

# Determination of Distribution Coefficients for Radionuclides of Concern at the Westinghouse Hematite Facility

REV. 0

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## ABBREVIATIONS AND ACRONYMS

ASTM	American Society for Testing and Materials
bgs	below ground surface
CSSG	clayey silty sandy gravel
DCGL	derived concentration guideline level
DOE	U.S. Department of Energy
DQO	data quality objective
DSCC	deep silty-clay/clay
EC&HS	Environmental Compliance and Health and Safety
EPA	U.S. Environmental Protection Agency
GEO	GEO Consultants, LLC
HU	hydrostratigraphic unit
IDW	investigation-derived waste
ISCORS	Interagency Steering Committee on Radiation Standards
JCD	Jefferson City Dolomite
LSC	Liquid scintillation counting
$K_d$	distribution coefficient
KPA	kinetic phosphorescence analysis
MCAWW	Methods for Chemical Analysis of Water and Wastes
NAD83	North American Datum of 1983
NSSC	near surface silt, silty clay
ORP	oxidation reduction potential
QA	quality assurance
QC	quality control
RESRAD	Residual Radioactivity, a computer code for evaluating radioactive sites
SAP	Sampling and Analysis Plan
SAIC	Science Applications International Corporation

## EXECUTIVE SUMMARY

The nuclear manufacturing facility at Hematite, Missouri was used for the production of nuclear fuels from natural, depleted, and enriched uranium. More than 45 years of processing nuclear materials and formerly authorized on-site disposal of process waste has resulted in radionuclide contamination of surface and near-surface soils at the Hematite Site. As part of the decommissioning process by Westinghouse, derived concentration guideline levels (DCGLs) for residual soils must be determined for radionuclides of concern. DCGLs will be calculated using the Residual Radioactivity (RESRAD) model, in which the soil distribution coefficient or  $K_d$  is an input parameter for simulating radionuclide leaching from contaminated soils. The primary objective of the study described in this report is to determine appropriate  $K_d$  factors for uranium (U), technetium (Tc), thorium (Th), plutonium (Pu), americium (Am), and neptunium (Np) to be used for modeling radionuclide leaching from unconsolidated soils at the Hematite Site. Because higher-than-background levels of U isotopes ( $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ ) and Tc (as  $^{99}\text{Tc}$ ) have been measured during previous characterization events, site-specific  $K_d$  factors for these radionuclides were measured in the laboratory using soil samples collected from the Hematite Site. Th, Pu, Am, and Np are contaminants of concern based on site history but have not been detected during previous characterization efforts. Thus, it was deemed sufficient to obtain  $K_d$  factors for these radionuclides from the published literature.

Site-specific measurements for  $K_d$  were performed on samples collected from areas of concern within the Hematite Site. Six boreholes were drilled to refusal or bedrock (~30 to 35 ft), and 18 soil samples (3 depth intervals per borehole) were collected for  $K_d$  testing, radionuclide analysis, and general soil characterization procedures. Groundwater used for the  $K_d$  tests was taken from an uncontaminated background monitoring well. All samples collected from the site consisted of very fine-grained, brown silty clay. The sand/gravel unit described in previous characterization efforts was encountered in four out of six boreholes but at a thickness of less than 1 ft, not enough to obtain representative samples for  $K_d$  testing. The fine-grained nature of the soil samples was confirmed by particle size distribution measurements, which showed the soils to consist of >96% silt and clay sized fractions and ~30% clay. Soil pH ranged from 5.8 to 8.3, total organic carbon ranged from 2.2 to 14 g/kg and iron (extracted through hot-acid digestion) ranged from 11.1 to 21.2 g/kg. Uranium activities were detected at significant levels in samples from the restricted areas, and in shallowest sample from the Tile Barn/Cistern Burn Pit area. Except for one sample from the restricted areas, technetium was not detected above the laboratory reporting limits in the samples collected for this study.

$K_d$  testing was performed following ASTM 4319-93, Standard Test Method for Distribution Ratios by the Short-term Batch Method, as recommended in the RESRAD data collection handbook. Two types of  $K_d$  tests were performed: (1) desorption tests where a measured mass of soil was contacted with a measured volume of uncontaminated groundwater over a period of 14 days, and (2) adsorption tests where soil was contacted with uncontaminated groundwater spiked to predetermined levels of U (as the uranyl ion or  $\text{UO}_2^{2+}$ ) and  $^{99}\text{Tc}$  (as the pertechnetate ion  $\text{TcO}_4^-$ ). For uranium, lower overall  $K_d$  values were observed in the adsorption tests, when compared to the desorption tests. Average  $K_d$ s from the adsorption and desorption tests were calculated, and the mean of the averages was considered the "best" estimate for U  $K_d$  for the Hematite Site. Although the desorption tests are likely to be more representative of contaminant leaching under field conditions, the adsorption data were still considered to yield a reasonable but conservative site-specific  $K_d$  for uranium. For Tc, significant removal of Tc was observed from the liquid phase of the soil/water mixtures within 3 days. This "apparent" sorption could be due

to the reduction of Tc(VII) to Tc(VI) and adsorption or precipitation of the latter, rather than electrostatic interactions of Tc(VII) with soil mineral surfaces. The resulting  $K_d$ s for Tc are significantly higher than published values, but the validity of  $K_d$  obtained from this study is supported by results that were repeated in multiple soil samples at several time intervals, and recovery of the Tc on the solid residues.

The following table shows recommended  $K_d$  values for radionuclides of interest to the Hematite Site. The U and Tc  $K_d$  values are site-specific in that these were measured using soil samples collected from the site. Because there were no distinct trends with depth in the  $K_d$  measurements for both U and Tc, spatial variability is best addressed by assuming that the unconsolidated sediments overlying bedrock at the Hematite Site can be characterized by a single  $K_d$  parameter that has either a log-normal (for U) or uniform (for Tc) distribution. The  $K_d$  values for the rest of the radionuclides are based on published literature values.

Radionuclides of Concern	Recommended $K_d$ value (mL/g)	Remarks
Uranium	175	Site specific measurement with range of 6.6 and 471.4 mL/g; grossly approximates a lognormal distribution.
Technetium	106	Site specific measurement with range of 15.1 and 172.9 mL/g; approximates a uniform distribution between 0 and 200 mL/g.
Plutonium	2000	RESRAD default value, reasonable when compared to published literature.
Thorium	60000	RESRAD default value, reasonable when compared to published literature.
Neptunium	2	At low end of published literature values.
Americium	1000	Consistent with published literature values, more reasonable than default $K_d$ of 20.

# 1. INTRODUCTION

## 1.1 BACKGROUND

The nuclear manufacturing facility at Hematite, Missouri, referred to in this report as the Hematite Site, was formerly used for the production of nuclear fuels from natural, depleted, and enriched uranium. The Hematite Site consists of 228 acres of property, 8 acres of which were used for operations. After taking ownership of the facility in 2000, Westinghouse Electric Company ceased operations and is proceeding with plant decommissioning.

More than 45 years of processing nuclear materials and formerly authorized on-site disposal of process waste has resulted in radionuclide contamination of surface and near-surface soils at the Hematite Site. These soils or unconsolidated sediments consist of a fine-grained silty clay/clay layer and a sand-gravel unit, with a total thickness of approximately 30 to 40 ft beneath the site [LBG 2003]. As part of the decommissioning process by Westinghouse, derived concentration guideline levels (DCGLs) for residual soils must be determined for radionuclides of concern in accordance with the requirements of 10CFR20, Subpart E. DCGLs will be calculated using the Residual Radioactivity (RESRAD) model [Yu et al. 2001], in which the soil distribution coefficient or  $K_d$  is an input parameter for simulating radionuclide leaching from contaminated soils. The  $K_d$  factor is defined as the concentration of a chemical species on the solid fraction divided by the concentration in the aqueous phase:

$$K_d = \frac{S}{C_w},$$

where  $S$  is mass of chemical species sorbed per unit mass of soil, and  $C_w$  is mass of chemical species per volume of solution. When the  $K_d$  parameter is used to model the leaching of chemicals from contaminated soils, the underlying assumption is that rapid equilibrium is reached between the dissolved and sorbed concentrations of a chemical species, and that these two concentrations are linearly related through the  $K_d$  factor. In theory, the  $K_d$  factor is used to characterize the *reversible* adsorption of a chemical species on solid surfaces including soil minerals and organic matter. However, other chemical processes, including mineral precipitation, diffusion into dead-end pores and attachment to microbes, can influence the experimental measurement of  $K_d$ . Although research efforts have attempted to differentiate adsorption from these other processes, there are no universally accepted standard methods for doing so.

There are two laboratory approaches for measuring  $K_d$ : the "batch" and the "column" methods. The "batch" method for measuring  $K_d$  consists of equilibrating a measured mass of soil with a selected contact solution (e.g., synthetic or site groundwater). In the more commonly used adsorption mode for  $K_d$  testing, the contact solution is spiked with a measured mass of the chemical species of interest which then adsorbs onto the soil during equilibration. It is also possible to use contaminated soils, in which case the chemical species of interest desorbs from the soil into the contact solution. The concentration of the chemical species is then monitored in the contact liquid over time. When this concentration reaches a steady state, it is assumed that the liquid and solid concentrations are in equilibrium, and  $K_d$  is calculated from their ratio. The liquid concentration is directly measured, while the solid concentration is usually inferred from a mass balance knowing the initial mass of chemical species in the soil/water mixture. In the "column" procedure for measuring  $K_d$ , a soil column (i.e., a cylinder packed with soil) is flushed

with the contact solution under a controlled flow rate. The  $K_d$  factor is then determined by analyzing the breakthrough of the chemical species of interest at the effluent end of the soil column. The "column" procedure is a closer simulation of the physical processes occurring in the field, however the experimental set-up and data interpretation are more difficult when compared to the "batch" procedure. Moreover, batch and column loading of uranyl complexes was compared in one study and no significant differences were observed [Bostick et al. 2002]. Thus, the "batch" procedure is more commonly used when a large number tests are needed to characterize spatial variability.  $K_d$  measurements in this study were performed using a "batch" procedure.

## 1.2 STUDY OBJECTIVES AND REPORT ORGANIZATION

The primary objective of the study described in this report is to determine appropriate  $K_d$  factors for uranium (U), technetium (Tc), thorium (Th), plutonium (Pu), americium (Am), and neptunium (Np) to be used for modeling radionuclide leaching from unconsolidated soils at the Hematite Site. Because higher-than-background levels of U isotopes ( $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ ) and Tc (as  $^{99}\text{Tc}$ ) have been measured during previous characterization events, site-specific  $K_d$  factors for these radionuclides were measured in the laboratory using soil samples collected from the Hematite Site. The laboratory  $K_d$  measurements were conducted following ASTM D 4319-93, *Standard Test Method for Distribution Ratios by the Short-Term Batch Method*, which is the procedure recommended in the RESRAD data collection manual [Yu et al., 1993]. Th, Pu, Am, and Np are contaminants of concern based on site history but have not been detected during previous characterization efforts. Thus, it was deemed sufficient to obtain  $K_d$  factors for these radionuclides from the published literature.

A secondary objective for the activities described in this report is to obtain radionuclide contamination data as well as basic geochemical and physical properties of soil samples collected from selected areas of concern within the Hematite Site. These data were used in assessing the laboratory-measured U and Tc  $K_d$  factors, through comparisons with published studies on similar soils, and in selecting  $K_d$  factors for Th, Pu, Am, and Np from literature values.

This report describes the site-specific laboratory measurement of  $K_d$  factors for U and Tc on soil samples collected from the Hematite Site. It also includes the selection of appropriate  $K_d$  factors for Th, Pu, Am, and Np from literature  $K_d$  values. The report is organized as follows:

- Section 2 contains the methods used to collect and characterize soil and groundwater samples from the Hematite Site for this study and the laboratory procedures followed to measure site-specific  $K_d$  factors for U and Tc.
- Section 3 describes results of physical, geochemical, and radionuclide (U isotopes and  $^{99}\text{Tc}$ ) analyses of soil and groundwater samples collected from the Hematite Site for this study.
- Section 4 provides results of laboratory U and Tc  $K_d$  measurements and a discussion of these results in comparison with published literature values.
- Section 5 contains literature  $K_d$  values for the other radionuclides (Th, Am, Pu, Np).
- Section 6 summarizes the primary findings from this study and includes a table containing  $K_d$  values for U, Tc, Th, Pu, Am, and Np recommended for use in RESRAD modeling and DCGL calculations for the Hematite Site.

## **2. PROCEDURES FOR DETERMINING SITE-SPECIFIC URANIUM AND TECHNETIUM DISTRIBUTION COEFFICIENTS**

### **2.1 SOIL AND GROUNDWATER SAMPLE COLLECTION METHODS**

Laboratory  $K_d$  measurements for U and Tc were performed on soil samples collected from areas of concern within the Hematite site. A bulk sample of groundwater from a background well was collected and used in preparing contact solutions for the  $K_d$  tests. Details regarding soil and groundwater sample collection are described below.

#### **2.1.1 Borehole locations**

Soil samples were collected from six boreholes located based on site history, previous subsurface characterization [LBG 2003], and a recently conducted gamma walkover survey [SAIC 2003]. Coordinates of these boreholes were measured via a Global Positioning System and are shown in Table 1. Areas surrounding borehole locations are described below (see Fig. 1 for borehole location map):

1. Duels Mountain (Borehole BHKD1) - Refers to a pile of excavated and potentially contaminated soil stored along the southeast corner of the fence line.
2. Burial Pits (Borehole BHKD2) - Approximately 40 burial pits are known to exist outside the fenced area based on available plant documentation.
3. Tile Barn Cistern Burn Pit (Borehole BHKD3) - The roof of the Red Room (referring to Building 240, Area 240-2 formerly used for highly enriched U conversion processes) was reportedly buried in an area south of the Tile Barn.
4. Restricted Area No.1 (Borehole BHKD4) - This borehole is located in "restricted areas" where elevated gamma radiation was detected during the walkover survey [SAIC 2003].
5. Restricted Area No. 2 (Borehole BHKD5) - This borehole is also located in "restricted areas" where elevated gamma radiation was detected during the walkover survey [SAIC 2003].
6. Evaporation Pond (Borehole BHKD6) - Past waste management practices have included the disposal of water containing trichloroethylene and  $^{99}\text{Tc}$  from cylinder washing.

**Table 1. Borehole coordinates in MO-East State Plane (NAD83) coordinate system**

<b>Borehole ID</b>	<b>Area</b>	<b>EASTING (ft)</b>	<b>NORTHING (ft)</b>
BHKD 1	Duel's Mountain	827489.34	864930.41
BHKD 2	Burial Pits	827677.93	864996.11
BHKD 3	Tile Barn Cistern Burn Pit	826723.31	864800.19
BHKD 4	Restricted Area #1	827245.45	864663.76
BHKD 5	Restricted Area #2	827255.37	864725.49
BHKD 6	Evaporation Ponds	827320.86	864645.66

\*NAD83: North American Datum of 1983

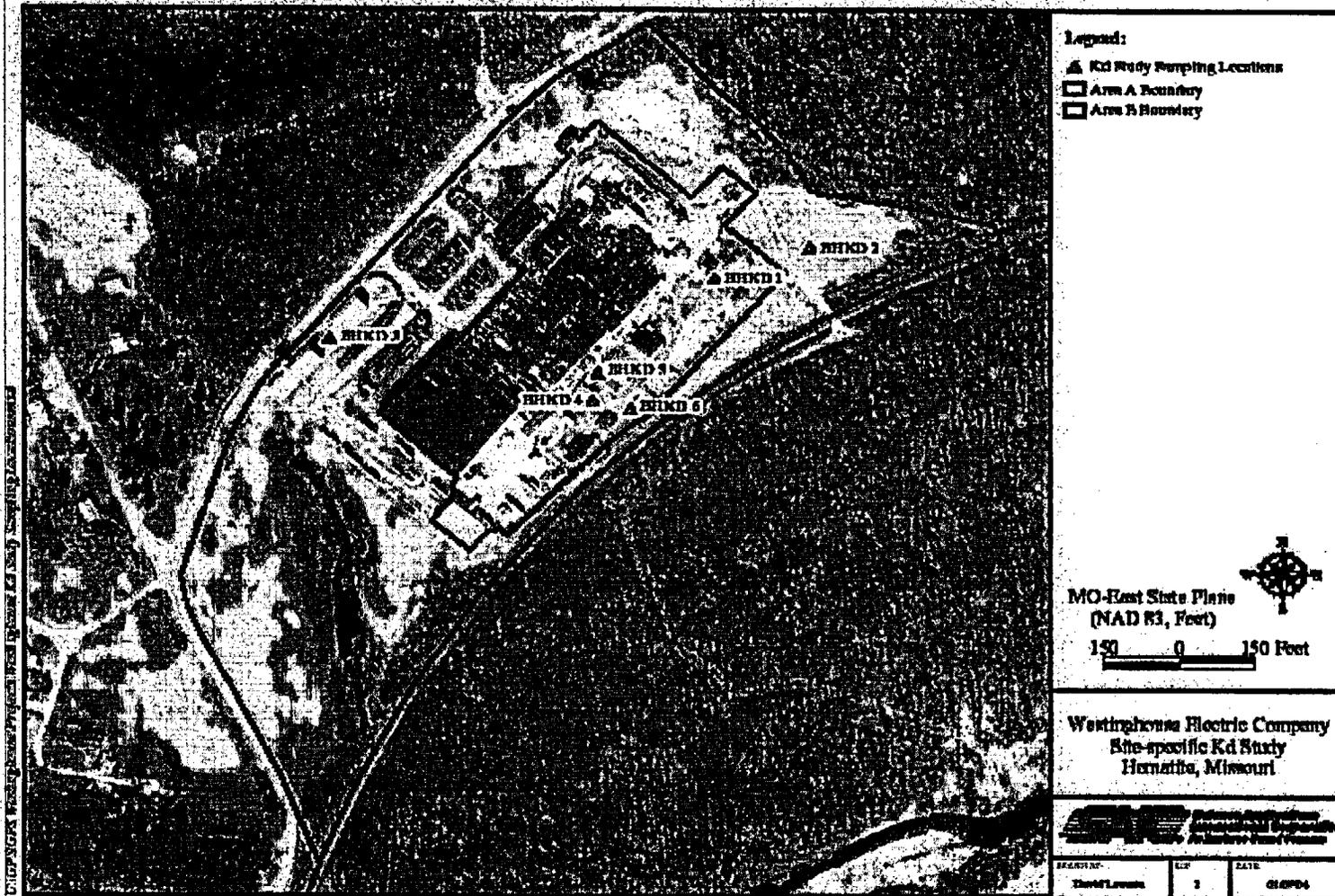


Fig. 1. Locations of boreholes where samples were collected for laboratory  $K_d$  measurements

### 2.1.2 Borehole Drilling and Soil Coring Procedures

Continuous soil cores were collected in 3 to 4 ft long, 2-in diameter acetate sleeves using a direct-push drill rig. This coring method was chosen over auger drilling because it is more economical and capable of collecting relatively intact samples from unconsolidated sediments at depths anticipated for the Hematite Site (<35 ft). In addition, this method of drilling/coring minimized the amount of investigation-derived waste (IDW) generated during the project.

Immediately after collection, cores contained in acetate sleeves were laid out on field tables and sleeves were cut for better visual examination. Gross gamma and beta scanning of the soil cores was performed to delineate contaminated zones within each core and allow collection of contaminated soil samples needed for the desorption  $K_d$  tests (see Section 2.2). Geologic descriptions were logged, with particular attention to mottling and appearance of iron oxide in order to estimate probable redox conditions of the soil. Water saturation of the cores were visually examined, recorded, and used to estimate the location of the water table.

Field geologists attempted to delineate the hydrostratigraphic units (HU) described during previous site investigations. Within the unconsolidated sediments, these units included a “near-surface silt/silty clay” unit (NSSC), a “deeper silty-clay/clay” unit (DSSC), and a “clayey, silty, sandy-gravel” unit (CSSG) [LBG 2003]. An attempt was made to collect samples for  $K_d$  measurements from each HU within each borehole. However, as will be shown later (Section 3.1), it was impossible to visually differentiate between the NSSC and the DSSC layers in the field. Furthermore, the CSSG layer was not encountered at a significant thickness before drill refusal. Soil samples (~1 kg) were collected from each borehole from three depths, focusing on intervals with elevated gamma and/or beta radiation from the core scans. This approach was used to increase the likelihood of collecting contaminated samples for desorption  $K_d$  measurements (see Section 2.2).

