml in a Glass or Mylar Container	NA
<p>* Sampling material extracted at lab location from soil cores collected from boreholes and sealed in the field.  ** To be extracted from soil core using centrifugal method.</p>					

## 5 SAMPLING

### 5.1 SAMPLE LOCATIONS

Data for the project may be obtained from several sources including samples obtained during the installation of the well planned for FY01, data from a CPT investigation, samples from existing cores obtained from previous drilling programs at the site, and samples from exposed surface deposits that are outside of any environmentally controlled areas and are representative of the site soils. These are discussed in detail in the following sections.

#### 5.1.1 Borehole Samples

The borehole sampling locations were determined from the stratigraphic profile for the site developed from data obtained during previous well installations (BHI 1995). The sampling locations and intervals are described below.

1. Samples from the Hanford formation will be taken starting at 20 feet below grade from each distinct lithologic horizon (i.e., sands, gravels, etc.) observed from the drill cuttings. If no change in the lithology is observed over thirty feet of drilling, a sample should be collected.
2. Continuous soil samples will be obtained from 5 feet above the estimated top of the Early Palouse soils to 5 feet below the bottom of the Plio-Pleistocene unit. The continuous sampling will assure collection of the required samples of the formation that otherwise might be drilled through without sampling, as it is known that the thickness of the caliche layer varies throughout the area.
3. Samples from the Ringold formation will be taken starting at 5 feet below the bottom of the Plio-Pleistocene unit. Samples will be taken from each distinct lithologic horizon (i.e., sands, gravels, etc.) observed from the drill cuttings. If no change in the lithology is observed over thirty feet of drilling, a sample should be collected. Samples from the unsaturated Ringold formation, with duplicates, will be acquired every 10 feet starting at 30 feet below the bottom of the Plio-Pleistocene. Samples from the saturated Ringold formation, with duplicates, will be acquired at an interval of 15 feet starting 5 feet below the water table. The duplicate samples shall be used for the geochemical model validation efforts. Sampling will continue to 30 feet below the water table.

Based on the sampling plan described above and the stratigraphic profile from wells 299-W19-34A, MSE estimates that 20 split-spoon samples will be acquired. The sampling locations are summarized in ~~Table 8~~ Table 12.

**Table 812. Summary of Estimated Borehole Sampling**

Description	Estimated Thickness	Sampling Interval	Number of Samples*
Hanford 1 Formation	70 ft	Every 30 ft	2
Hanford 2 Formation	117 ft	Every 30 ft	4

Description	Estimated Thickness	Sampling Interval	Number of Samples*
Early Palouse and Plio-Pleistocene Units	18 ft	Continuous	12
Ringold Formation (Unsaturated)	44 ft	Every 10 ft	4**
Ringold Formation (Saturated)	N/A	Every 30 ft	4**
<b>TOTAL NUMBER OF SAMPLES</b>	249 ft	N/A	27

\* Assumes split-spoon will sample 2 ft to 2.5 ft per sample.

\*\* Duplicate samples will be acquired.

During the drilling and sampling activities, the MSE onsite geologist may recommend altering the sampling locations in the field, depending on drilling and sampling conditions. Any recommendations made by the MSE geologist will be discussed with the on-site BHI Subcontractor Technical Representative (STR). Changes to the sampling will be made only after receiving the approval of the BHI STR. Any deviations to the planned sampling locations and/or procedures must be documented in the field logbook.

MSE also recognizes the practical limitations to subsurface sampling, and if it is found that sampling of certain intervals is not possible, the MSE onsite geologist may recommend sampling to proceed to the next interval.

### 5.1.2 Cone Penetrometer Testing

The proposed cone penetrometer testing (CPT) is planned to optimize the sampling during the drilling program. Data obtained from the CPT will include soil gas CO<sub>2</sub> concentrations, soil moisture, and gross lithology. The CPT would eliminate the need for soil gas samples from the upper portion of the borehole (this is estimated to be the upper 140 feet, but is dependent on the depth that can be achieved with the CPT rig). The data would also be used to direct the collection of split-spoon samples from those sections of the borehole with the highest soil moisture; therefore ensuring usable data will be obtained from the samples collected during drilling. If an acceptable depth, as determined by the MSE representative, is not met, another hole(s) will be attempted. In order for optimization of the sampling, the CPT would need to be run prior to drilling and in the same general location as the proposed borehole.

### 5.1.3 Existing Core Samples

Samples from existing soil cores from the Hanford site may be used for the study if the MSE project geologist determines the core to be representative of the site and applicable to the study.

## **5.2 SAMPLE METHODS**

### **5.2.1 Carbon Dioxide Measurements**

Collection of gas samples from the formation(s) is necessary to measure the carbon dioxide (CO<sub>2</sub>) content in air present in unsaturated sediments. The CO<sub>2</sub> measurement is critical to the project because CO<sub>2</sub> of the formation gas, being in chemical equilibrium with CO<sub>2</sub> dissolved in soil moisture, is one of the main factors controlling mobility of uranium in the unsaturated zone (see Section 3.1.2). Since the unsaturated zone is considered to be the uranium source for the contaminated groundwater, it is imperative to determine the mobility of this source. Once recognized, the leach rate of uranium from the unsaturated zone at the water table interface can be quantified. This will allow for a successful simulation of uranium transport in the groundwater, whose cleanup is the ultimate objective. An adequate simulation of uranium transport in the groundwater will require information and data on uranium mobility in both the unsaturated and saturated zones.