The soil samples were collected using pre-cleaned spatulas and placed in 1-L, wide-mouth, pre-cleaned polyethylene bottles. The bottles were then sealed with a chain-of-custody label affixed over the cap, and the bottles were labeled with the following information:

- borehole number
- sample label
- sampling depth interval
- date and time collected
- sampler name

Samples were labeled according to the following scheme: BHKD1-03, where the first field (BHKD1) corresponds to the borehole number, and the second field (03) corresponds to the upper limit of the sampling interval (e.g., 3 ft below ground surface). The soil samples were then packaged in ice and transported within 24 hours to the laboratory, together with completed chain-of-custody forms. A second 1-kg sample of soil was also collected for archiving, and labeled as BHKD1-03-ARCH. In total, 36 soil samples were collected, 18 of which were sent immediately to the laboratory for  $K_d$  measurements and other analyses while the remainder were archived and stored on site.

### 2.1.3 Groundwater Sample Collection and Field Analyses

Groundwater uncontaminated by radionuclides needed for preparing contact solutions in the laboratory  $K_d$  tests was collected from OB-1, a background-monitoring well located approximately 1000 to 1200 ft south/southwest from the center of the Hematite plant's main area. OB-1 is a 2-in diameter polyvinyl chloride (PVC) well with a depth of 26.2 ft and 16.2-ft well screen located within the unconsolidated sediments. Groundwater from this well was collected using a peristaltic pump and directly placed in a 20-L container. The headspace of the 20-L container was purged with nitrogen gas, immediately capped and a chain-of-custody seal affixed to the cap. Smaller volume groundwater samples were also collected in 40-mL vials for  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{238}\text{U}$ ,  $^{99}\text{Tc}$  activity analyses, major cation (Ca, K, Mg, Na) and anion ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) analyses. The groundwater samples were brought to the laboratory where they were stored at  $\sim 4^\circ\text{C}$  prior to analyses or use in  $K_d$  tests. The samples for cation analyses were preserved with nitric acid as soon as they were received in the laboratory. The purpose of nitrogen gas purging (for the 20-L sample) and cool storage is to maintain, to the extent possible, the dissolved oxygen content of the groundwater as well as minimize biological activity and chemical processes that can alter the water chemistry.

### 2.1.4 Field Analyses

Gross gamma/beta scans were performed on the soil cores in the field using zinc sulfide (alpha/beta) and 2" x 2" sodium iodide (gamma) hand-held meters. The field radiological measurements were used to determine sampling locations within each boring.

A number of groundwater parameters (pH, temperature, oxidation reduction potential (ORP), specific conductivity, and dissolved oxygen) were measured in the field at monitoring well OB-1 using a multi-parameter water quality instrument. Alkalinity and dissolved Fe were measured within 24 hours using single parameter test kits. Groundwater parameters were also measured in WS-14, a 2-in diameter PVC well screened within the unconsolidated sediments and located within 50 ft of BHKD2 in the Burial Pits area. Of the six boreholes, only BHKD2 was located near an existing groundwater monitoring well.

## 2.2 LABORATORY METHODS

### 2.2.1 Radionuclide Analysis

Upon receipt, the laboratory collected sub-samples from each of the 18 soil samples for isotopic U analysis via alpha spectroscopy following NAS/DOE 3050, and  $^{99}\text{Tc}$  analysis via liquid scintillation counting (LSC) following DOE TC-02-RC. A sub-sample of the groundwater sample from OB-1 was analyzed for total U via kinetic phosphorescence analysis (KPA) following ASTM D5174, and  $^{99}\text{Tc}$  via LSC following DOE TC-02-RC.

### 2.2.2 Distribution Coefficient Measurement

$K_d$  factors for U and  $^{99}\text{Tc}$  were measured following ASTM 4319-93, *Standard Test Method for Distribution Ratios by the Short-term Batch Method*, as recommended in the RESRAD data collection handbook [Yu, et al., 1993]. The ASTM method uses the term "distribution ratio" (or

$R_d$ ) instead of "distribution coefficient" (or  $K_d$ ) to avoid implying that equilibrium is attained in the measurements. In this study, the tests were performed for a maximum of 14 days, at which point steady-state concentrations in the contact solutions was observed in most of the tests and assumed to represent equilibrium conditions.

Two types of  $K_d$  tests were performed: (1) desorption tests where a measured mass of soil (20 g) was contacted with a measured volume of OB-1 groundwater (80 mLs) over a period of 14 days, and (2) adsorption tests where 20 g of soil was contacted with 80-mLs of OB-1 groundwater spiked to predetermined levels of U (as the uranyl ion or  $UO_2^{2+}$ ) and  $^{99}Tc$  (as the pertechnetate ion  $TcO_4^-$ ).

Although the adsorption test protocol is more commonly applied in research and practice due to the ability to control and accurately quantify radionuclide levels in the soil/water mixtures, the desorption tests more closely simulate radionuclide leaching from contaminated soils in the field. Before the  $K_d$  tests were initiated, the field-sampled radionuclide levels were reviewed to select soil samples containing U and  $^{99}Tc$  at high enough levels such that detectable radionuclide levels would likely be present in the contact solution. Furthermore, the  $K_d$  tests were performed in two batches to allow modifications in the  $K_d$  test procedures (e.g., spike levels) between batches to improve test measurements. Initially, desorption tests were performed on four of the samples with the highest levels of U. Two additional soil samples were later determined to have a sufficient amount of U that would possibly result in measurable U levels in the contact solutions during a desorption  $K_d$  test, based on the  $K_d$  factors measured from Batch 1. These two samples were subjected to desorption  $K_d$  testing in Batch 2. None of the soil samples collected for this study contained  $^{99}Tc$  that exceeded the laboratory-reporting limit (10 pCi/g). Table 2 shows the samples that were used for each type of  $K_d$  test. The target spike levels in Batch 1 were 10,000  $\mu\text{g/L}$  and 150 pCi/L for U and  $^{99}Tc$ , respectively, and 1000  $\mu\text{g/L}$  and 25,000 pCi/L for U and  $^{99}Tc$ , respectively, in Batch 2. The values shown in Table 2 are based on analyses of the contact solutions. The actual Tc concentration in Batch 1 is higher than the target level, suspected to be due to errors in dispensing the minute volume of Tc standard solution when the contact solutions were prepared.

**Table 2. Test conditions for distribution coefficient measurements**

Type of $K_d$ Test	Samples	Radionuclide levels in contact solution*
<i>Batch 1</i>		
Desorption test	BHKD3-8 BHKD5-1; -19; -27	Unspiked*
Adsorption test	BHKD2-4; -13; -23	10,000 $\mu\text{g/L}$ U; 600 pCi/L $^{99}Tc$
<i>Batch 2</i>		
Desorption test	BHKD4-14 BHKD6-1	Unspiked*
Adsorption test	BHKD1-4; -23; -28 BHKD3-16; -23 BHKD4-2; 24 BHKD6-11; 26	950 $\mu\text{g/L}$ U; 27,800 pCi/L

\*A bulk groundwater sample (20 L) from a background well (OB-1) was used for preparing contact solutions. Refer to Table 8 for radionuclide levels in groundwater sample.

Although visual observations of soil samples and field analyses in this study indicate mildly reducing conditions (discussed in Section 3), there are no available site-wide redox measurements. Thus, no attempts were made to strictly control the oxidizing conditions during the  $K_d$  tests. Furthermore, measured  $K_d$  factors under oxidizing conditions should be lower (and more conservative) because it will be unlikely for U (VI) (the oxidation state of U in  $UO_2^{2+}$ ) to reductively precipitate as U (IV). Table 3 summarizes procedural details on how ASTM D 4319 was applied to  $K_d$  measurements on the Hematite samples, including any deviations from the recommended procedures.

For each soil sample, eight soil/water mixtures were prepared to enable sacrificial sampling of each mixture for  $^{99}Tc$  and U analysis of the supernatant at eight predetermined time intervals (Days 3, 7, 10, 14, 21, 28, 35, 45). However, Batch 1 test results indicated steady-state U and  $^{99}Tc$  levels in the contact liquid (see Section 4.1) were achieved in 14 days. Thus, the supernatant in the soil/water mixtures were analyzed on Days 3, 7, 10, and 14 in both Batch 1 and Batch 2  $K_d$  tests.  $^{99}Tc$  and total U in the supernatant/contact liquids were quantified through LSC and KPA, respectively.

**Table 3. Procedural details regarding application of ASTM\* D 4319, "Standard Test Method for Distribution Ratios by the Short-term Batch Method," to Hematite samples. (Specific procedures are given in Section 7 of ASTM D 4319)**

ASTM Method Subsection	Notes regarding application to Hematite samples
7.1	Soil samples were disaggregated using a ball mill grinder to maximize homogenization and minimize variability between soil/water mixtures prepared for each soil sample.
7.2	Organic matter was not removed prior to $K_d$ testing. This step is not necessary since the intent of the measurements was to obtain model parameters for leaching from field soils with its natural organic content.
7.3	Characterization of soil samples prior to $K_d$ tests included: pH, total and organic carbon, moisture content, particle size distribution, total Fe and Mn, U isotopes and $^{99}\text{Tc}$ (refer to Section 2.2.1 and 2.2.3 for methods). Characterization of OB-1 groundwater used as contact solution included: pH, DO, ORP, dissolved Fe, alkalinity, specific conductivity, $\text{NO}_3^-$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , Ca, K, Mg, Na).
7.4	Bulk samples were ground to ensure homogeneity among subsamples collected for preparing soil/water mixtures. Soil samples were air-dried before disaggregation (Section 7.1). Air-drying was deemed acceptable since <i>in situ redox</i> conditions at Hematite are largely unknown.
7.5	OB-1 groundwater was used to pre-treat/pre-wash soil samples in Batch 1. This step was eliminated in Batch 2 to avoid loss of natural U from the soil samples, which could bias $K_d$ estimates if the field-sampled U concentration were used in calculations.
7.6	Two types of treatment solution/contact liquid were used: (1) unspiked OB-1 groundwater for desorption tests, and (2) OB-1 groundwater spiked with U and $^{99}\text{Tc}$ using certified standard solutions (refer to Table 2 for concentrations). The pH of soil/liquid mixtures was adjusted to 6.6, value measured for OB-1 in the field.
7.7	Specific conductance of each solution was not measured nor required in this study.
7.8	Contact periods for each soil sample were 3, 7, 10, and 14 days. Steady-state conditions were achieved within 14 days.
7.9	pH of mixtures was measured in Batch 2 samples. Eh measurement was not necessary since mixtures were kept under atmospheric conditions.
7.10	Analysis of total U and $^{99}\text{Tc}$ in the supernatant were measured via KPA and LSC, respectively.
7.11	Supernatant liquids were filtered before analysis.
7.12	Mass balance was assessed through solid residue analyses of Day 14 soil/water mixtures (see 7.13 below).
7.13	Filtered residues for Day 14 were measured in selected soil samples to assess mass balance.

\*American Society for Testing Materials

### 2.2.3 Laboratory Measurement of Other Soil and Groundwater Parameters

Other soil and groundwater parameters measured in the laboratory include the following.

Moisture content	MCAWW 160.3 MOD
Soil pH	SW846 9045A
Particle Size Distribution	ASTM D422
Total organic carbon/soil	SW846 9060
Total carbon/soil	SW846 9060
Total Fe/soil	SW846 6010B
Total Mn/soil	SW846 6010B
Major cations/groundwater	SW846 6010B
Major anions/groundwater	SW846 9056A

Except for the particle size distribution, all parameters were measured in all 18-soil samples collected from the boreholes. Particle size distributions were measured in soil samples from two boreholes (BHKD5 and BHKD6).

### 2.3 QUALITY CONTROL PROCEDURES

Established field quality control (QC) procedures were followed to ensure that field activities comply with the approved Quality Assurance (QA) Program Plan. Field Technical Procedures used for this project were listed in the project SAP [GEO and SAIC, 2003]. The laboratory adhered to all the QA/QC requirements specified in the analysis methods used in this study.

Data validation technical reviews were performed in accordance with the *Contract Laboratory Program Data Validation Functional Guidelines for Evaluating Inorganic Analytical Data*, and the *Laboratory Data Validation Guidelines for Evaluating Radionuclide Analyses and Radiochemical Data Verification and Validation*. These reviews were based on the information and documentation supplied by the laboratory. There were only minor findings in these reviews, none of which affected the accuracy of the  $K_d$  values calculated from the analytical data. Complete data validation reports can be found in Appendix A.

### 3. PHYSICAL AND CHEMICAL CHARACTERISTICS OF STUDY SOIL SAMPLES

#### 3.1 SOIL TYPES AND PARTICLE SIZE DISTRIBUTIONS

Soil samples were collected from three depth intervals from each borehole and were described as brown silty clay with increasing degrees of limonite and gray mottling and the presence of chert and/or limestone fragments at lower depths (see Table 4 and complete boring logs in Appendix B). Gray mottling indicates dissolution of ferric iron (i.e.,  $\text{Fe}^{3+}$  in iron oxides) as ferrous iron ( $\text{Fe}^{2+}$ ), a microbial process that requires anaerobic conditions under normal environmental pH conditions. Thus, it appears the soils are poorly aerated, consistent with the fine soil texture (i.e., poorly draining soil) observed in the samples. Note that the samples are assumed to be representative of soils from areas of concern within the Hematite Site.

The NSSC and DSCC layers previously identified by LBG [2003] could not be distinguished in the field. What appears to be the sand/gravel unit identified by LBG [2003] was encountered in four of the six boreholes (see Table 4 and complete boring logs in Appendix B), but all were observed to have a thickness of less than 1 ft before drill refusal. Drill refusal in all six boreholes occurred between 27 and 33 ft below ground surface, and was assumed to correspond to the depth of the Jefferson City Dolomite bedrock. Particle size distribution analyses in 6 samples from 2 boreholes (Table 5 and Appendix C) supports the field descriptions, with 5 out of six of the samples containing more than 96% silt/clay (~30% clay). One sample with coarser grained particles was taken from the lowest sampling interval in BHKD6, also consistent with the noted presence of clayey sand gravel in the last 6 in of this interval (see Table 4). Water saturation was encountered at 21 to 22 ft in BHKD2 and BHKD3 and at 28 ft in BHKD4 and BHKD5. Soil was moist but not saturated throughout the drilled depths of BHKD1 (33 ft) and BHKD6 (30 ft).

#### 3.2 SOIL CHEMICAL CHARACTERISTICS

Chemical characteristics of soil samples collected from the Hematite site for this study are shown in Table 6. Soil pH ranged from 6.5 to 7.5 for a majority of the soil samples. The lowest soil pH (5.8 and 6.0) were measured in the shallowest samples from BHKD4 and BHKD6, respectively. The highest pH values (8.1 and 8.3) were measured in mid-depth and deepest samples collected from BHKD1. Total and organic carbons levels were less than 1% in most of the measurements. In some samples, organic carbon levels were higher than total carbon (which consists of both organic and inorganic carbon). This was attributed to sub-sample heterogeneity coupled with low levels of inorganic carbon in the soil. In general, the chemical characteristics of the soil samples did not vary significantly among the soil samples, and no trends were observed when these parameters were plotted vs sample depth (see Appendix D for graphs).

**Table 4. Field descriptions of soil samples collected for  $K_d$  testing and other analyses**

Borehole	Location	Sample Interval (ft)		Field Description
		Upper Limit	Lower Limit	
BHKD1	Duels Mt	4	8.6	Silty clay, brown with 10% gray mottling
		23	28	Silty clay, brown with 5% mottling and limestone or dolomite fragments
		28	33*	Silty clay, brown with 5% mottling and limestone or dolomite fragments
BHKD2	Burial Pits	4	10	Silty clay, brown with 5% mottling
		13	17	Silty clay, brown with 15% mottling
		23	34*	Silty clay, brown with 15% mottling with chert fragments; silty sand gravel from 33.5-34 ft (bottom)
BHKD3	Tile Barn/Cistern Burn Pit	8	13	Silty clay, brown with 15% iron oxide gray mottling
		16	20	Silty clay, brown with 5% iron oxide mottling
		23	27*	Silty clay, brownish gray with 10% mottling and dolomite fragments
BHKD4	Restricted Area #1	2	14	Silty clay, brown with manganese (Mn) and chert nodules
		14	21	Silty clay, brown and 10% mottling
		24	30*	Silty clay, grayish brown with 15 mottling; sand with gravel 29.5-30
BHKD5	Restricted Area #2	1	12	Silty clay, brown with Mn nodules
		19	24	Silty clay, brown Mn nodules and 15% iron oxide mottling
		27	31*	Silty clay, brownish gray with 20% iron oxide mottling; clayey sand with gravel from 30.5- 31
BHKD6	Evaporation Pond	1	8	Silty clay, brown with iron oxide mottling
		11	16	Silty clay, brown with iron oxide mottling
		26	30*	Silty clay, brown with iron oxide mottling, clayey sand with gravel from 29-30 ft

\*Total depth of boreholes

**Table 5. Particle size distribution analyses results**

Sample ID	Location	Sample Interval (ft)	%Gravel	%Sand	%Silt	% Clay
BHKD5-01	Restricted Area #2	1-12	0	3.5	66.3	30
BHKD5-19	Restricted Area #2	19-24	0	2.8	66.2	31
BHKD5-27	Restricted Area #2	27-31	3	39.2	32.8	25
BHKD6-01	Evaporation Ponds	1-8	0	3	67	30
BHKD6-11	Evaporation Ponds	11-16	0	2.4	69.5	28
BHKD6-26	Evaporation Ponds	26-30	0	1.9	68.1	30

**Table 6. Physical and chemical characteristics of soil samples collected for K<sub>d</sub> testing**

Sample ID	PH	Moisture (%)	Total Carbon (g/kg)	Total Organic Carbon (g/kg)	Iron (g/kg)	Manganese (g/kg)
BHKD1-4	6.6	21.3%	1.36	2.26	19.8	1.5
-23	8.1	28.0%	4.12	4.64	22.2	1.55
-28	8.3	13.0%	1.49	2.32	16.3	0.458
BHKD2-4	7.3	19.8%	2.45	3.2	19.4	0.367
-13	6.6	21.3%	1.36	2.26	17.1	0.577
-23	6.7	24.2%	8.9	14.9	19	0.311
BHKD3-8	7.3	20.8%	5.55	3.93	20.3	0.955
-16	7.4	22.3%	2.7	3.78	22	0.364
-23	7.5	24.0%	3.75	3.74	22.2	1.04
BHKD4-2	6.0	18.8%	2.56	2.207	22	0.449
-14	7.2	22.0%	2.26	2.98	19.9	0.623
-24	7.1	23.7%	2.55	4.27	17.9	1.12
BHKD5-1	7.2	20.6%	3.45	3.32	20.8	0.535
-19	6.6	23.1%	3.07	3.4	20.9	0.283
-27	7.0	24.8%	6.25	5.35	11.1	0.216
BHKD6-1	5.8	20.0%	2.35	6.88	21.2	1.85
-11	6.8	21.2%	1.99	2.58	14.3	0.479
-26	7.7	22.0%	9.49	14	11.1	0.221
Minimum	5.8	13%	1.36	2.2	11.1	0.216
Maximum	8.3	28%	9.49	14	21.2	1.85

### 3.3 URANIUM AND TECHNETIUM ACTIVITIES IN SOIL SAMPLES

Soil samples collected from the restricted areas (BHKD5) contained the highest uranium concentrations (see Fig. 2) and highest radioactivity from  $^{234}\text{U}$  and  $^{235}\text{U}$  (see Table 7). Elevated U was also detected in the shallowest sample from the Tile Barn/Cistern Burn Pit area (BHKD3-8). Slightly elevated total U was measured in BHKD4-14 (from restricted area #1) and BHKD6-1 (from the Evaporation Ponds); elevated activities from  $^{234}\text{U}$  and  $^{235}\text{U}$  were also observed in these samples (see Table 7).

$^{99}\text{Tc}$  activity was not detected (0.5 pCi/g detection limit) in any of the samples from BHKD2 (Burial Pits) and BHKD3 (Tile Barn/Cistern Burn Pit). Activities were higher than the detection limit in the rest of the samples, but all were still below the laboratory's reporting limit (10 pCi/g). The highest  $^{99}\text{Tc}$  activity was measured in BHKD4-14.

All samples from BHKD5 and the shallowest sample from BHKD3 were deemed to have sufficient U levels for desorption testing in the first batch of  $K_d$  measurements. BHKD4-14 and BHKD6-1 were subjected to desorption testing in the second batch of  $K_d$  measurements because these had sufficient U to result in quantifiable levels in the contact solutions based on  $K_d$ s measured in the first batch.  $^{99}\text{Tc}$  was not measured in the first batch of desorption tests because the field-sampled activities in the soil samples (see Table 7) were below the reporting limit and were unlikely to be reliable for  $K_d$  calculations based on mass balance.

Table 7. Uranium isotope and Technetium-99 activities in soil samples

Borehole	Location	Upper Limit of Samp Int (ft)	Lower Limit of Samp Int (ft)	$^{234}\text{U}$ (pCi/g)	$^{235}\text{U}$ (pCi/g)	$^{238}\text{U}$ (pCi/g)	$^{99}\text{Tc}$ (pCi/g)
BHKD1	Duels Mt	4	8.6	6.14	0.26	1.48	6.6
		23	28	1.79	N.D.	1.04	6.23
		28	33	0.92	N.D.	0.73	2.84
BHKD2	Burial Pits	4	10	4.97	0.18	1.22	N.D.
		13	17	0.85	N.D.	0.93	N.D.
		23	34	0.72	N.D.	0.78	N.D.
BHKD3	Tile Barn/Cistern Burn Pit	8	13	21.5	1.31	12	N.D.
		16	20	1.48	0.15	0.93	N.D.
		23	27	1.63	0.24	1.01	N.D.
BHKD4	Restricted Area #1	2	14	3	N.D.	0.99	2.8
		14	21	20.2	0.66	3.32	13.8
		24	30	1.38	N.D.	0.94	0.82
BHKD5	Restricted Area #2	1	12	218	9.8	33.6	2.52
		19	24	90	4.12	14.5	1.18
		27	31	75.8	2.67	6.57	0.91
BHKD6	Evaporation Pond	1	8	11.6	0.45	2.06	2.55
		11	16	1	N.D.	0.91	2
		26	30	1.14	N.D.	0.66	5.86

Note: Shaded values are below the method-reporting limit (1 pCi/g for U isotopes and 10 pCi/g for  $^{99}\text{Tc}$ ) but above the detection limit (0.1 pCi/g for U isotopes and 1 pCi/g for  $^{99}\text{Tc}$ ). N.D.: not detected; value was below the method detection limit.

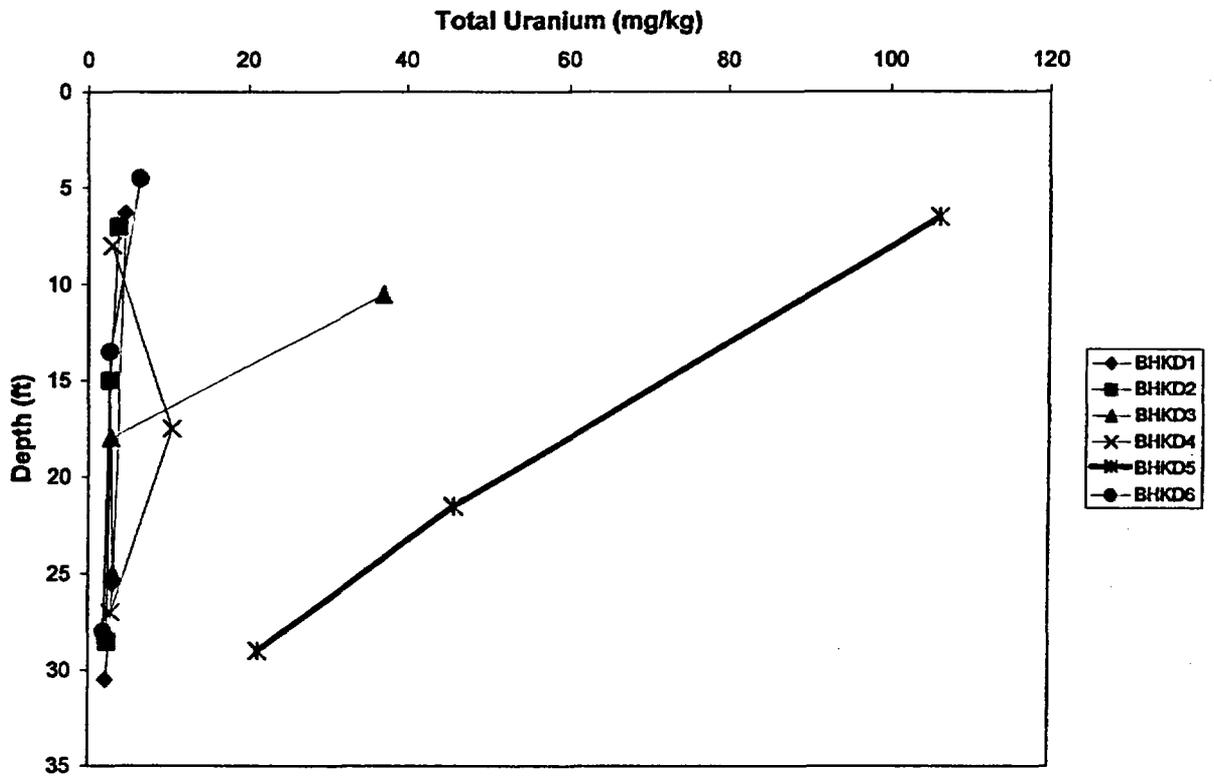


Fig. 2. Total uranium concentration in soil samples calculated from isotopic activities (Table 7) using the following conversion factors:  $6.2 \times 10^{-3}$  Ci/g  $^{234}\text{U}$ ,  $2.2 \times 10^{-6}$  Ci/g  $^{235}\text{U}$ , and  $3.3 \times 10^{-7}$  Ci/g  $^{238}\text{U}$ .

### 3.4 GROUNDWATER CHARACTERISTICS

Table 8 shows characteristics of groundwater used as contact solution for the  $K_d$  tests (OB-1). It also contains field parameters measured in WS-14, the only well located within 50 ft of one of the boreholes (BHKD2) drilled for this study. Note that the concentration of U in the OB-1 groundwater is significantly lower than the spike levels used in the adsorption  $K_d$  tests (see Table 2). The ORP in both wells indicated mildly reducing conditions, consistent with the presence of dissolved iron ( $Fe^{2+}$ ), but appear were inconsistent with the high dissolved oxygen measurements. It is suspected that the latter was affected by handling of the samples that can artificially aerate the groundwater.

**Table 8. Characteristics of Groundwater samples collected for this study**

Parameter	OB-1	WS-14
PH	6.57	5.93
Temperature °C	16.5	16.7
Oxidation Reduction Potential (ORP, mV)	27	57
Dissolved oxygen (mg/L)	1.42	4.79
Specific conductivity (mS/cm)	1.61	0.28
$^{234}U$ (pCi/L)*	1.27	Not measured
$^{235}U$ (pCi/L)*	0.03	Not measured
$^{238}U$ (pCi/L)*	0.66	Not measured
$^{99}Tc$ (pCi/L)	0.2	Not measured
Ca (mg/L)	83.5	Not measured
K (mg/L)	1.6	Not measured
Mg (mg/L)	28.1	Not measured
Na (mg/L)	19	Not measured
Cl (mg/L)	5	Not measured
$NO_3$ (mg/L)	3.5	Not measured
$SO_4$ (mg/L)	40.1	Not measured
Total Depth (ft)	27.1	Not measured
Depth to water (ft)	16.5	Not measured
$Fe^{**}$ (mg/L)	0.18	0.42
Alkalinity** (mg/L)	150	14

\*Calculated total U = 2.6 µg/L

\*\*Measured 24 hours later

## 4. RESULTS OF SITE-SPECIFIC $K_d$ STUDY FOR URANIUM AND TECHNETIUM-99

### 4.1 DESORPTION AND ADSORPTION KINETICS

Steady-state conditions were achieved within 14 days for both desorption and adsorption  $K_d$  tests (see Tables 9 and 10, Figs. 3 to 10). As mentioned in Section 2, the  $K_d$  tests were done in two batches to allow procedure modifications based on results of the first batch of tests. Tc was not quantified in the Batch 1 desorption tests because Tc activities were below the reporting limit in the soil samples (see Section 3.3 and Table 7). In addition, the Day 3 U analyses for BHKD2-4, -13, -23, BHKD4-14, and BHKD6-1 were not included in Figs. 4 and 5 because these were inconsistent with analyses on subsequent days (i.e., values were significantly higher or lower) and were deemed likely to be in error.

Table 9. Uranium concentrations in contact solutions during  $K_d$  tests

Sample ID	Batch No. and Test Type*	Initial U in contact solution ( $\mu\text{g/L}$ )	Uranium in contact solution ( $\mu\text{g/L}$ )					Std. Dev Day 7-14
			Day 3	Day 7	Day 10	Day 14	Average Day 7-14	
BHKD1-4	2, Ads	950	175	254	242	177	224	41
-23	2, Ads	950	491	420	321	335	359	54
-28	2, Ads	950	141	348	253	318	306	49
BHKD2-4	1, Ads	10000	0.606	9300	10100	10100	9833	462
-13	1, Ads	10000	0.291	9400	9900	9300	9533	321
-23	1, Ads	10000	0.291	8400	8700	9100	8733	351
BHKD3-8	1, Des	0	127	168	184	191	181	12
-16	2, Ads	950	28	12	19.3	18.7	17	4
-23	2, Ads	950	162	190	157	192	180	20
BHKD4-2	2, Ads	950	185	174	121	148	148	27
-14	2, Des	0	850	163	137	127	142	19
-24	2, Ads	950	40	34	20.9	8.83	21	13
BHKD5-1	1, Des	0	675	760	730	679	723	41
-19	1, Des	0	252	102	108	79.2	96	15
-27	1, Des	0	73.8	84	73.6	65.6	74	9
BHKD6-1	2, Des	0	840	7.7	4.5	7.79	7	2
-11	2, Ads	950	26	31	21.1	9.21	20	11
-26	2, Ads	950	13	16	6.51	4.88	9	6

\*Ads: adsorption; Des: desorption

**Table 10. Tc activities in contact solutions during  $K_d$  tests**

Sample ID	Batch No. and Test Type*	Initial Tc in contact solution (pCi/L)	Tc in contact solution (pCi/L)					
			Day 3	Day 7	Day 10	Day 14	Average (Day 7-14)	Std. Dev. (Day 7-14)
BHKD1-4	2, Ads	27800	1370	916	990	938	948	38
-23	2, Ads	27800	2610	3540	13200	724	5821	6543
-28	2, Ads	27800	565	548	635	6270	2484	3279
BHKD2-4	1, Ads	600	27	27	6.5	7.2	14	12
-13	1, Ads	600	64	68	29.7	4.8	34	32
-23	1, Ads	600	36	12	6.7	8.2	9	3
BHKD3-8	1, Des	0	N.A.	N.A.	N.A.	N.A.	----	----
-16	2, Ads	27800	1380	718	710	694	707	12
-23	2, Ads	27800	688	697	585	638	640	56
BHKD4-2	2, Ads	27800	3090	1300	1080	859	1080	221
-14	2, Des	0	N.A.	N.A.	-9.1	-15	----	----
-24	2, Ads	27800	1850	1250	1110	760	1040	252
BHKD5-1	1, Des	0	N.A.	N.A.	N.A.	N.A.	----	----
-19	1, Des	0	N.A.	N.A.	N.A.	N.A.	----	----
-27	1, Des	0	N.A.	N.A.	N.A.	N.A.	----	----
BHKD6-1	2, Des	0	N.A.	N.A.	10	-6	----	----
-11	2, Ads	27800	2160	1860	1330	1300	1497	315
-26	2, Ads	27800	1170	783	618	550	650	120

\*N.A. = Not applicable

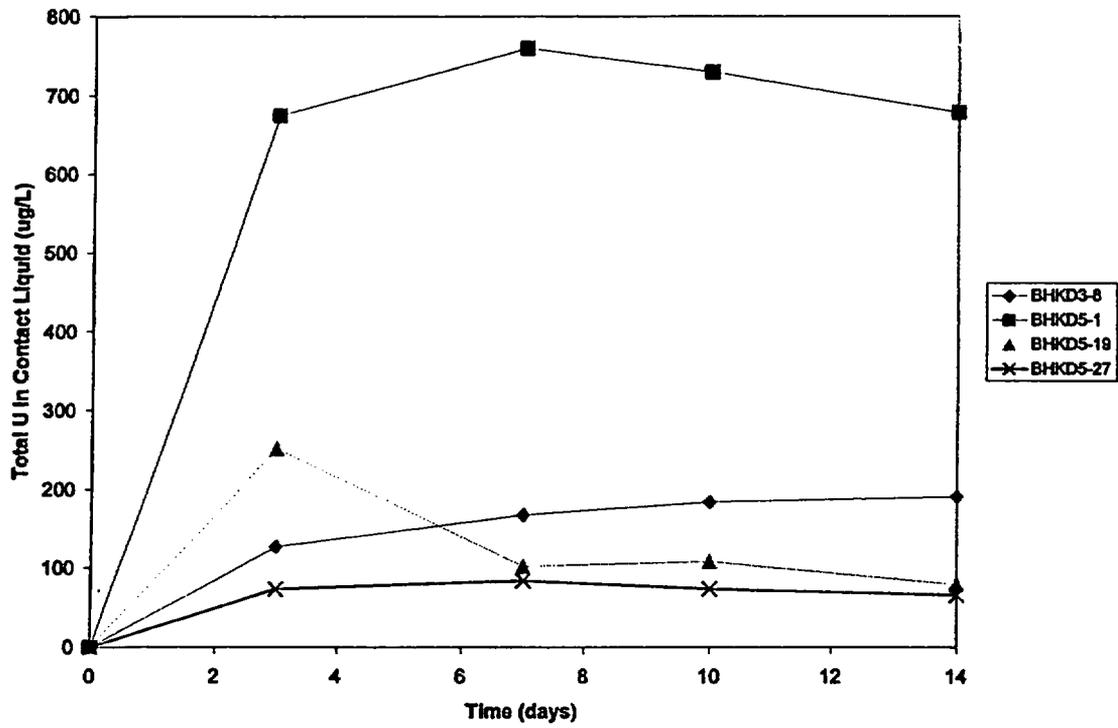
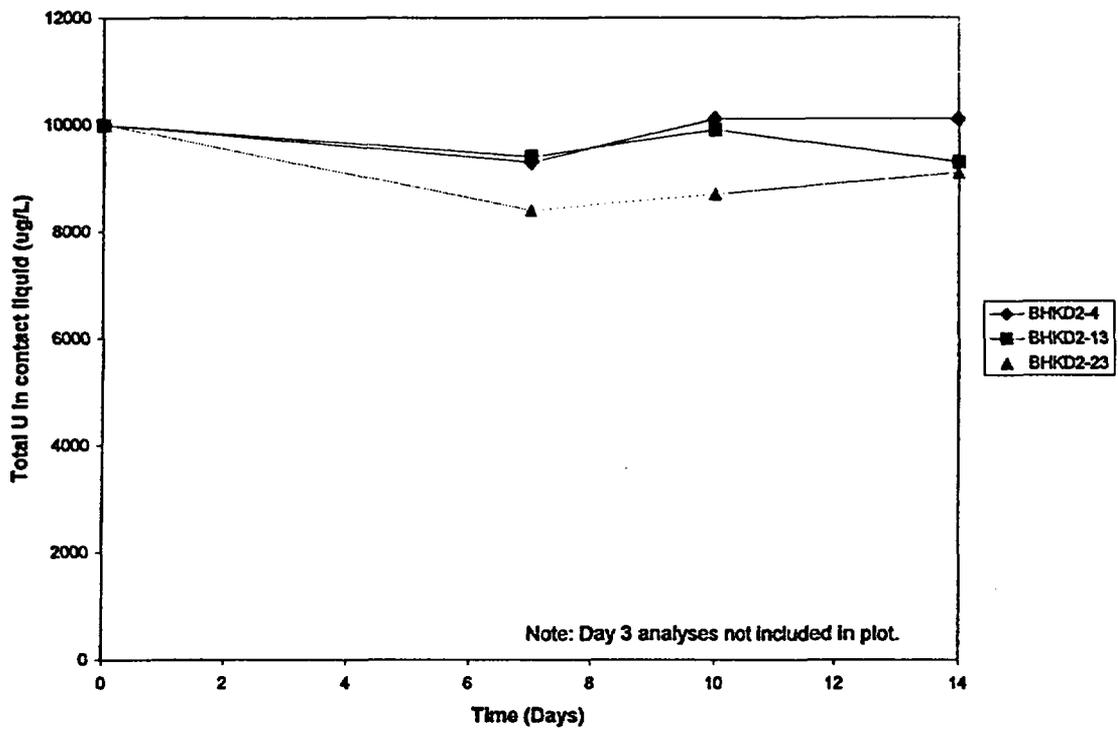
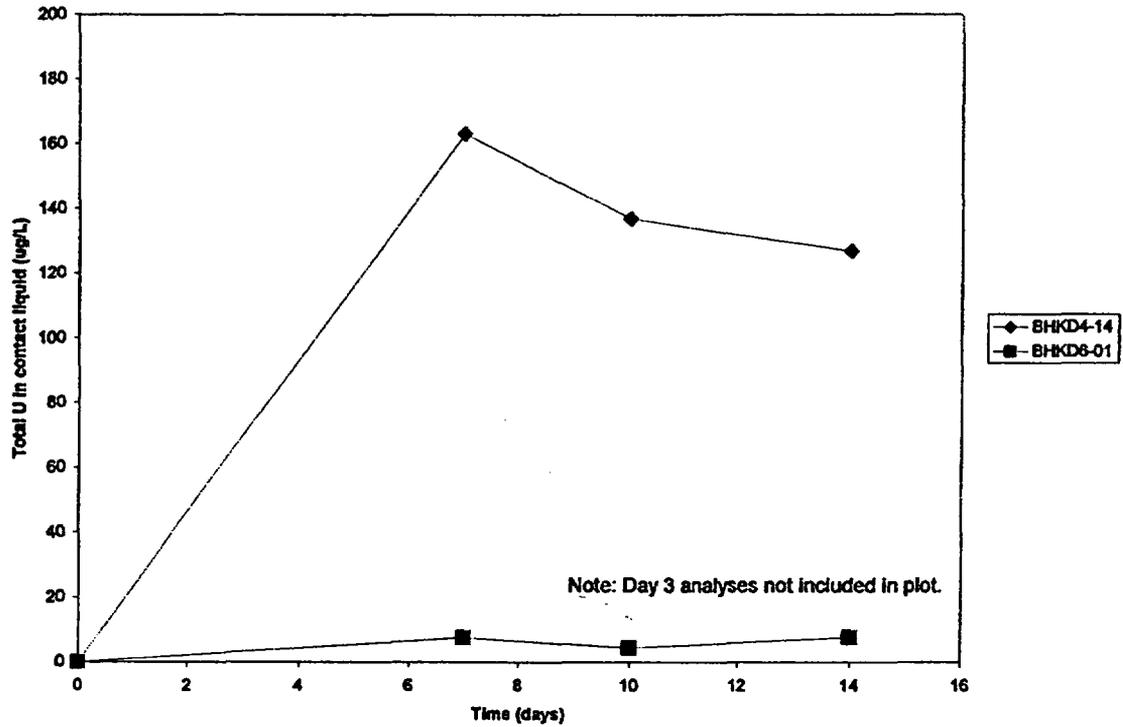