It is estimated that the thickness of the unsaturated zone at the borehole location is approximately 210 feet. Assuming samples of the formation gas can be acquired to a depth of approximately 140 feet using a cone penetrometer testing (CPT) rig, gas samples from the remaining portion of the unsaturated zone will be acquired from the borehole drilled by the cable tool method. For this portion of the sampling, real time measurements of CO<sub>2</sub> concentration will be acquired and graphed to determine whether atmospheric air was evacuated from the borehole and the gas sample is representative of the formation gas. This will be recognized by a flattening of the diagram of carbon dioxide concentration versus time. The CO<sub>2</sub> sampling will be contingent on scheduling and funding.

At least one formation gas sample from each sampling interval of the cable tool borehole and, if possible the CPT hole, will also be sent to the laboratory to validate the sample quality. Analyses will be completed to determine the degree of contamination, if any, of the sample with atmospheric air. Contamination will be evaluated using an isotopic analysis for the ratio of stable isotope of carbon (<sup>13</sup>C) to carbon (<sup>12</sup>C) in the collected gas sample.

#### **5.2.1.1 Carbon Dioxide Sampling of CPT Hole**

Based on previous experience of Applied Research Associates, Inc. (ARA), the CPT should be able to penetrate sediments to the depth of the first caliche-layer occurrence, which is assumed to be 140 feet below ground surface (bgs). Carbon dioxide concentrations in this interval will be measured continuously at the outlet of a vacuum pump that is drawing gas at the tip of the penetrating cone. A gas analyzer capable of measuring CO<sub>2</sub> concentration ranging from 0 ppm to 500,000 ppm with resolution of 100 ppm will be used.

Costs for the CPT and necessary permitting efforts will be covered by MSE. The subcontractor shall secure the necessary permits to push the hole in close proximity to the planned borehole prior to drilling activities. MSE will be responsible for these subcontracted costs. It is expected that the CPT work will be completed within one working day.

### **5.2.1.2 Carbon Dioxide Sampling of Borehole**

It is estimated that 5 formation gas samples will be acquired from the borehole, assuming it is drilled using the cable-tool method. The sampling interval will range from 140 feet to 210 feet bgs. Samples will be drawn according to the following:

- 1 sample from the Hanford 2 formation;
- 1 or 2 samples from the Early Palouse and Plio-Pleistocene unit (contains the caliche layer of interest); and
- 2 samples from the unsaturated Ringold formation.

Formation-gas samples can be acquired once the drillers have completed their tasks on days when designated sampling horizons have been reached. The procedure for collecting gas samples includes:

1. With the last 2 ft of the borehole left uncased, the drill string will be removed from the borehole.
2. Using a custom-made cap the top of the internal casing will be sealed so it is airtight. The cap will be equipped with an airtight cut-off valve and a nipple, which will be connected to an air hose.
3. A flexible air-hose will be connected to an electrical blower.
4. The blower will be turned on and CO<sub>2</sub> concentration in the blower's exhaust (gas from formation) will be measured using a carbon dioxide analyzer. The operation will cease when readings of carbon dioxide concentrations reach a constant level.
5. The instrumentation will be removed to have the borehole ready for the following day drilling.

The following arrangements will be made and special conditions met if necessary:

- Electric power for the blower will be supplied by a generator;
- If required by site conditions, the blower (and generator if used) will be explosion proof;
- The blower will be capable of evacuating one air-volume of the borehole in 5 minutes provided the vacuum does not exceed 6 inches of mercury (longer time will be necessary if the formation is tight, i.e., low permeable);
- Air samples will not be contaminated by the blower infrastructure;
- Manpower for the gas sampling operation will be provided by MSE-TA; and
- All instrumentation, operational and analytical costs associated with the CO<sub>2</sub> sampling will be covered by MSE.

## **5.2.2 Split-Spoon Samples**

Soil samples will be obtained during drilling using a 5-inch outside diameter (OD) split-spoon sampler with a two-foot body. Liners will be used inside the split-spoon samplers to contain the sample material. Sampling shall follow the applicable sections of BHI-EE-01, Procedure Number 4.0, Soil and Sediments Sampling, Rev. 2 for split spoon sampling.

## **5.3 SAMPLE MANAGEMENT**

Samples obtained for this study will be released by BHI to the contract laboratory in accordance with BHI-EE-10 Procedure 8.0 and any other necessary radiological release authorization. MSE will have a laboratory contract in place prior to the start of the sampling activities. The contract laboratory will be certified to accept and handle radioactive and hazardous waste. BHI will work with MSE to obtain the necessary release authorization(s). MSE will be responsible for packaging and shipping the samples.