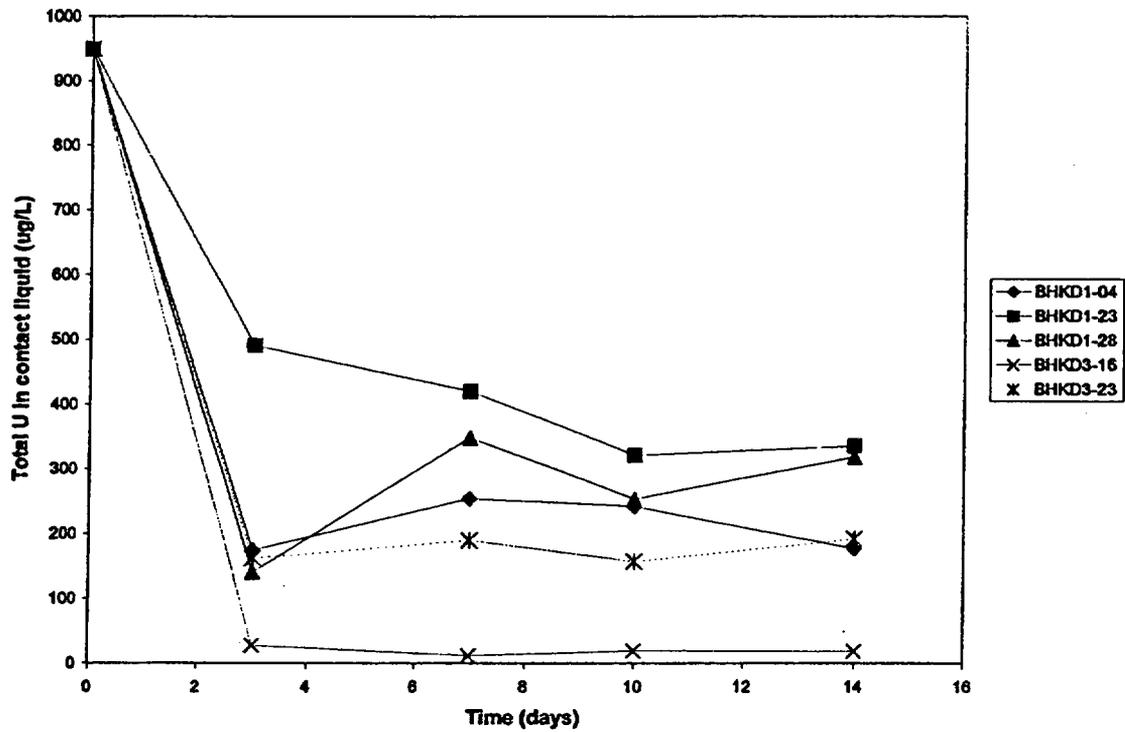
Fig. 3. Total U concentration in contact solutions vs time for Batch 1 desorption tests. Contact solutions consisted of groundwater from well OB-1 considered as a background well (U and <sup>99</sup>Tc at 2.6 µg/L and 0.2 pCi/L, respectively)



**Fig. 4. Total U concentration in contact solutions vs time for Batch 1 adsorption tests. Contact solutions consisted of groundwater from background well OB-1 spiked with standard solutions to achieve initial uranium and technetium concentrations of 10,000  $\mu\text{g/L}$  and 600 pCi/L.**



**Fig. 5. Total U concentration in contact solutions vs time for Batch 2 desorption tests. Contact solutions consisted of groundwater from well OB-1 considered as a background well (U and <sup>99</sup>Tc at 2.6 µg/L and 0.2 pCi/L, respectively).**



**Fig. 6. Total uranium concentration in contact solutions vs time for Batch 2 adsorption tests on samples from BHKD1 and BHKD3. Contact solutions consisted of groundwater from background well OB-1 spiked with standard solutions to achieve initial uranium and technetium concentrations of 950 µg/L and 27,800 pCi/L, respectively.**

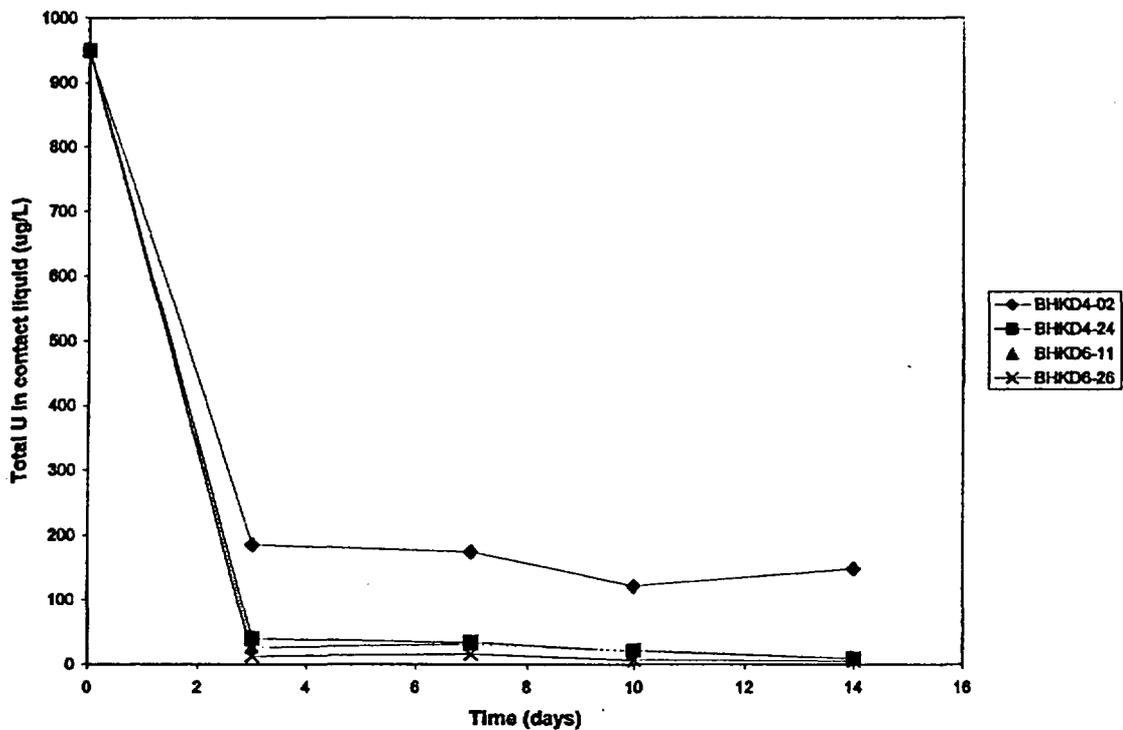
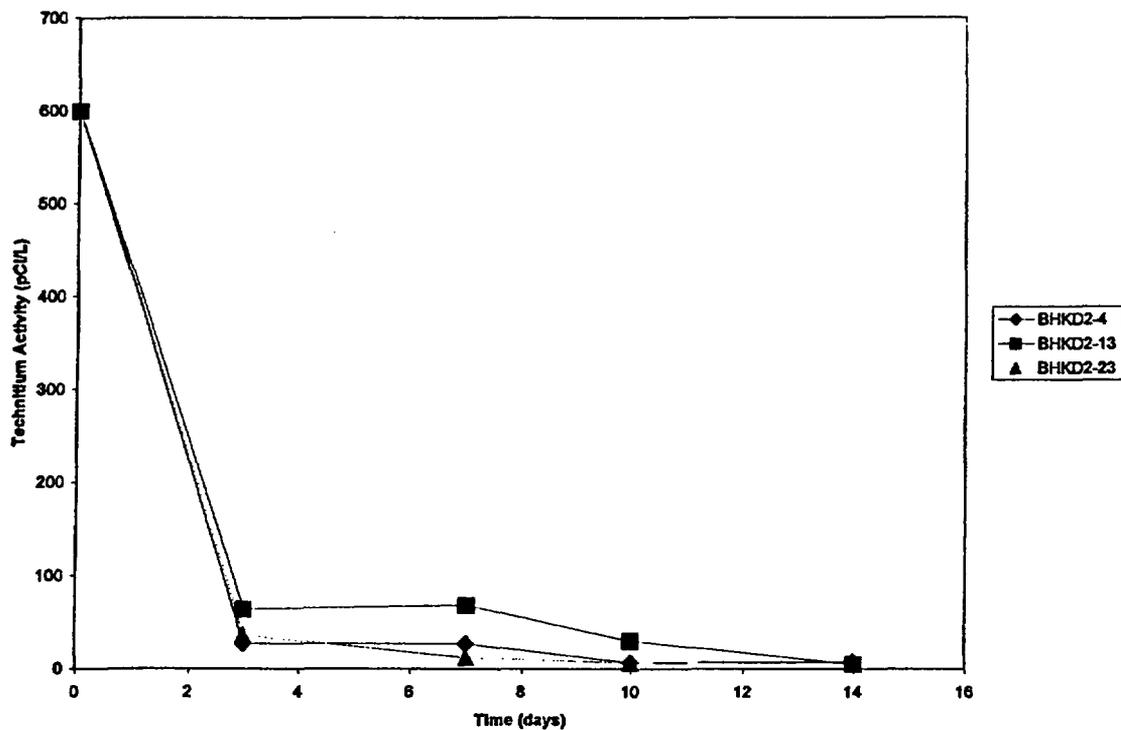
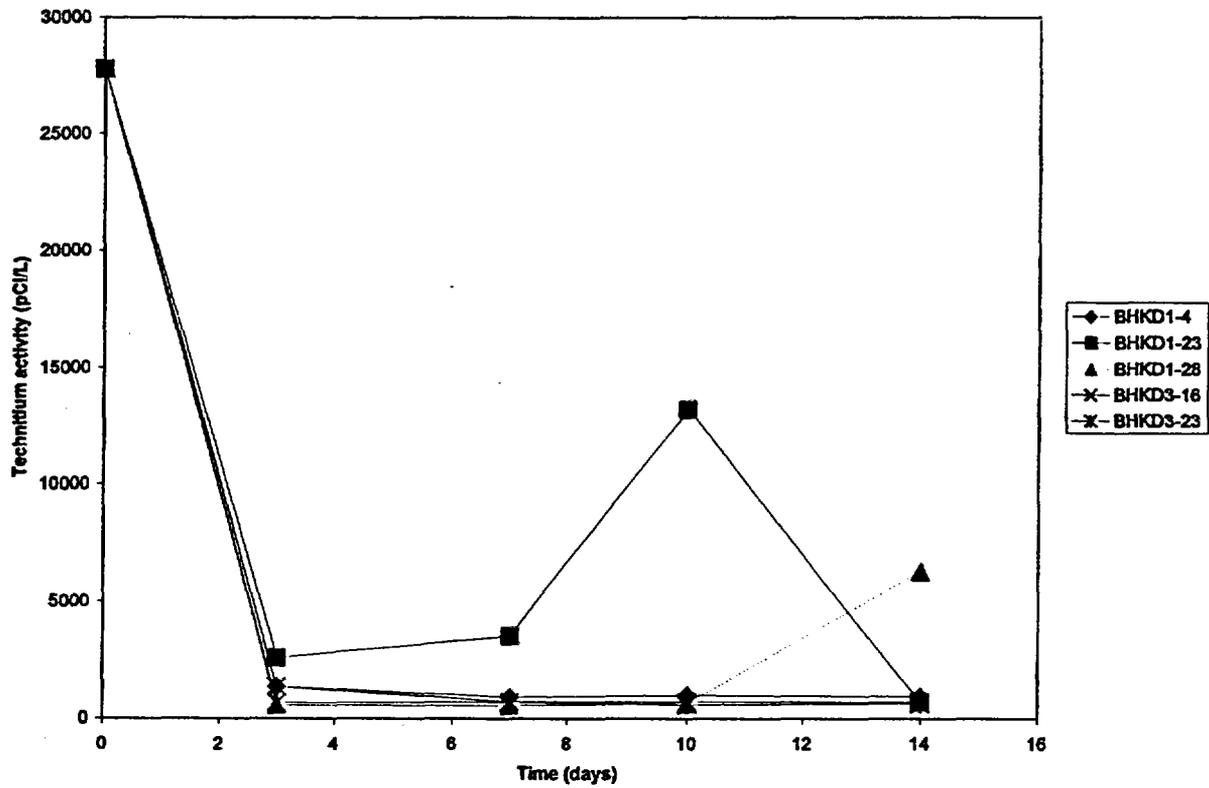


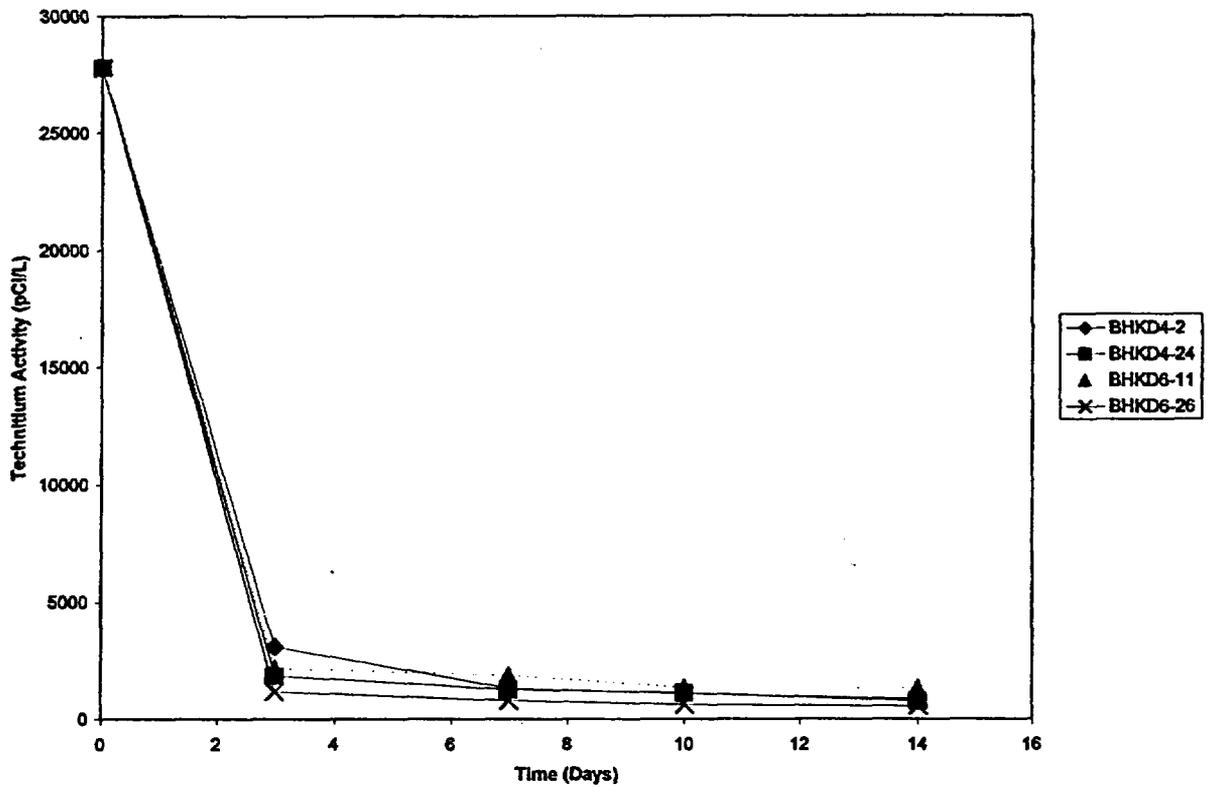
Fig. 7. Total U concentration in contact solutions vs time for Batch 2 adsorption tests on samples from BHKD4 and BHKD6. Contact solutions consisted of groundwater from background well OB-1 spiked with standard solutions to achieve initial U and Tc concentrations of 950 µg/L and 27,800 pCi/L, respectively.



**Fig. 8. Tc activities in contact solutions vs time for Batch 1 adsorption tests on samples from BHKD2. Contact solutions consisted of groundwater from background well OB-1 spiked with standard solutions to achieve initial U and Tc concentrations of 10,000  $\mu\text{g/L}$  and 600 pCi/L, respectively.**



**Fig. 9. Tc activities in contact solutions vs time for Batch 2 adsorption tests on samples from BHKD1 and BHKD3. Contact solutions consisted of groundwater from background well OB-1 spiked with standard solutions to achieve initial U and Tc concentrations of 950  $\mu\text{g/L}$  and 27,800 pCi/L, respectively.**



**Fig. 10. Tc activities in contact solutions vs time for Batch 2 adsorption tests on samples from BHKD4 and BHKD6. Contact solutions consisted of groundwater from background well OB-1 spiked with standard solutions to achieve initial U and Tc concentrations of 950  $\mu\text{g/L}$  and 27,800 pCi/L, respectively.**

A relatively high U spike level (10,000 µg/L) was selected for the Batch 1 adsorption tests, in anticipation of  $K_d$  values that can be as high as 10,000 mL/g [EPA 1999]. If the  $K_d$  factor were this high, then a high spike level would be required to adequately quantify U in the contact solutions after equilibration with the soil samples. Measured U concentrations in the contact solutions did not vary much from the spike level in the Batch 1 adsorption tests (see Table 9, BHKD2-4, 13, and 23, and Fig. 4), indicating very little to no adsorption onto the soil. On the other hand, Batch 1 desorption samples exhibited  $K_d$  factors that were greater than 100 mL/g. When the spike level was reduced to 950 µg/L U in Batch 2, adsorption was observed in all samples (see Figs. 6 and 7). It is possible that the low adsorption observed in Batch 1 was due to the high U concentration in the contact solution that led to saturation of the active sites on the solid surfaces. Table 11 shows results of U analyses on select Day 14 solid residues, as well as mass balance calculations that show good recovery in most of the samples.

**Table 11. Mass balance calculations for U in soil/water mixtures**

Sample ID	As-sampled U in soil (mg/kg)	Initial U in contact solution (ug/L)	Initial Mass of U in soil/water mixture (mg)	U in solid residue on Day 14* (mg/kg)	U in contact solution on Day 14 (ug/L)	Mass of U in soil/water mixture on Day 14 (mg)	Mass Balance**
BHKD1-4	4.60	950	0.168	7.4	177	0.162	96%
-23	3.15	950	0.139	8.2	335	0.192	138%
-28	2.21	950	0.120	5.4	318	0.134	111%
BHKD2-4	3.78	10000	0.876	N.M.	10100	----	----
-13	2.82	10000	0.856	N.M.	9300	----	----
-23	2.36	10000	0.847	N.M.	9100	----	----
BHKD3-8	36.96	0	0.739	30.2	191	0.618	84%
-16	2.89	950	0.134	7.9	18.7	0.160	120%
-23	3.17	950	0.139	7.9	192	0.174	124%
BHKD4-2	3.00	950	0.136	9.2	148	0.195	144%
-14	10.36	0	0.207	10.8	127	0.225	109%
-24	2.85	950	0.133	5.5	8.83	0.110	83%
BHKD5-1	106.31	0	2.126	116.0	679	2.375	112%
-19	45.83	0	0.917	36.8	79.2	0.742	81%
-27	21.13	0	0.423	22.1	65.6	0.447	106%
BHKD6-1	6.45	0	0.129	6.4	7.79	0.129	100%
-11	2.76	950	0.131	6.1	9.21	0.123	94%
-26	2.00	950	0.116	6.7	4.88	0.134	116%

\*These were corrected for dissolved U in the water phase of the solid residue samples. The moisture content in the solid residues (~45%) were measured and used for these corrections, together with measured U in Day 14 contact solutions.

\*\*Mass balance = Ratio between mass of U on Day 14 and initial mass of U in soil/water mixtures.

The Tc activities in the contact solutions from the Batch 1 adsorption  $K_d$  tests (Table 10, Fig. 8) were significantly lower than the initial contact solution activity of 600 pCi/L, indicating that Tc was being removed from solution in the soil/water mixtures. Published studies on  $\text{TcO}_4^-$  adsorption are fairly consistent in that all show very low  $K_d$  values (0.1 to 1 mL/g, Krupka and Serne 2002) under aerobic conditions. The negative  $\text{TcO}_4^-$  ion is not expected to adsorb on soil surfaces that are predominantly negatively charged under typical pH values found in the subsurface environment. Because 600 pCi/L is equivalent to a mass concentration of  $\sim 35$  ng/L, it was thought that the observed disappearance of Tc from solution was a “concentration effect”, and that there were enough positively charged sites on the soil surfaces to interact electrostatically with the minute amount of Tc in solution. For Batch 2, the Tc spike level was increased to 27,800 pCi/L ( $\sim 1.6$   $\mu\text{g/L}$ ).

Even at this elevated concentration, Tc was still removed from solution, dropping by an order of magnitude by Day 14 in most of the samples. The Day 14 Tc activities in the deeper samples from BHKD1 were the exception to this trend (Table 10, Fig. 9). The Tc activities in the contact solutions for BHKD1-23 were erratic, with values that fluctuated between a minimum of 724 pCi/L on Day 14, and a maximum of 13,200 pCi/L on Day 10. Tc activities in BHKD1-28 on Days 3, 7 and 10 were relatively consistent (548 to 635 pCi/L), but Tc activity was much higher on Day 14 (6,270 pCi/L). These results could be due to heterogeneity among subsamples collected from a bulk sample used to prepare the soil/water mixtures. Nevertheless, 10 out of 12 Tc adsorption tests showed significant removal of Tc from solution by Day 3, and relatively monotonic Tc activities that either leveled off or decreased gradually through Day 14 (Table 10, Figs. 8-10).

Determining the actual mechanism by which Tc was being removed from solution is beyond the scope of this study. However, published experimental studies on the behavior of Tc in geologic media can shed light on the observations in this study. The Tc added to the contact solutions was in the +7 oxidation state [Tc (VII)] in the form of  $\text{TcO}_4^-$ . The latter is known to be very soluble and not strongly adsorbed at neutral and basic pH conditions (Krupka and Serne 2002). Significant removal of Tc in this study could be due to chemical reduction of Tc (VII) to Tc(IV) which is more highly sorbed and can form relatively insoluble Tc oxides. Chemical reduction of Tc (VII) has been observed by others through biotic processes (e.g., aided by metal reducing bacteria) and abiotic reactions (e.g., interaction with reduced iron) (Krupka and Serne 2002).

It is somewhat surprising that Tc (VII) reduction occurred in the soil/water mixtures prepared for this study because the mixtures were not kept under anaerobic conditions, which is typically done in experiments where Tc (VII) reduction was observed (e.g., Sheppard, Sheppard and Evenden, 1990). However, significant recovery of Tc in the solid residues (see Table 12) from filtration of the soil/water mixtures is consistent with its removal from solution. Thus, the evidence from this study points towards  $\text{TcO}_4^-$  being removed from solution and “adhering” to the Hematite soil samples, either through adsorption or chemical reduction followed by precipitation.

**Table 12. Mass balance calculations for Tc in soil/water mixtures**

Sample ID	As-sampled <sup>99</sup> Tc in soil (pCi/g)	Initial <sup>99</sup> Tc in contact solution (pCi/L)	Total <sup>99</sup> Tc activity in soil/water mixture (pCi)	<sup>99</sup> Tc in solid residue on Day 14* (pCi/g)	<sup>99</sup> Tc in contact solution on Day 14 (pCi/L)	Total <sup>99</sup> Tc activity in soil/water mixture on Day 14 (pCi)	Mass Balance**
BHKD1-4	6.60	27800	2356	71.4	938	1503.7	64%
-23	6.23	27800	2349	86.6	724	1790.1	76%
-28	2.84	27800	2281	67.7	6270	1855.0	81%
BHKD2-4	0.00	600	48	N.M.	7.2	----	----
-13	0.00	600	48	N.M.	4.8	----	----
-23	0.00	600	48	N.M.	8.2		
BHKD3-8	0.00	0	0	N.M.	N.M.	----	----
-16	0.00	27800	2224	100.4	694	2064.2	93%
-23	0.00	27800	2224	87.3	638	1796.6	81%
BHKD4-2	2.80	27800	2280	81.5	859	1698.7	75%
-14	13.80	0	276	N.M.	-15		
-24	0.82	27800	2240	74.0	760	1540.4	69%
BHKD5-1	2.52	0	50.4	N.M.		----	----
-19	1.18	0	23.6	N.M.		----	----
-27	0.91	0	18.2	N.M.		----	----
BHKD6-1	2.55	0	51	N.M.	-6	----	----
-11	2.00	27800	2264	89.9	1300	1902.7	84%
-26	5.86	27800	2341	73.2	550	1507.0	64%

\*These were corrected for dissolved <sup>99</sup>Tc in the water phase of the solid residue samples. The moisture content in the solid residues (-48%) were measured and used for these corrections, together with measured <sup>99</sup>Tc in Day 14 contact solutions.

\*\*Mass balance = Ratio between total <sup>99</sup>Tc activity on Day 14 and initial total <sup>99</sup>Tc activity in soil/water mixtures.

## 4.2 CALCULATED DISTRIBUTION COEFFICIENTS

Distribution coefficients ( $K_d$ ) were calculated from the ratio between the U or Tc adsorbed onto the soil ( $S$ ) and the average of Day 7, 10, and 14 U or Tc concentration in the contact solutions ( $C_w$ , Table 9 and 10 for U and Tc, respectively). For the desorption tests, the adsorbed U or Tc concentration was calculated via mass balance as follows:

$$S = \frac{S_i M - C_w V}{M}, \quad [1]$$

where  $S_i$  is the field-sampled U or Tc concentration in the soil samples (Table 7),  $V$  is the volume of contact solution (0.08 L) and  $M$  is the mass of soil (0.02 kg) used in the  $K_d$  tests. Because the U or Tc soil concentrations ( $S$ ) were measured following hot acid digestion of the soil samples, it is possible that a fraction of the field-sampled U or Tc in the soil is in precipitated form or occluded in the soil's mineral structure and not *reversibly* sorbed onto the soil. Thus, using the total (acid-digested) U and Tc soil concentration in calculations for the desorption tests can result in overestimated  $K_d$  factors. Researchers have used methods for selective extraction of defined U fractions (e.g., Kaplan and Serkiz, 2000, Senko et al, 2002, Sowder et al. 2003), however use of these methods was beyond the scope of this project. The initial contaminant concentrations to be used in RESRAD modeling will also consist of analyses results from acid-digested samples. Thus, calculating  $K_{ds}$  from the desorption test results assuming that the acid-digested U or Tc represents the "leachable" fraction in contaminated soil is a reasonable approach.

For the adsorption tests, the U or Tc concentrations sorbed onto the soil ( $S$ ) was calculated as follows:

$$S = \frac{(C_{wi} - C_w)V}{M},$$

where  $C_{wi}$  is the initial U or Tc concentration in the spiked contact solution. Neglecting the contribution of the initial U or Tc in the soil samples to the final concentration in the contact solution is a conservative approach, resulting in a lower estimate for  $S$  and lower calculated  $K_d$ .

### 4.2.1 Uranium

The average U  $K_d$  factors from the adsorption and desorption tests are 117.8 and 232.7 mL/g, respectively (Table 13). These averages were calculated without  $K_d$  values from BHKD2 and BHKD6-1. As mentioned previously (Section 4.1), it is suspected that results from BHKD2 were compromised by the high U concentration in the Batch 1 contact solution (10,000  $\mu\text{g/L}$ ). The  $K_d$  value from BHKD6-1 is more than twice the next lower value and was not considered when calculating the average  $K_d$  (a conservative approach). Significant variability in the measured  $K_{ds}$  is reflected by standard deviations that are comparable to the average values (see Table 13). The degree of variability is not entirely surprising, and has been observed by others [EPA 1999, Krupka and Serne 2002]. Higher average  $K_d$  values in the desorption tests can be due to the sorbed U concentration in the soil-water mixtures being estimated from the U extracted from the soil samples via acid digestion. This digestion procedure extracts not only U that is adsorbed on to the soil (e.g., through electrostatic interactions with soil surfaces), but also likely

dissolves some U that is in precipitated form or occluded in the soil minerals. The latter should not, in theory, be included in the initial soil concentration ( $S_i$ ) when estimating sorbed concentration,  $S$  (see Eqn. [1]). Higher  $K_d$  values in the desorption tests can also be due to an "aging effect" in field-contaminated samples, as described by Kaplan et al. [2001] who also measured  $K_d$  factors via desorption that were higher than  $K_d$  values based on adsorption measurements. Desorption from field-contaminated samples more closely simulates the leaching of radionuclides from contaminated soils, the process that is being modeled by RESRAD in DCGL calculations.

The lower average  $K_d$  in the adsorption tests can also be from soil samples with low potential for adsorption being fortuitously selected for adsorption testing. For example, all three samples from BHKD1 were subjected to adsorption testing and exhibited low  $K_d$  values. In a histogram of adsorption  $K_d$ s (excluding data from BHKD2 suspected to have been compromised by high U spike in Batch 1 contact solution), 3 out of 5 data points in the 0-100 mL/g range were results from one borehole (BHKD1, Fig. 11). There were no other consistent trends with borehole location or depth in the  $K_d$  measurements (see Fig. 12).

The "best" estimate for uranium  $K_d$  applicable to the Hematite Site is 175 mL/g, which is the mean of the averages from the adsorption and desorption test samples (excluding data from BHKD2 and BHKD6-1, discussed earlier in this subsection). This approach for estimating the "best"  $K_d$  was chosen over averaging the entire data set (158.8 mL/g), which unduly weights the adsorption  $K_d$  values (9 data points) over the desorption  $K_d$  values (5 data point). The approach used to arrive at the "best" estimate for Uranium  $K_d$  balances the more conservative estimation of  $K_d$  in the adsorption tests (i.e., by neglecting the contribution of the field-sampled U in the soil), with the less conservative approach (i.e., by using U in acid-digested soil samples) in calculating  $K_d$  factors from the desorption tests.

Histograms of measured  $K_d$  values for U (Fig. 11) from both adsorption and desorption tests (excluding data from BHKD2 and BHKD6-1, justification discussed earlier in this subsection) shows a more skewed distribution for the adsorption tests when compared to the desorption tests. If RESRAD modeling will include uncertainty analysis, it is recommended that parameters for characterizing the statistical distribution of  $K_d$  be obtained from a data set that consists of (1) the adsorption test results from this study excluding the 3 data from BHKD2, and the two highest and the two lowest  $K_d$  values, and (2) the desorption test results excluding  $K_d$  from BHKD6-1. This trimmed data set, which consists of an equal number of adsorption and desorption data points, grossly approximates a lognormal distribution (Fig. 11). Because there were no distinct depth trends in the  $K_d$  measurements (Fig. 12), spatial variability is best addressed by assuming that the unconsolidated sediments overlying bedrock at the Hematite Site can be characterized by a single  $K_d$  parameter that has a lognormal distribution.

The range and "best" estimate for U  $K_d$  from this study are compared with published literature values in Table 14. The latter include (1) a compilation by Sheppard and Thibbault (1990), where the  $K_d$  values are categorized according to soil texture, (2) a compilation by EPA (1999), where a look-up table, based on a large number of published experimental results, is formulated with pH as the independent variable, and (3) measurements by Kaplan and Serkiz (2001) following a desorption procedure using field-contaminated soil from the Department of Energy's Savannah River Site. The ranges for loam (>80% silt-sized and smaller fractions) and clay (>35% clay-sized fractions) from Sheppard and Thibbault (1990) are given in Table 14, because these textures best describe the soil collected from the Hematite Site for this study.  $K_d$  ranges for pH 6, 7 and 8 from EPA (1999) are shown in Table 14, also based on the characteristics of soil and groundwater from the Hematite Site (see Section 3). The Interagency

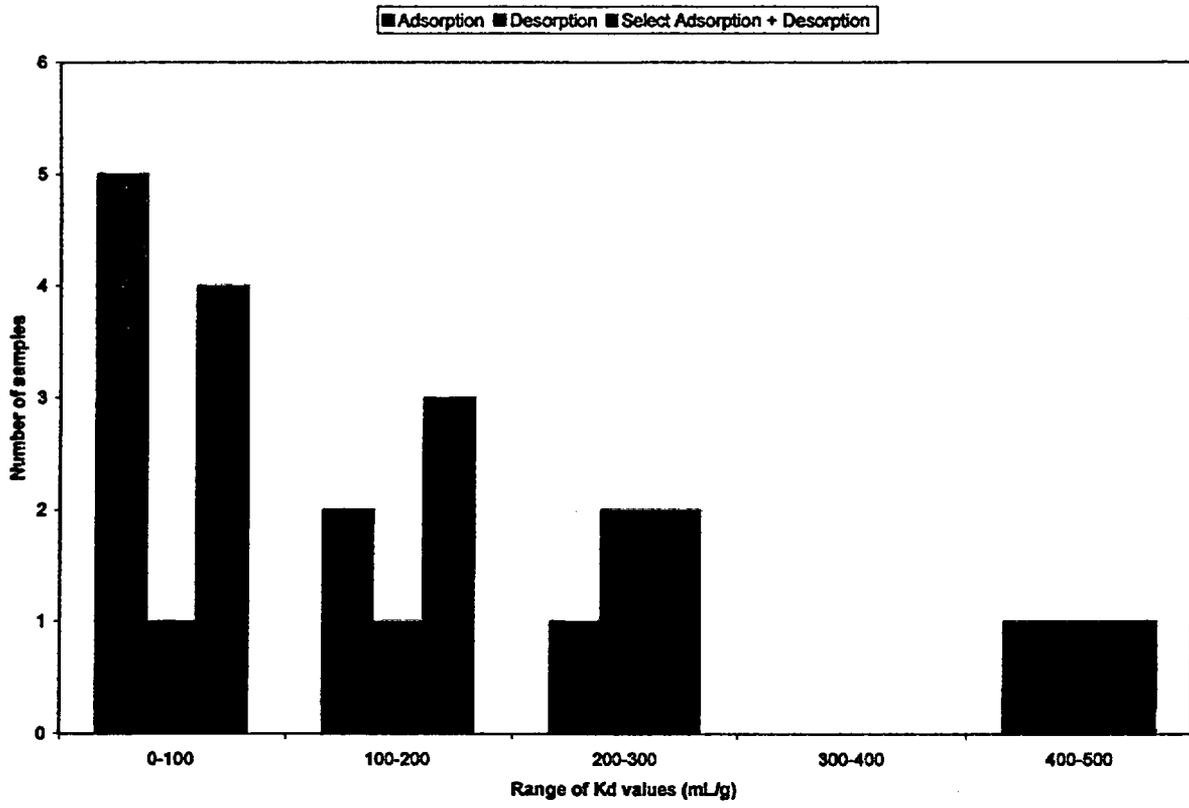
Steering Committee on Radiation Standards (ISCORS) recently performed a RESRAD dose modeling effort for radionuclides in sewage sludge used for agricultural and land reclamation. The baseline  $K_d$  value for U in the ISCORS model in this modeling study is also shown in Table 14. Note that the  $K_d$  range from this study is near the lower end of the published range of  $K_d$  values in Table 14. Thus, the  $K_d$  values in this study, including the best estimate for Uranium  $K_d$  for RESRAD modeling, appear to be reasonable and conservative.

**Table 13. Calculated distribution coefficients for U based on average U concentration in contact solutions on Days 7, 10, and 14**

Sample ID	Location	Adsorption Test $K_d$ (mL/g)	Desorption Test $K_d$ (mL/g)	Remarks
BHKD1-4	Duel's Mountain	12.9	-----	Initial U at 950 $\mu\text{g/L}$
-23		6.6	-----	Initial U at 950 $\mu\text{g/L}$
-28		8.4	-----	Initial U at 950 $\mu\text{g/L}$
BHKD2-4	Burial Pits	0.1*	-----	Initial U at 10,000 $\mu\text{g/L}$
-13		0.2*	-----	Initial U at 10,000 $\mu\text{g/L}$
-23		0.6*	-----	Initial U at 10,000 $\mu\text{g/L}$
BHKD3-8	Tile Barn/ Cistern Burn Pit	-----	200.2	Unspiked
-16		224.0	-----	Initial U at 950 $\mu\text{g/L}$
-23		17.2	-----	Initial U at 950 $\mu\text{g/L}$
BHKD4-2	Restricted Area #1	21.7	-----	Initial U at 950 $\mu\text{g/L}$
-14		-----	68.8	Unspiked
-24		174.9	-----	Initial U at 950 $\mu\text{g/L}$
BHKD5-1	Restricted Area #2	-----	143.0	Unspiked
-19		-----	471.4	Unspiked
-27		-----	280.1	Unspiked
BHKD6-1	Evaporation Ponds	-----	963.8**	Unspiked
-11		181.9	-----	Initial U at 950 $\mu\text{g/L}$
-26		412.2	-----	Initial U at 950 $\mu\text{g/L}$
Average		117.8	232.7	Excludes BHKD2 and BHKD6-1
Std. dev.		141.4	154.2	Excludes BHKD2 and BHKD6-1
Mean of adsorption and desorption averages		175		Excludes BHKD2 and BHKD6-1

\*Very low adsorption in these tests suspected to have been due to high initial U in contact solution, resulting in saturation of adsorption sites on soil surfaces.

\*\*This value is very high compared to other values.



**Fig. 11. Histograms of measured distribution coefficients ( $K_d$ ) for U. “Adsorption” and “desorption” data sets exclude data from BHKD2 and BHKD6-1. “Select Adsorption + Desorption” data set consists of adsorption results excluding data from BHKD2, two highest and two lowest values, and desorption results excluding data from BHKD6-1.**

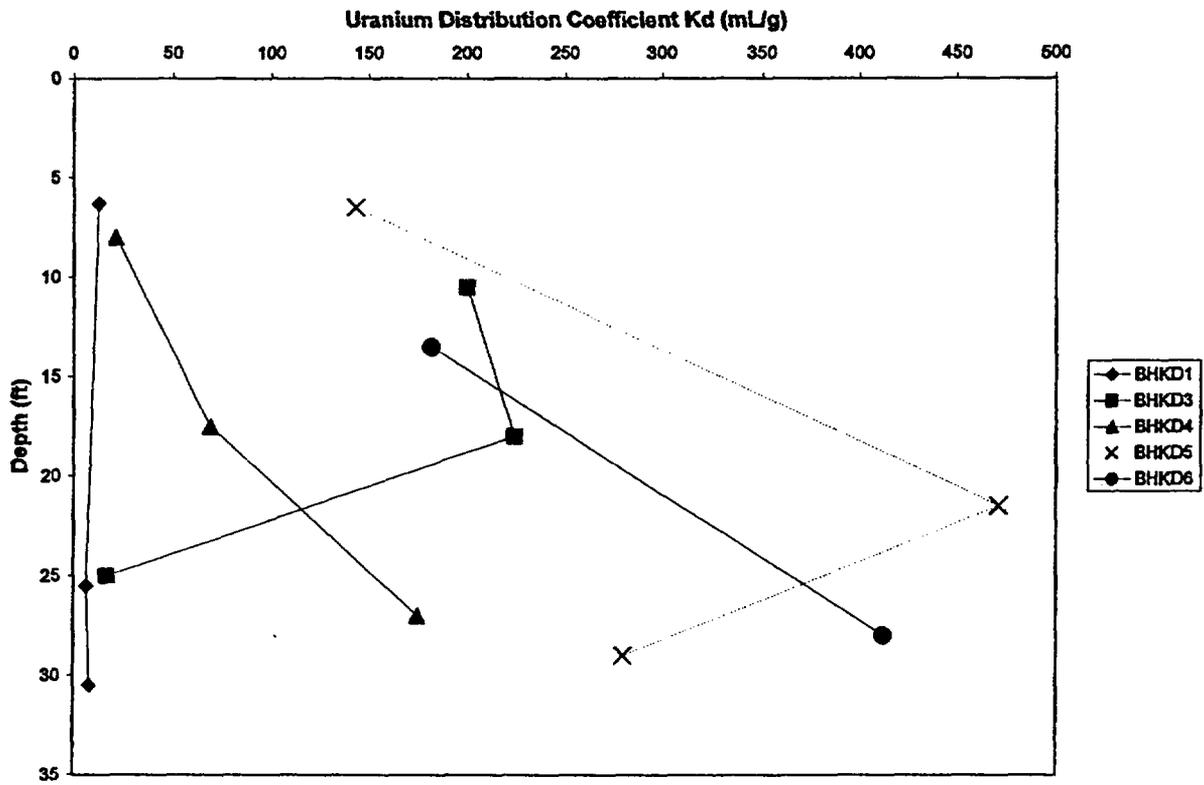


Fig. 12. Distribution coefficients ( $K_d$ ) for uranium measured in Hematite Site soil samples plotted vs sample depth. Note that both adsorption and desorption test results are shown in the graph, and results from BHKD2 and BHKD6-1 are not plotted.

**Table 14. Comparison of measured distribution coefficients for U in this study with published values**

Source	Soil Type or Characteristic	Minimum $K_d$ (mL/g)	Maximum $K_d$ (mL/g)	"Best" Estimate for $K_d$ (mL/g)
This Study*	>96% silt-sized and smaller particles pH 5.8-8.3	6.6	471.4	175
RESRAD default	-----	-----	-----	50
Sheppard and Thibault ., 1990	Loam	0.2	4,500	15**
Sheppard and Thibault., 1990	Clay	46	395,100	1600**
EPA 1999	pH 6	100	1,000,000	-----
EPA 1999	pH 7	63	6,300,000	-----
EPA 1999	pH 8	0.4	250,000	-----
Kaplan et al, 2001	pH 4-5.8 (desorption tests) 20%-40% silt-sized and smaller particles	170	6493	-----
ISCORS***, 2003	-----	-----	-----	126

\*Data set excludes data from BHKD2 and BHKD6-1 (see Section 4.2.1 for justification). "Best" estimate for  $K_d$  is the mean of the average  $K_d$ s from the adsorption and desorption tests.