Upon completion of the analysis, the sample material will be disposed of according to approved and established procedures. The laboratory shall be responsible for the disposal. Samples will not be returned to Hanford for disposal.

## **5.4 FIELD MEASUREMENTS AND OBSERVATIONS**

### **5.4.1 Soil Moisture**

The weight percent soil moisture will be measured in the field using the Calcium Carbide Gas Pressure Test Method according to ASTM D4944-98.

### **5.4.2 Geologic Logging**

Lithologic descriptions made from observations during drilling and from inspection of core will be made according to the BHI-EE-01 Procedure Number 7, Revision 3, Geologic Logging.

### **5.4.3 Borehole Geophysical Measurements and Logging Intervals**

High-resolution spectral gamma and neutron moisture data will be acquired using the standard borehole geophysical logging procedures after each major string of casing is installed. MSE will procure a qualified borehole logging subcontractor prior to the beginning of the drilling activities. It is estimated that two strings of casing will be logged. If possible, MSE will have the logging completed off-hours, after the drilling is completed, to prevent interference with the drilling activities. If logging does interfere with the drilling activities, BHI will provide cost for driller standby and the associated labor for the BHI crew.

### **5.4.4 Hydrogeologic Information**

Relevant hydrogeologic information needed for geochemical and transport modeling will be taken from existing reports. This includes moisture retention curves for unsaturated sediments that were developed at the Hanford Site.

## **5.5 WASTE MANAGEMENT**

BHI shall be responsible for waste management during the well installation and sample acquisition activities. BHI will manage any waste generated according to an approved waste control plan.

## 6 REFERENCES

- BHI March 1995, Borehole Summary Report for the 200-UP-2 Operable Unit, BHI-00034.
- BHI, November 1998, ERC Training Procedures, BHI-HR-02, Bechtel Hanford, Inc., Richland, Washington
- BHI, September 2000, ERC Quality Assurance Program Plans, BHI-QA-03, Bechtel Hanford, Inc., Richland, Washington
- BHI, January 2001, Environmental Investigations Procedures, BHI-EE-01, Bechtel Hanford, Inc., Richland, Washington
- DOE/RL January 1, 1997. Waste Site Grouping for 200 Areas Soil Investigations DOE/RL-96-81 Rev. 0
- DOE/RL April 1, 1999. 200 Areas Remedial Investigation/Feasibility Study Implementation Plan-Environmental Restoration Program DOE/RL-98-28 Rev. 0
- DOE/RL March 2000. Fiscal Year 1999 Annual Summary Report for the 200-UP-1, 200-ZP-1, and 100-NR-2 Pump-and-Treat Operations and Operable Units DOE/RL-99-79 Rev. 0
- DOE/RL December 1, 2000. Hanford First Five-Year Review Report (DRAFT)
- Dzombak, D.A. and Morel, F.M.M., 1990, Surface complexation modeling, Hydrous ferric oxide. Wiley-Interscience, New York 1990
- EPA, 1996, Guidance for Data Quality Assessment, EPA QA/G-9, U.S. Environmental Protection Agency, Washington, D.C.
- EPA February 1997. Declaration of the Record of Decision, Interim Action Record of Decision for the 200 Area UP-1 OU 043623
- EPA, 1999, EPA Requirements for Quality Assurance Project Plans, EPA QA/R-5, U.S. Environmental Protection Agency, Washington, D.C.
- Langmuir, D. 1997, Aqueous Environmental Geochemistry. Prentice Hall, Upper Saddle River, NJ.
- MSE, 2001, Data Quality Objectives Summary Report for Development of a Conceptual Geochemical Model for Uranium Mobility in the Unsaturated Zone and Saturated Sediments at the 200 West Area of the DOE Hanford Site, Washington.
- MSE, 2001, Multi-Year Implementation and Project Management Plan for Development of a Conceptual Geochemical Model for Uranium Mobility in the Unsaturated Zone and Saturated Sediments at the 200 West Area of the DOE Hanford Site, Washington, MSE Technology Applications, Butte, Montana
- Pabalan, R. T., Turner, D.R. Bertetti, F.P., and Prikryl, J.D., 1998, Uranium (VI) sorption onto selected mineral surfaces. Chapter 3 in Adsorption of Metals by Geomedia. Variables, Mechanisms and Model Applications. E.A. Jenne ed., Academic Press, San Diego CA, 99-130

Turner, D.R., 1995, *A uniform approach to surface complexation modeling of Radionuclide sorption*. Report CN-WRA 95-001. Center for Nuclear Waste Regulatory Analysis, San Antonio TX.

WHC June 1, 1988. *U1/U2 Uranium Plume Characterization, Remedial Action Review and Recommendation for Future Action* WHC-EP-0133

Yang, In C., Gordon W Rattray, and Pei Yu. *Interpretation of Chemical and Isotopic Data from Boreholes in the Unsaturated Zone at Yucca Mountain, Nevada*. USGS Water-Resources Investigations Report 96-4058. Denver, Colorado, 1996.