\*\*Geometric mean; data observed to be log normally distributed.

\*\*\*Interagency Steering Committee on Radiation Standards

#### 4.2.2 Technetium

The  $K_d$  values measured for Tc ranged from 15.1 to 172.9 mL/g and one data point at 263.7 mL/g (Table 15). The values appear to be relatively uniformly distributed between 0 and 200 mL/g, as shown by the histogram in Fig. 13. The lowest  $K_d$  values were obtained from BHKD1-23 and BHKD1-28, which were the samples that exhibited fluctuating concentrations in the contact solutions (Fig. 9). As a result, the Tc contact solution activity averaged over Day 7, 10, and 14 (used to calculate  $K_d$ ) had a large standard deviation reflecting significant uncertainty in the  $K_d$  obtained from these time-averaged Tc activities. Exclusion of these data points was considered, but was eventually ruled out because the  $K_d$ s from these samples were on the low end and inclusion of these data points would constitute a conservative approach. Aside from BHKD1 samples exhibiting the lowest  $K_d$  values, no other trends were observed with borehole location or depth (Fig. 14).

Based on the measured  $K_d$  values (excluding data from the BHKD2-23), the best estimate for Tc  $K_d$  applicable to the Hematite site is 106 mL/g. Although this is significantly higher than published literature values measured under aerobic conditions, this value is considered to be valid based on the general consistency of the results (i.e., out of 9 samples, 7 exhibited significant and consistent removal of Tc from solution over 4 time intervals spanning 14 days, see Figs. 8-10) as well as recovery of Tc in the solid residues (Table 12).

Determining the mechanism for the removal of  $\text{TcO}_4^-$  from solution is beyond the scope of this study, but a mechanism can be hypothesized based on published literature. Because  $\text{TcO}_4^-$  is known to be highly soluble due to its negative charge and the negative character of soil surfaces at neutral pH, removal of Tc from contact solutions and its association with the soil is unlikely to be an electrostatic process, but is more likely from a reduction reaction where Tc(VII) is reduced to less soluble Tc(IV) either through abiotic reactions with reduced chemical species (e.g.,  $\text{Fe}^{2+}$ ) or microbial processes. The rapid removal of Tc (within 3 days) is more indicative of abiotic reactions, rather than biological processes particularly for metal-reducing bacteria that are active mainly under anaerobic conditions. It is also possible that Tc removal from solution observed in this study is due to the very low concentration of Tc used in these studies (maximum of 1,600 ng/L in the contact solution equivalent to a soil concentration 0.0064 mg/kg for 20 g: 80 mL soil:water mixtures). Gu and Dowlen (1996) conducted their experiments under similar Tc soil concentrations, while Sheppard et al. (1990b) applied Tc to their study soils at an effective soil concentration of 3.9 mg/kg. Note that historical Tc levels in groundwater at the Hematite site are significantly lower than the lowest contact solution spike level in this study (600 pCi/L).

If uncertainty analysis will be performed during RESRAD modeling, it is recommended that statistical parameters be obtained from the range of values shown in Table 15, excluding the high value from BHKD2-23. The histogram in Fig. 13 grossly approximates a uniform distribution between 0 and 200 mL/g. Because there were no distinct trends with depth in the  $K_d$  measurements (Fig. 14), spatial variability is best addressed by assuming that the unconsolidated sediments overlying bedrock at the Hematite Site can be characterized by a single  $K_d$  parameter that has a uniform distribution.

**Table 15. Calculated distribution coefficients for Technetium based on average Tc concentration in contact solutions on Days 7, 10, and 14**

Sample ID	Location	$K_d$ (mL/g)	Remarks
BHKD1-4	Duel's Mountain	113.3	Initial $^{99}\text{Tc}$ at 27,800 pCi/L
-23		15.1	Initial $^{99}\text{Tc}$ at 27,800 pCi/L
-28		40.8	Initial $^{99}\text{Tc}$ at 27,800 pCi/L
BHKD2-4	Burial Pits	172.9	Initial $^{99}\text{Tc}$ at 600 pCi/L
-13		66.2	Initial $^{99}\text{Tc}$ at 600 pCi/L
-23		263.7	Initial $^{99}\text{Tc}$ at 600 pCi/L
BHKD3-8	Tile Barn/ Cistern Burn Pit	N.M.	Used for U desorption testing
-16		153.2	Initial $^{99}\text{Tc}$ at 27,800 pCi/L
-23		169.8	Initial $^{99}\text{Tc}$ at 27,800 pCi/L
BHKD4-2	Restricted Area #1	99.0	Initial $^{99}\text{Tc}$ at 27,800 pCi/L
-14		N.M.	Used for U desorption testing
-24		102.9	Initial $^{99}\text{Tc}$ at 27,800 pCi/L
BHKD5-1	Restricted Area #2	N.M.	Used for U desorption testing
-19		N.M.	Used for U desorption testing
-27		N.M.	Used for U desorption testing
BHKD6-1	Evaporation Ponds	N.M.	Used for U desorption testing
-11		70.3	Initial $^{99}\text{Tc}$ at 27,800 pCi/L
-26		167.0	Initial $^{99}\text{Tc}$ at 27,800 pCi/L
Average		106	Excludes BHKD2-23 (high compared to other data)
Std. Dev.		54.7	Excludes BHKD2-23 (high compared to other data)

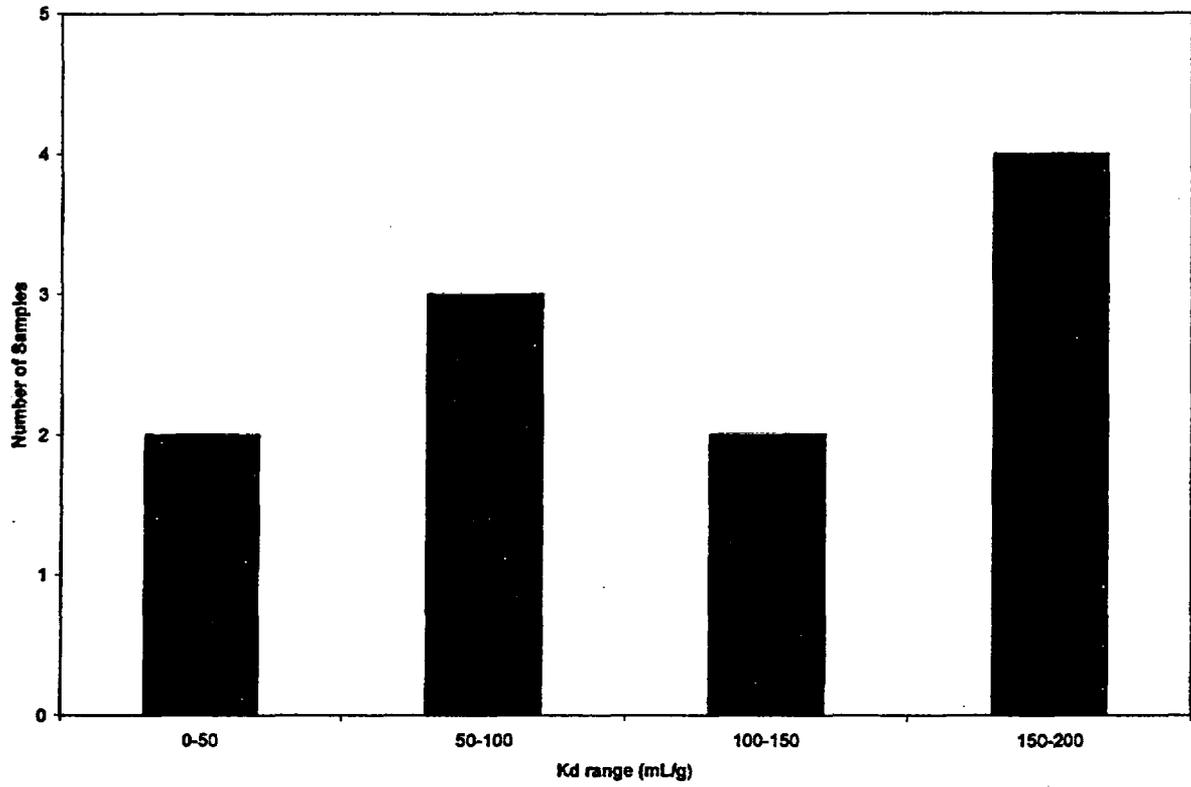
\*N.M. = Not measured

**Table 16. Comparison of measured distribution coefficients for technetium in this study with published values**

Source	Soil Type or Characteristic	Minimum $K_d$ (mL/g)	Maximum $K_d$ (mL/g)	"Best" Estimate for $K_d$ (mL/g)
This Study*	>96% silt-sized and smaller particles pH 5.8-8.3	15.1	172.9	106
RESRAD default	-----	-----	-----	0
Sheppard and Thibault, 1990	Loam	0.01	0.4	0.1*
Sheppard and Thibault, 1990	Clay	1.16	1.32	1*
Sheppard, Sheppard and Evenden, 1990	Clay-Loam, aerobic	-----	-----	-0.2**
Sheppard, Sheppard and Evenden, 1990	Clay-Loam, anaerobic	-----	-----	50
Gu and Dowlen 1996	Silty and sandy clay, aerobic	-----	-----	No sorption; $K_d$ s not reported
Gu and Dowlen 1996	Silty and sandy clay, anaerobic	20	100	-----

\*Geometric mean, based on assumed log-normal distribution for  $K_d$

\*\*Negative values have been reported elsewhere and attributed to ion exclusion



**Fig. 13. Histogram of Technetium  $K_d$  values, excluding high value from BHKD2-23. All  $K_d$  values obtained via adsorption testing.**

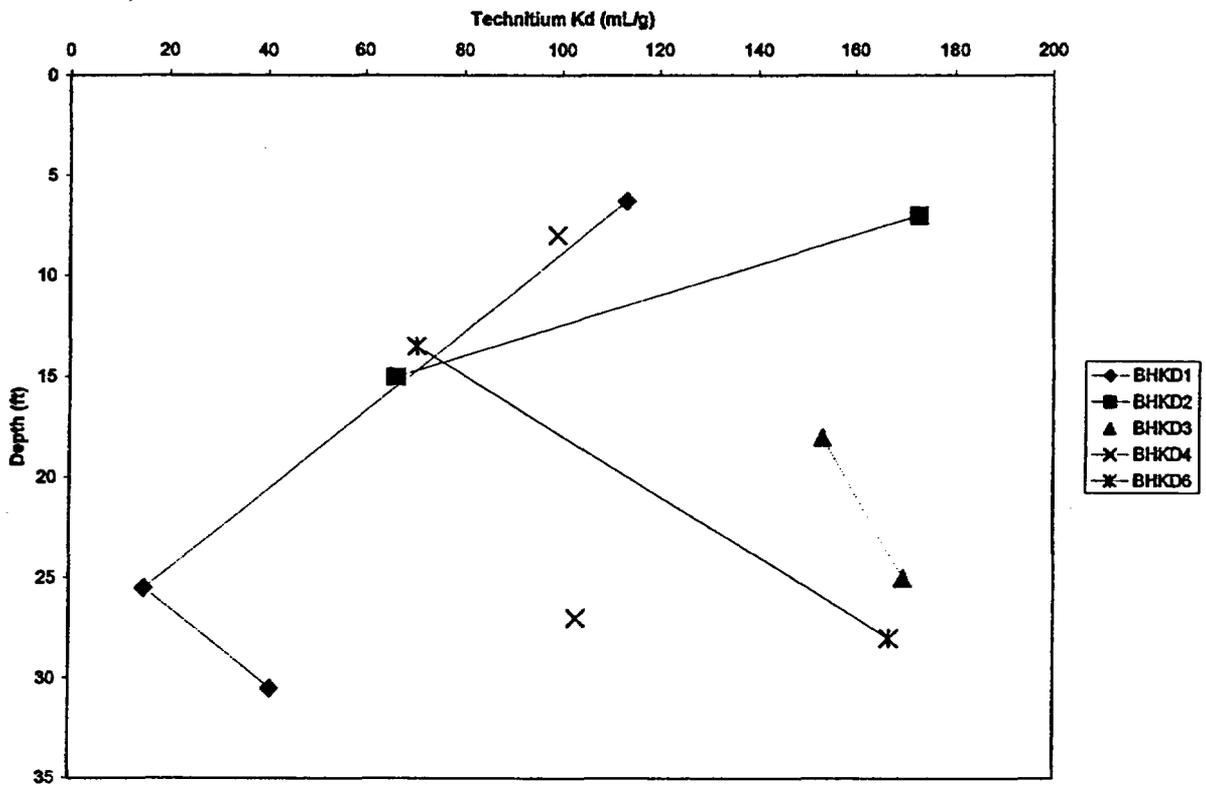


Fig. 14. Distribution coefficients ( $K_d$ ) for technetium measured in Hematite Site soil samples plotted vs sample depth. High value from BHKD2-23 not plotted.

## 5. LITERATURE $K_d$ VALUES FOR OTHER RADIONUCLIDES

The published compilation of distribution coefficients by Sheppard and Thibault (1990) was primarily used to select appropriate  $K_d$  values for Pu, Th, Np, and Am based on soil characteristics of the samples collected from the Hematite Site (Section 3). Sheppard and Thibault (1990) categorized the data by the texture of the soils used in the measurements. These categories were "sand" (containing > 70% sand-sized particles), clay (containing >35% clay-sized particles), "loam" (containing an even distribution of sand- clay- and silt-sized particles or consisted of up to 80% silt-sized particles), and "organic soils" (contained >30% organic matter). This categorization is consistent with the positive correlation between soil texture and specific surface area, and adsorption being a chemical interaction between a chemical species and chemically active surfaces on soil particles. For each category, Sheppard and Thibault (1990) provide the number of data points, geometric mean, minimum and maximum  $K_d$  measurements included in the data compilation. Given the particle size distribution measurements (Section 3.1), the samples from this study can be classified under the "clay" category. However, since the clay-sized fraction in the Hematite samples (~30%) is near the boundary for clay soils selected by Sheppard and Thibault (1990),  $K_d$  values for "loam" were also considered as shown below. Note that the "loam"  $K_d$  values are typically lower, and that inclusion of Sheppard and Thibault's "loam" data in selecting  $K_d$  values for the Hematite Site is a conservative approach.

EPA's compilation of  $K_d$  measurements (EPA 1999) was also considered when selecting  $K_d$  values for Pu and Th. Np and Am were not included in the EPA (1999) compilation but are covered in a forthcoming report (EPA 2003 unpublished).

### 5.1 PLUTONIUM

Table 17 shows summary statistics for Pu  $K_d$  values for loam and clay from Sheppard and Thibault (1990), and the range of values in EPA (1999) where a look-up table (with clay content and soluble carbonate as independent variables) is formulated based on one study that included 17 soil samples from 9 different locations within the Department of Energy complex. Given these published values, the RESRAD default value appears reasonable for application at the Hematite Site. This value is between Sheppard and Thibault's (1990) geometric means for loam and clay, and is within the range of  $K_d$ s for soils with 31 to 50% clay in EPA's look-up table. The baseline  $K_d$  value for Pu used in the ISCORS dose modeling effort for sewage sludge is also shown in Table 17.

**Table 17. Published  $K_d$  values for plutonium**

Source	Soil Type or Characteristic	Minimum $K_d$ (mL/g)	Maximum $K_d$ (mL/g)	"Best" Estimate for $K_d$ (mL/g)
Sheppard and Thibault (1990)	Loam (21 data points)	100	5933	1200*
Sheppard and Thibault (1990)	Clay (18 data points)	316	190000	5100*
EPA 1999	Soluble carbonate 0.1 – 6 meq/L; clay (31-50%)	380	2700	----
ISCORS 2003	-----	-----	-----	953
RESRAD default	-----	----	----	2000

\*Geometric mean, based on assumed lognormal distribution

## 5.2 THORIUM

Table 18 shows summary statistics for Thorium (Th)  $K_d$  values in clay from Sheppard and Thibault (1990), and the range of values in EPA (1999) where a look-up table (with pH as the independent variable) was formulated based on several published studies. The RESRAD default value of 60000 mL/g is recommended for application at Hematite. Although it is an order of magnitude higher than the geometric mean for clay in Sheppard and Thibault (1990), it is well within the range in EPA's look-up table, which is based on several studies and many more data points when compared to 5 data points used by Sheppard and Thibault for calculating their geometric mean. The baseline  $K_d$  value for Th used in the ISCORS dose modeling effort for sewage sludge is also shown in Table 18.

**Table 18. Published  $K_d$  values for thorium**

Source	Soil Type or Characteristic	Minimum $K_d$ (mL/g)	Maximum $K_d$ (mL/g)	"Best" Estimate for $K_d$ (mL/g)
Sheppard and Thibault (1990)	Loam (no data)	---	---	---
Sheppard and Thibault (1990)	Clay (5 data points)	244	160000	5800*
EPA 1999	pH 5-8	1700	170000	----
ISCORS 2003	-----	-----	-----	5884
RESRAD default	-----	----	----	60000

\*Geometric mean, based on an assumed lognormal distribution

### 5.3 NEPTUNIUM

Table 19 shows summary statistics for neptunium (Np)  $K_d$  values in loam and clay from Sheppard and Thibault (1990), as well as results from a number of studies found in the literature. The baseline  $K_d$  value for Np used in the ISCORS dose modeling effort for sewage sludge is also shown in Table 19. Note that the "default"  $K_d$  value in RESRAD is -1, which is a flag that invokes calculation of the default value using a correlation with the plant root uptake transfer factor [Yu et al., 2001]. In current version of RESRAD (v.6), the correlation for a loamy soil is used and results in a calculated  $K_d$  for Neptunium of 257. For the Hematite Site, a value of 2 mL/g is recommended which is near the low end of  $K_d$ s shown in Table 19. If the calculated DCGL based on this conservative  $K_d$  is significantly smaller than in situ Np levels and will require significant clean-up efforts, site-specific laboratory measurements may be warranted.

**Table 19. Published  $K_d$  values for neptunium**

Source	Soil Type or Characteristic	Minimum $K_d$ (mL/g)	Maximum $K_d$ (mL/g)	"Best" Estimate for $K_d$ (mL/g)
Sheppard and Thibault (1990)	Loam (11 data points)	1.3	79	25*
Sheppard and Thibault (1990)	Clay (4 data points)	79	2575	55*
EPA 1999	Not included in compendium	----	----	----
Kaplan et al., 1996	Silty loam and coarse sand, pH 8.3	2.17	19.86	---
Kaplan et al., 1995	Loamy sand and silt loam	2.4	21.7	
Turner et al., 1998	Montmorillonite clay, maximum at pH 8-8.5 in presence of atmospheric CO <sub>2</sub>	----	100 mL/g	--
ISCORS 2003	----	----	----	17
RESRAD default	----	----	---	-1**

\*Geometric mean, based on an assumed log-normal distribution

\*\*This is a flag that invokes the calculation of a default  $K_d$  value using correlations with plant/soil concentration ratios. This results in a default  $K_d$  of 257 mL/g in the current version of RESRAD (v.6).

### 5.4 AMERICIUM

Table 20 shows summary statistics for americium (Am)  $K_d$  values in loam and clay from Sheppard and Thibault (1990), as well as results from a study referenced by Cantrell et al. (2000) where  $K_d$  values were measured in sandy material from the Department of Energy's Hanford Site. The baseline  $K_d$  value for Np used in the ISCORS dose modeling effort for sewage sludge is also shown in Table 20. The default RESRAD  $K_d$  value is very low (20 mL/g), and is outside the range of  $K_d$ s for loam and clay reported by Sheppard and Thibault (1990). For the Hematite site, it is recommended that 1000 mL/g be used. This value is more consistent with the published values referenced in Table 20, but is still conservative given that it is much lower than the geometric means for loam and clay in Sheppard and Thibault (1990).

**Table 20. Published  $K_d$  values for Americium**

Source	Soil Type or Characteristic	Minimum $K_d$ (mL/g)	Maximum $K_d$ (mL/g)	"Best" Estimate for $K_d$ (mL/g)
Sheppard and Thibault (1990)	Loam (20 data points)	400	48309	9600*
Sheppard and Thibault (1990)	Clay (11 data points)	25	40000	8400*
EPA 1999	Not included in compendium	----	----	----
Cantrell et al. (2000)	Sandy material	----	----	>1200 mL/g
ISCORS 2003	-----	-----	-----	825
RESRAD default	-----	-----	-----	20

\*Geometric mean, based on an assumed log-normal distribution

## 6. SUMMARY AND RECOMMENDATIONS

Site-specific measurements for  $K_d$  were performed on samples collected from areas of concern within the Hematite Site. A total of six boreholes were drilled to refusal or bedrock (~30 to 35 ft), and 18 soil samples (3 depth intervals per borehole) were collected for  $K_d$  testing, radionuclide analysis and general soil characterization procedures. The following is a summary of primary findings from this study:

1. All samples collected consisted of very fine-grained, brown silty clay, likely corresponding to the NSSC and DSSC HU identified in previous characterization reports [LBG 2003]. However, these two layers could not be visually distinguished in the field. Furthermore, the sand/gravel HU described by LBG (2003) was encountered in four out of six boreholes but at a thickness of less than 1 ft, not enough to obtain representative samples for  $K_d$  testing. The fine-grained nature of the soil samples was confirmed by particle size distribution measurements, which showed the soils to consist of >96% silt and clay sized fractions and ~30% clay.
2. General soil characteristics did not vary significantly over the site as shown in the summary table below. Furthermore, there were no observable trends with depth in these parameters.

**Table 21. Summary of Hematite soil properties measured in this study**

	pH	Moisture (%)	Total Carbon (g/kg)	Total Organic Carbon (g/kg)	Iron (g/kg)	Manganese (g/kg)
<b>Minimum</b>	5.8	13%	1.36	2.2	11.1	0.216
<b>Maximum</b>	8.3	28%	9.49	14	21.2	1.85

3. Uranium activities were detected at significant levels in samples from the restricted areas (BHKD5), and in shallowest sample from the Tile Barn/Cistern Burn Pit (BHKD3-8). Slightly elevated U activities were also observed in the mid-depth sample from another location in the restricted areas (BHKD4-14) and the shallowest sample from the Evaporation Ponds (BHKD6-1). Technetium was not detected at significant levels in any of the samples collected for this study.
4.  $K_d$  testing was performed following ASTM 4319-93, Standard Test Method for Distribution Ratios by the Short-term Batch Method, as recommended in the RESRAD data collection handbook. Two types of  $K_d$  tests were performed: (1) desorption tests where a measured mass of soil was contacted with a measured volume of uncontaminated groundwater over a period of 14 days, and (2) adsorption tests where soil was contacted with uncontaminated groundwater spiked to predetermined levels of U (as the uranyl ion or  $UO_2^{2+}$ ) and  $^{99}Tc$  (as the pertechnetate ion  $TcO_4^-$ ). The  $K_d$  tests were performed in two

batches, to enable modifications in procedures for the second batch of tests based on the first batch of results.

5. In general, steady-state conditions were achieved in the soil/water mixtures within 14 days during the  $K_d$  tests. For Uranium, lower overall  $K_d$  values were observed in the adsorption tests, when compared to the desorption tests. Average  $K_d$ s from the adsorption and desorption tests were calculated (excluding data suspected to have been compromised by high U in the contact solution prepared for the first group of tests, and one  $K_d$  measurement that was much higher than the rest of the data) and the mean of the averages was considered the "best" estimate for U  $K_d$  for the Hematite Site. Although the desorption tests are likely to be more representative of contaminant leaching under field conditions, the adsorption data was still considered to achieve a reasonable but conservative site-specific  $K_d$  for Uranium.

For Tc, significant removal of Tc was observed from the liquid phase of the soil/water mixtures within 3 days. This "apparent" sorption could be due to the combined reduction of Tc (VII) to Tc (VI) and adsorption or precipitation of the latter, rather than electrostatic interactions of Tc (VII) with soil mineral surfaces. The resulting  $K_d$ s for Tc are significantly higher than published values, but the validity of  $K_d$  obtained from this study is supported by results that were repeated in multiple soil samples at several time intervals, and recovery of the Tc on the solid residues.

6. The following table shows the recommended  $K_d$  values for radionuclides of interest to the Hematite Site. The U and Tc  $K_d$  values are site-specific in that these were measured using soil samples collected from the site. Because there were no distinct trends with depth in the  $K_d$  measurements for both U and Tc, spatial variability is best addressed by assuming that the unconsolidated sediments overlying bedrock at the Hematite Site can be characterized by a single  $K_d$  parameter that has either a log-normal (for U) or uniform (for Tc) distribution. The  $K_d$  values for the rest of the radionuclides are based on published literature values.

**Table 22. Recommended  $K_d$  values for RESRAD modeling at Hematite Site**

Radionuclides of Concern	Recommended $K_d$ value (mL/g)	Remarks
Uranium	175	Site specific measurement with range of 6.6 and 471.4 mL/g; grossly approximates a lognormal distribution.
Technetium	106	Site specific measurement with range of 15.1 and 172.9 mL/g; approximates a uniform distribution between 0 and 200 mL/g.
Plutonium	2000	RESRAD default value, reasonable when compared to published literature.
Thorium	60000	RESRAD default value, reasonable when compared to published literature.
Neptunium	2	At low end of published literature values.
Americium	1000	Consistent with published literature values, more reasonable than default $K_d$ of 20.

## 7. REFERENCES

- Bostick, B.C., S. Fendorf, M. Bennett, P. Jardine, and S. Brooks. 2002. Uranyl surface complexes formed on subsurface media from DOE facilities. *Soil Sci. Soc. Am. J.* 66:99-108.
- Environmental Protection Agency (EPA). 1999. *Understanding Variation in Partition Coefficient,  $K_d$  Values, Vol. II Review of Geochemistry and Available  $K_d$  Values for Cadmium, Cesium, Chromium, Lead, Plutonium, Radon, Strontium, Thorium, Tritium (3H), and Uranium.* EPA 402-R-99-004B.
- GEO Consultants, LLC and Science Applications International Corporation, 2003 (July). *Distribution Coefficient Sampling and Analysis Plan for the Hematite Site, Rev A*, prepared for the Westinghouse Electric Company, Hematite Facility, Festus, MO.
- Gu, B, and Dowlen, K. 1996. *An Investigation of Groundwater Organics, Soil Minerals and Activated Carbon on the Complexation, Adsorption and Separation of Technetium-99*, ORNL/TM-13154, Oak Ridge National Laboratory, Oak Ridge, TN.
- Interagency Steering Committee on Radiation Standards. 2003. *Assessment of Radioactivity in Sewage Sludge: Modeling to Assess Radiation Doses, Draft Report for Comment*, NUREG-1783, U.S. Nuclear Regulatory Commission, Washington, DC.
- Kaplan, D. I.; Serkiz, S. M. 2001. Quantification of thorium and uranium sorption to contaminated sediments. *Journal of Radioanalytical and Nuclear Chemistry*, 248, 529-535.
- Kaplan, D. I. and Serne, R. J. 1995 (March). *Distribution Coefficient Values Describing Iodine, Neptunium, Selenium, Technetium, and Uranium Sorption.* PNL-10379, Sup. 1. Pacific Northwest Laboratory, Richland, WA
- Kaplan, D. I.; Serne, R. J.; Owen, A. T.; Conca, J.; Wietsma, T. W.; Gervais, T. L. 1996 (August). *Radionuclide Adsorption Distribution Coefficient Measured in Hanford Sediments for the Low Level Waste Performance Assessment Project.* PNNL-11485, Pacific Northwest National Laboratory, Richland, WA.
- Krupka, K. M.; Serne, R. J. 2002. *Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Sediments.* Pacific Northwest National Laboratory, PNNL-14126.
- Leggette, Brashears and Graham, Inc. (LBG), 2003 (May). *Remedial Investigation Feasibility Study Work Plan, Revision 0*, prepared for the Westinghouse Electric Company, Hematite Facility, Festus, MO.
- Science Applications International Corporation, 2003 (June). *Gamma Survey Data Evaluation Report*, prepared for the Westinghouse Electric Company, Hematite Facility, Festus, MO.
- Senko, J., Istok, J., Suflita, J., Krumholtz, L. 2002. *In-Situ Evidence for Uranium Immobilization and Remobilization.* *Environ. Sci. Technol.*, 26, 1491-1496.

- Sheppard, C., Sheppard, M. and Evenden, W. 1990. A Novel Method Used to Examine Variation in Tc Sorption Among 34 Soils, Aerated and Anoxic, *J. Environ. Radioactivity*, 11, 215-233.
- Sowder, A.G., P.M. Bertsch, and P.J. Morris. 2003. Partitioning and availability of uranium and nickel in contaminated riparian sediments. *Journal of Environmental Quality*. 32:885-898.
- Turner, D. R.; Pabalan, R. T.; Bertetti, F. P. 1998. Neptunium (V) sorption on montmorillonite: An experimental and surface complexation modeling study. *Clays and Clay Minerals*, 46, 256-269.
- Yu, C., Luiero, C., Cheng, J.-J., Jones, J. G., Wang, Y. Y., Chin, Y. P., and Faillace, E., 1993. *Data Collection Handbook to Support Modeling Impacts*, Argonne National Laboratory, Argonne, IL.
- Yu, C., Zielin, J., Cheng, J.-J., LePoire, D. J., Gnanaprajasan, E., Kamboj, S., Arnish, J., Wallo III, A., William, W. A., and Peterson, H. 2001. *User's Manual for RESRAD Version 6*, ANL/EAD-4, Argonne National Laboratory, Argonne, IL.

**Appendix A**  
**Data Validation Reports**

# DATA VALIDATION REPORT

Date:

September 4, 2003

To: <b>Steve Passig</b>	From: <b>Jerry Everett</b>
Laboratory: <b>Severn Trent - St. Louis</b>	SDG #: <b>F3H010120</b>

Attached you will find the results from the data validation technical review for the Westinghouse/Hematite samples and analyses that are associated with the above referenced laboratory and sample delivery group (SDG) number. These data points have been selected for data validation and the sample index on the following page specifically identifies the samples and analyses associated with this validation review.

The FUSRAP validation technical review was performed in accordance with the *Contract Laboratory Program Data Validation Functional Guidelines for Evaluating Inorganic Analytical Data*, and the *Laboratory Data Validation Guidelines for Evaluating Radionuclide Analyses and Radiochemical Data Verification and Validation*. It was based on the information and documentation supplied by the associated laboratory. The analyses were evaluated against criteria established in the related analytical procedures and the Westinghouse/Hematite data quality requirements.

Attachment A to this report provides the Sample Data Summary Sheets for the samples associated with the above referenced request. These summary sheets identify the analytical values and the qualifiers for each sample and parameter. Attachment B outlines the validation qualifiers and reason codes used in the validation of the data.

Report Summary	
Total Number of Samples	14
Total Number of Data Points	108
Total Number of Rejected Data Points	0
Percent Completeness (approval to rejection ratio)	100.0%

## Sample Index

Date:

September 4, 2003

Laboratory:

Severn Trent – St. Louis

SDG #:

F3H010120

WESTINGHOUSE Sample ID	Target Analyses
BHKD4-02	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD4-14	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD4-24	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD5-01	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD5-19	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD5-27	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD6-01	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD6-11	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, Ph
BHKD6-26	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
OB-1-KD	Isotopic Uranium, Technetium-99
OB-1-ANION	Chloride, Nitrate, Sulfate
OB-1-CATION	Calcium, Potassium, Magnesium, Sodium
WS-14-ANION	Chloride, Nitrate, Sulfate
WS-14-CATION	Calcium, Potassium, Magnesium, Sodium

**ANALYTICAL CATEGORY: Anions**

- Chloride, Nitrate, and Sulfate were determined by SW846 Method 9056A.
  - 1. The following items (as applicable) have been addressed during the validation review:
    - sample custody, integrity & preservation
    - sample handling & preparation
    - holding times
    - instrument calibration & performance
    - dilution factors
    - detection limits
    - laboratory background & carry-over
    - appearance & interpretation of chromatography<sup>†</sup>
    - retention times<sup>†</sup>
    - overall appearance of the data
    - Quality Control:
      - calibration checks & blanks
      - laboratory blanks (method, TCLP)
      - laboratory control samples
      - matrix spike samples
      - matrix duplicates
      - field blanks (if available)
      - field duplicates (if available)
- <sup>†</sup> - for ion chromatography only.
2. The above items were found to be acceptable, except as follows:
  - None
3. Additional comments:
  - Contamination with chloride was seen in the calibration blanks. Calibration blanks are run to verify that carry over does not occur and that no contamination is being introduced during the run. Chloride data associated with the bracketed samples were greater than five times the contamination level. Therefore, qualification of the chloride data were not necessary.

**ANALYTICAL CATEGORY: Metals**

- Metals were analyzed by Inductively Coupled Plasma (ICP).

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & blanks
  - laboratory blanks (method, TCLP)
  - laboratory control samples
    - matrix spike samples
  - matrix duplicates
  - field blanks (if available)
  - field duplicates (if available)
  - CRDL standards
  - interference check standards
  - analytical bench spikes
  - serial dilutions

2. The above items were found to be acceptable, except as follows:

- Blank Contamination

The continuing calibration blank was contaminated with potassium at a concentration of 1600 ug/l. This is evidence of possible laboratory contamination. The positive potassium result in sample OB-1-CATION was less than five times the contamination level. The reported sample concentration was qualified with a *U*.

3. Additional comments:

- Contamination with iron and manganese were seen in the calibration blanks. Calibration blanks are run to verify that carry over does not occur and that no contamination is being introduced during the run. Iron and manganese data associated with the bracketed samples were greater than five times the contamination level. Therefore, qualification of iron and manganese were not necessary.
- Detection limits in samples OB-1-CATION and WS-14-CATION have been changed.

**ANALYTICAL CATEGORY: Miscellaneous**

- Total Organic Carbon and Total Carbon were determined by SW846 Method 9060; pH was determined by SW846 Method 9045A; and percent moisture was determined by MCAWW 160.3.

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & blanks
  - laboratory blanks (method, TCLP)
  - laboratory control samples
    - matrix spike samples
  - matrix duplicates
    - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- None.

3. Additional comments:

- None.

**ANALYTICAL CATEGORY: Radiochemical**

- Isotopic uranium was determined by alpha spectroscopy (NAS/DOE 3050/RP), and technetium was determined by Liquid scintillation counters (DOE TC-02-RC).

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & background
  - preparation blanks
  - laboratory control samples
  - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- Instrument Counting Error

Several samples have reported results that are less than the MDA and the uncertainty is greater than the result. The non-detect results for these samples were qualified *UU*.

Several samples have reported results that are greater than the MDA and the sample uncertainty is 50% to 100% of the sample result. The reported values for these samples were qualified with a *J*.

- Blank Contamination

Uranium-234 was present in the associated method blank at  $0.1 \pm 0.11$  pCi/g. This may indicate that contamination could have been introduced during the laboratory preparation. The normalized absolute difference between the sample OB-1-KD and the method blank was less than 2.58 and was qualified as estimated, *J*.

3. Additional comments:

- MDC values for Isotopic uranium in sample BHKD6-01 have been changed.

# **ATTACHMENT A**

**WESTINGHOUSE Sample Data Summary Sheets**

# ATTACHMENT B

## KEY TO THE WESTINGHOUSE DATA VALIDATION QUALIFIERS

QUALIFIERS	
=	Indicates that the data met all QA/QC requirements, and that the parameter has been positively identified and the associated concentration value is accurate.
U	Indicates that the data met all QA/QC requirements, and that the parameter was analyzed for but was not detected above the reported sample quantitation limit.
J	Indicates that the parameter was positively identified; the associated numerical value is the approximate concentration of the parameter in the sample.
UJ	Indicates that the parameter was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
N	The analysis indicates the presence of a parameter for which there is presumptive evidence to make a "tentative identification."
R	Indicates that the sample results for the parameter are rejected or unusable due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the parameter cannot be verified.

## Data Validation Reason Codes

### Holding Times

- A01 Extraction holding times were exceeded.
- A02 Extraction holding times were grossly exceeded.
- A03 Analysis holding times were exceeded.
- A04 Analysis holding times were grossly exceeded.
- A05 Samples were not preserved properly.
- A06 Professional judgment was used to qualify the data.

### GC/MS Tuning

- B01 Mass calibration was in error, even after applying expanded criteria.
- B02 Mass calibration was not performed every 12 hours.
- B03 Mass calibration did not meet ion abundance.
- B04 Professional judgment was used to qualify the data.

### Initial/Continuing Calibration – Organics

- C01 Initial calibration RRF was <0.05.
- C02 Initial calibration RSD was >30%.
- C03 Initial calibration sequence was not followed as required.
- C04 Continuing calibration RRF was <0.05.
- C05 Continuing calibration %D was >25%.
- C06 Continuing calibration was not performed at the required frequency.
- C07 Resolution criteria were not met.
- C08 RPD criteria were not met.
- C09 RSD criteria were not met.
- C10 Retention time of compounds was outside windows.
- C11 Compounds were not adequately resolved.
- C12 Breakdown of endrin or DDT was >20%.
- C13 Combined breakdown of endrin/DDT was >30%.
- C14 Professional judgment was used to qualify the data.

### Blanks

- F01 Sample data were qualified as a result of the method blank.
- F02 Sample data were qualified as a result of the field blank.
- F03 Sample data were qualified as a result of the equipment rinsate.
- F04 Sample data were qualified as a result of the trip blank.
- F05 Gross contamination exists.
- F06 Concentration of the contaminant was detected at a level below the CRQL.
- F07 Concentration of the contaminant was detected at a level less than the action limit, but greater than the CRQL.
- F08 Concentration of the contaminant was detected at a level that exceeds the action level.
- F09 No laboratory blanks were analyzed.
- F10 Blank had a negative value >2x's the IDL.
- F11 Blanks were not analyzed at required frequency.
- F12 Professional judgment was used to qualify the data.

#### **Surrogate/Radiological Chemical Recovery**

- G01 Surrogate/radiological chemical recovery was above the upper control limit.
- G02 Surrogate/radiological chemical recovery was below the lower control limit.
- G03 Surrogate recovery was <10%.
- G04 Surrogate/radiological chemical recovery was zero.
- G05 Surrogate/radiological chemical recovery was not present.
- G06 Professional judgment was used to qualify the data.
- G07 Radiological chemical recovery was <20%.
- G08 Radiological chemical recovery was >150%.

#### **Matrix Spike/Matrix Spike Duplicate**

- H01 MS/MSD recovery was above the upper control limit.
- H02 MS/MSD recovery was below the lower control limit.
- H03 MS/MSD recovery was <10%.
- H04 MS/MSD pairs exceed the RPD limit.
- H05 No action was taken on MS/MSD results.
- H06 Professional judgment was used to qualify the data.
- H07 Radiological MS/MSD recovery was <20%.
- H08 Radiological MS/MSD recovery was >160%.
- H09 Radiological MS/MSD samples were not analyzed at the required frequency.

#### **Laboratory Duplicate**

- J01 Duplicate RPD/normalized absolute difference (NAD) was outside the control limit.
- J02 Duplicate sample results were >5x the CRDL.
- J03 Duplicate sample results were <5x the CRDL.
- J04 Professional judgment was used to qualify the data.
- J05 Duplicate was not analyzed at the required frequency.

### **Target Compound Identification**

- M01 Incorrect identifications were made.
- M02 Qualitative criteria were not met.
- M03 Cross contamination occurred.
- M04 Confirmatory analysis was not performed.
- M05 No results were provided.
- M06 Analysis occurred outside 12 hr GC/MS window.
- M07 Professional judgment was used to qualify the data.
- M08 The %D between the two pesticide/PCB column checks was >25%.

### **Laboratory Control Samples (LCSs)**

- P01 LCS recovery was above upper control limit.
- P02 LCS recovery was below lower control limit.
- P03 LCS recovery was <50%.
- P04 No action was taken on the LCS data.
- P05 LCS was not analyzed at required frequency.
- P06 Radiological LCS recovery was <50% for aqueous samples; <40% for solid samples.
- P07 Radiological LCS recovery was >150% for aqueous samples; >160% for solid samples.
- P08 Professional judgment was used to qualify the data.

### **Field Duplicate**

- Q01 No action was taken on the basis of field duplicate RPDs.
- Q02 Radiological field duplicate normalized absolute difference (NAD) was outside the control limit.
- Q03 Duplicate sample results were >5x the CRDL.
- Q04 Duplicate sample results were <5x the CRDL.

### **Radiological Calibration**

- R01 Efficiency calibration criteria were not met.
- R02 Energy calibration criteria were not met.
- R03 Resolution calibration criteria were not met
- R04 Background determination criteria were not met.
- R05 Quench curve criteria were not met.
- R06 Absorption curve criteria were not met.
- R07 Plateau curve criteria were not met.
- R08 Professional judgment was used to qualify the data.

### **Radiological Calibration Verification**

- S01 Efficiency verification criteria were not met.
- S02 Energy verification criteria were not met.
- S03 Resolution verification criteria were not met
- S04 Background verification criteria were not met.
- S05 Cross-talk verification criteria were not met.
- S06 Professional judgment was used to qualify the data.

### **Radionuclide Quantitation**

- T01 Detection limits were not met.
- T02 Analytical uncertainties were not met and/or not reported.
- T03 Inappropriate aliquot sizes were used.
- T04 Professional judgment was used to qualify the data.
- T05 Analytical result is less than the associated MDA, but greater than the counting uncertainty.
- T06 Analytical result is less than both the associated counting uncertainty and MDA.
- T07 Negative analytical result where the absolute value exceeds 2x the associated MDA.

### **System Performance**

- V01 High background levels or a shift in the energy calibration were observed.
- V02 Extraneous peaks were observed.
- V03 Loss of resolution was observed.
- V04 Peak-tailing or peak splitting that may result in inaccurate quantitation were observed.
- V05 Professional judgment was used to qualify the data.

# DATA VALIDATION REPORT

Date:

September 4, 2003

To: Steve Passig	From: Jerry Everett
Laboratory: Severn Trent – St. Louis	SDG #: F3G310383

Attached you will find the results from the data validation technical review for the Westinghouse/Hematite samples and analyses that are associated with the above referenced laboratory and sample delivery group (SDG) number. These data points have been selected for data validation and the sample index on the following page specifically identifies the samples and analyses associated with this validation review.

The FUSRAP validation technical review was performed in accordance with the *Contract Laboratory Program Data Validation Functional Guidelines for Evaluating Inorganic Analytical Data*, and the *Laboratory Data Validation Guidelines for Evaluating Radionuclide Analyses and Radiochemical Data Verification and Validation*. It was based on the information and documentation supplied by the associated laboratory. The analyses were evaluated against criteria established in the related analytical procedures and the Westinghouse/Hematite data quality requirements.

Attachment A to this report provides the Sample Data Summary Sheets for the samples associated with the above referenced request. These summary sheets identify the analytical values and the qualifiers for each sample and parameter. Attachment B outlines the validation qualifiers and reason codes used in the validation of the data.

Report Summary	
Total Number of Samples	9
Total Number of Data Points	90
Total Number of Rejected Data Points	0
Percent Completeness (approval to rejection ratio)	100.0%

# Sample Index

Date:

September 4, 2003

Laboratory:

Severn Trent - St. Louis

SDG #:

F3G310383

WESTINGHOUSE Sample ID	Target Analyses
BHKD1-04	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD1-23	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD1-28	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD2-04	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD2-13	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD2-23	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD3-08	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD3-16	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH
BHKD3-23	Iron, Manganese, Total Carbon, TOC, Isotopic Uranium, Technetium-99, percent moisture, pH

**ANALYTICAL CATEGORY: Metals**

- Iron and manganese were analyzed by Inductively Coupled Plasma (ICP).

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & blanks
  - laboratory blanks (method, TCLP)
  - laboratory control samples
    - matrix spike samples
  - matrix duplicates
  - field blanks (if available)
  - field duplicates (if available)
  - CRDL standards
  - interference check standards
  - analytical bench spikes
  - serial dilutions

2. The above items were found to be acceptable, except as follows:

- None.

3. Additional comments:

- Contamination with iron and manganese were seen in the calibration blanks. Calibration blanks are run to verify that carry over does not occur and that no contamination is being introduced during the run. Iron and manganese data associated with the bracketed samples were greater than five times the contamination level. Therefore, qualification of the iron and manganese data was not necessary.
- The matrix spike recovery for iron was high. The spiked sample analysis is designed to provide information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology. When the sample concentration is greater than 4X the spike concentration spike recoveries are not evaluated. Therefore qualification of the data is not necessary.
- The matrix spike recovery for manganese was low. The spiked sample analysis is designed to provide information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology. When the sample concentration is greater than 4X the spike concentration, spike recoveries are not evaluated. Therefore qualification of the data is not necessary.

**ANALYTICAL CATEGORY: Miscellaneous**

- Total Organic Carbon and Total Carbon were determined by SW846 Method 9060; pH was determined by SW846 Method 9045A; and percent moisture was determined by MCAWW 160.3.

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & blanks
  - laboratory blanks (method, TCLP)
  - laboratory control samples
  - matrix spike samples
  - matrix duplicates
  - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- None.

3. Additional comments:

- The matrix spike recoveries for total carbon and total organic carbon were high. The spiked sample analysis is designed to provide information about the effect of each sample matrix on the sample preparation procedures and the measurement methodology. When the sample concentration is greater than 4X the spike concentration spike recoveries are not evaluated. Therefore qualification of the date is not necessary.

**ANALYTICAL CATEGORY: Radiochemical**

- Isotopic uranium was determined by alpha spectroscopy (NAS/DOE 3050/RP), and technetium was determined by Liquid scintillation counters (DOE TC-02-RC).

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & background
  - preparation blanks
  - laboratory control samples
  - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- Instrument Counting Error

Several samples have reported results that are less than the MDA and the uncertainty is greater than the result. The non-detect results for these samples were qualified *UJ*.

Several samples have reported results that are greater than the MDA and the sample uncertainty is 50% to 100% of the sample result. The reported values for these samples were qualified with a *J*.

3. Additional comments:

- Contamination with technetium-99 was seen in the method blank. Method blanks are run to verify that contamination is being introduced during the run. Technetium-99 data associated with the method blank were greater than the contamination level. Therefore, qualification of the data was not necessary.

# **ATTACHMENT A**

## **WESTINGHOUSE Sample Data Summary Sheets**

## ATTACHMENT B

### KEY TO THE WESTINGHOUSE DATA VALIDATION QUALIFIERS

QUALIFIERS	
=	Indicates that the data met all QA/QC requirements, and that the parameter has been positively identified and the associated concentration value is accurate.
U	Indicates that the data met all QA/QC requirements, and that the parameter was analyzed for but was not detected above the reported sample quantitation limit.
J	Indicates that the parameter was positively identified; the associated numerical value is the approximate concentration of the parameter in the sample.
UJ	Indicates that the parameter was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
N	The analysis indicates the presence of a parameter for which there is presumptive evidence to make a "tentative identification."
R	Indicates that the sample results for the parameter are rejected or unusable due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the parameter cannot be verified.

## Data Validation Reason Codes

### Holding Times

- A01 Extraction holding times were exceeded.
- A02 Extraction holding times were grossly exceeded.
- A03 Analysis holding times were exceeded.
- A04 Analysis holding times were grossly exceeded.
- A05 Samples were not preserved properly.
- A06 Professional judgment was used to qualify the data.

### GC/MS Tuning

- B01 Mass calibration was in error, even after applying expanded criteria.
- B02 Mass calibration was not performed every 12 hours.
- B03 Mass calibration did not meet ion abundance.
- B04 Professional judgment was used to qualify the data.

### Initial/Continuing Calibration – Organics

- C01 Initial calibration RRF was <0.05.
- C02 Initial calibration RSD was >30%.
- C03 Initial calibration sequence was not followed as required.
- C04 Continuing calibration RRF was <0.05.
- C05 Continuing calibration %D was >25%.
- C06 Continuing calibration was not performed at the required frequency.
- C07 Resolution criteria were not met.
- C08 RPD criteria were not met.
- C09 RSD criteria were not met.
- C10 Retention time of compounds was outside windows.
- C11 Compounds were not adequately resolved.
- C12 Breakdown of endrin or DDT was >20%.
- C13 Combined breakdown of endrin/DDT was >30%.
- C14 Professional judgment was used to qualify the data.

### Blanks

- F01 Sample data were qualified as a result of the method blank.
- F02 Sample data were qualified as a result of the field blank.
- F03 Sample data were qualified as a result of the equipment rinsate.
- F04 Sample data were qualified as a result of the trip blank.
- F05 Gross contamination exists.
- F06 Concentration of the contaminant was detected at a level below the CRQL.
- F07 Concentration of the contaminant was detected at a level less than the action limit, but greater than the CRQL.
- F08 Concentration of the contaminant was detected at a level that exceeds the action level.
- F09 No laboratory blanks were analyzed.
- F10 Blank had a negative value >2x's the IDL.
- F11 Blanks were not analyzed at required frequency.
- F12 Professional judgment was used to qualify the data.

#### **Surrogate/Radiological Chemical Recovery**

- G01 Surrogate/radiological chemical recovery was above the upper control limit.
- G02 Surrogate/radiological chemical recovery was below the lower control limit.
- G03 Surrogate recovery was <10%.
- G04 Surrogate/radiological chemical recovery was zero.
- G05 Surrogate/radiological chemical recovery was not present.
- G06 Professional judgment was used to qualify the data.
- G07 Radiological chemical recovery was <20%.
- G08 Radiological chemical recovery was >150%.

#### **Matrix Spike/Matrix Spike Duplicate**

- H01 MS/MSD recovery was above the upper control limit.
- H02 MS/MSD recovery was below the lower control limit.
- H03 MS/MSD recovery was <10%.
- H04 MS/MSD pairs exceed the RPD limit.
- H05 No action was taken on MS/MSD results.
- H06 Professional judgment was used to qualify the data.
- H07 Radiological MS/MSD recovery was <20%.
- H08 Radiological MS/MSD recovery was >160%.
- H09 Radiological MS/MSD samples were not analyzed at the required frequency.

#### **Laboratory Duplicate**

- J01 Duplicate RPD/normalized absolute difference (NAD) was outside the control limit.
- J02 Duplicate sample results were >5x the CRDL.
- J03 Duplicate sample results were <5x the CRDL.
- J04 Professional judgment was used to qualify the data.
- J05 Duplicate was not analyzed at the required frequency.

#### **Target Compound Identification**

- M01 Incorrect identifications were made.
- M02 Qualitative criteria were not met.
- M03 Cross contamination occurred.
- M04 Confirmatory analysis was not performed.
- M05 No results were provided.
- M06 Analysis occurred outside 12 hr GC/MS window.
- M07 Professional judgment was used to qualify the data.
- M08 The %D between the two pesticide/PCB column checks was >25%.

#### **Laboratory Control Samples (LCSs)**

- P01 LCS recovery was above upper control limit.
- P02 LCS recovery was below lower control limit.
- P03 LCS recovery was <50%.
- P04 No action was taken on the LCS data.
- P05 LCS was not analyzed at required frequency.
- P06 Radiological LCS recovery was <50% for aqueous samples; <40% for solid samples.
- P07 Radiological LCS recovery was >150% for aqueous samples; >160% for solid samples.
- P08 Professional judgment was used to qualify the data.

#### **Field Duplicate**

- Q01 No action was taken on the basis of field duplicate RPDs.
- Q02 Radiological field duplicate normalized absolute difference (NAD) was outside the control limit.
- Q03 Duplicate sample results were >5x the CRDL.
- Q04 Duplicate sample results were <5x the CRDL.

#### **Radiological Calibration**

- R01 Efficiency calibration criteria were not met.
- R02 Energy calibration criteria were not met.
- R03 Resolution calibration criteria were not met
- R04 Background determination criteria were not met.
- R05 Quench curve criteria were not met.
- R06 Absorption curve criteria were not met.
- R07 Plateau curve criteria were not met.
- R08 Professional judgment was used to qualify the data.

#### **Radiological Calibration Verification**

- S01 Efficiency verification criteria were not met.
- S02 Energy verification criteria were not met.
- S03 Resolution verification criteria were not met
- S04 Background verification criteria were not met.
- S05 Cross-talk verification criteria were not met.
- S06 Professional judgment was used to qualify the data.

### **Radionuclide Quantitation**

- T01 Detection limits were not met.
- T02 Analytical uncertainties were not met and/or not reported.
- T03 Inappropriate aliquot sizes were used.
- T04 Professional judgment was used to qualify the data.
- T05 Analytical result is less than the associated MDA, but greater than the counting uncertainty.
- T06 Analytical result is less than both the associated counting uncertainty and MDA.
- T07 Negative analytical result where the absolute value exceeds 2x the associated MDA.

### **System Performance**

- V01 High background levels or a shift in the energy calibration were observed.
- V02 Extraneous peaks were observed.
- V03 Loss of resolution was observed.
- V04 Peak-tailing or peak splitting that may result in inaccurate quantitation were observed.
- V05 Professional judgment was used to qualify the data.

## DATA VALIDATION REPORT

Date:

November 14, 2003

To: Steve Passig	From: Carol Johnson
Laboratory: Severn Trent – St. Louis	SDG #: F3I230103

Attached you will find the results from the data validation technical review for the Westinghouse/Hematite samples and analyses that are associated with the above referenced laboratory and sample delivery group (SDG) number. These data points have been selected for data validation and the sample index on the following page specifically identifies the samples and analyses associated with this validation review.

The Westinghouse/Hematite validation technical review was performed in accordance with the *Contract Laboratory Program Data Validation Functional Guidelines for Evaluating Inorganic Analytical Data*, and the *Laboratory Data Validation Guidelines for Evaluating Radionuclide Analyses and Radiochemical Data Verification and Validation*. It was based on the information and documentation supplied by the associated laboratory. The analyses were evaluated against criteria established in the related analytical procedures and the Westinghouse/Hematite data quality requirements.

Attachment A to this report provides the Sample Data Summary Sheets for the samples associated with the above referenced request. These summary sheets identify the analytical values and the qualifiers for each sample and parameter. Attachment B outlines the validation qualifiers and reason codes used in the validation of the data.

Report Summary	
Total Number of Samples	8
Total Number of Data Points	26
Total Number of Rejected Data Points	0
Percent Completeness (approval to rejection ratio)	100.0%

# Sample Index

*Date:*

**November 14, 2003**

*Laboratory:*

**Severn Trent - St. Louis**

*SDG #:*

**F3I230103**

WESTINGHOUSE Sample ID	Target Analyses
BHKD5-01	Total Uranium, Conductivity, pH
BHKD5-19	Total Uranium, Conductivity, pH
BHKD5-27	Total Uranium, Conductivity, pH
BHKD3-08	Total Uranium, Conductivity, Ph
BHKD2-04	Total Uranium, Technetium-99, Conductivity, pH
BHKD2-13	Total Uranium, Technetium-99, Conductivity, pH
BHKD2-23	Total Uranium, Technetium-99, Conductivity, pH
OB-1	Total Uranium, Technetium-99

**ANALYTICAL CATEGORY: Miscellaneous**

- Specific Conductance was determined by SW846 Method 9050; pH was determined by SW846 Method 9045A; and percent moisture was determined by MCAWW 160.3.

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & blanks
  - laboratory blanks (method, TCLP)
  - laboratory control samples
  - matrix spike samples
  - matrix duplicates
  - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- Holding Times for Conductivity were exceeded, resulting in the samples being qualified as estimated, *J*.

3. Additional comments:

- None

**ANALYTICAL CATEGORY: Radiochemical**

- Technetium was determined by Liquid scintillation counters (DOE TC-02-RC), and Total Uranium was determined by Laser Phosphorimetry Method ASTM 5174-91.

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & background
  - preparation blanks
  - laboratory control samples
  - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- Instrument Counting Error

Several samples have reported results that are less than the MDA and the uncertainty is greater than the result. The non-detect results for these samples were qualified *UJ*.

Method Blank

- Contamination with Technetium-99 and Isotopic Uranium was seen in the method blank. Method blanks are run to verify that contamination is being introduced during the run. Technetium-99 data associated with the method blank did not pass the Normalized Absolute Difference criteria. Samples were qualified as estimated, *J*.

Laboratory Control Sample

The percent recovery for Technetium-99 LCS, was above the upper control limit (UCL). Recoveries above the UCL could be the result of poor preparation or instrumentation problems, and may indicate a high bias to the data. Only positive sample results for qualified as estimated, *J*.

3. Additional comments:

None

# **ATTACHMENT A**

**WESTINGHOUSE Sample Data Summary Sheets**

# ATTACHMENT B

## KEY TO THE WESTINGHOUSE DATA VALIDATION QUALIFIERS

QUALIFIERS	
=	Indicates that the data met all QA/QC requirements, and that the parameter has been positively identified and the associated concentration value is accurate.
U	Indicates that the data met all QA/QC requirements, and that the parameter was analyzed for but was not detected above the reported sample quantitation limit.
J	Indicates that the parameter was positively identified; the associated numerical value is the approximate concentration of the parameter in the sample.
UJ	Indicates that the parameter was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
N	The analysis indicates the presence of a parameter for which there is presumptive evidence to make a "tentative identification."
R	Indicates that the sample results for the parameter are rejected or unusable due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the parameter cannot be verified.

## Data Validation Reason Codes

### Holding Times

- A01 Extraction holding times were exceeded.
- A02 Extraction holding times were grossly exceeded.
- A03 Analysis holding times were exceeded.
- A04 Analysis holding times were grossly exceeded.
- A05 Samples were not preserved properly.
- A06 Professional judgment was used to qualify the data.

### GC/MS Tuning

- B01 Mass calibration was in error, even after applying expanded criteria.
- B02 Mass calibration was not performed every 12 hours.
- B03 Mass calibration did not meet ion abundance.
- B04 Professional judgment was used to qualify the data.

### Initial/Continuing Calibration – Organics

- C01 Initial calibration RRF was <0.05.
- C02 Initial calibration RSD was >30%.
- C03 Initial calibration sequence was not followed as required.
- C04 Continuing calibration RRF was <0.05.
- C05 Continuing calibration %D was >25%.
- C06 Continuing calibration was not performed at the required frequency.
- C07 Resolution criteria were not met.
- C08 RPD criteria were not met.
- C09 RSD criteria were not met.
- C10 Retention time of compounds was outside windows.
- C11 Compounds were not adequately resolved.
- C12 Breakdown of endrin or DDT was >20%.
- C13 Combined breakdown of endrin/DDT was >30%.
- C14 Professional judgment was used to qualify the data.

### Blanks

- F01 Sample data were qualified as a result of the method blank.
- F02 Sample data were qualified as a result of the field blank.
- F03 Sample data were qualified as a result of the equipment rinsate.
- F04 Sample data were qualified as a result of the trip blank.
- F05 Gross contamination exists.
- F06 Concentration of the contaminant was detected at a level below the CRQL.
- F07 Concentration of the contaminant was detected at a level less than the action limit, but greater than the CRQL.
- F08 Concentration of the contaminant was detected at a level that exceeds the action level.
- F09 No laboratory blanks were analyzed.
- F10 Blank had a negative value >2x's the IDL.
- F11 Blanks were not analyzed at required frequency.
- F12 Professional judgment was used to qualify the data.

**Surrogate/Radiological Chemical Recovery**

- G01 Surrogate/radiological chemical recovery was above the upper control limit.
- G02 Surrogate/radiological chemical recovery was below the lower control limit.
- G03 Surrogate recovery was <10%.
- G04 Surrogate/radiological chemical recovery was zero.
- G05 Surrogate/radiological chemical recovery was not present.
- G06 Professional judgment was used to qualify the data.
- G07 Radiological chemical recovery was <20%.
- G08 Radiological chemical recovery was >150%.

**Matrix Spike/Matrix Spike Duplicate**

- H01 MS/MSD recovery was above the upper control limit.
- H02 MS/MSD recovery was below the lower control limit.
- H03 MS/MSD recovery was <10%.
- H04 MS/MSD pairs exceed the RPD limit.
- H05 No action was taken on MS/MSD results.
- H06 Professional judgment was used to qualify the data.
- H07 Radiological MS/MSD recovery was <20%.
- H08 Radiological MS/MSD recovery was >160%.
- H09 Radiological MS/MSD samples were not analyzed at the required frequency.

**Laboratory Duplicate**

- J01 Duplicate RPD/normalized absolute difference (NAD) was outside the control limit.
- J02 Duplicate sample results were >5x the CRDL.
- J03 Duplicate sample results were <5x the CRDL.
- J04 Professional judgment was used to qualify the data.
- J05 Duplicate was not analyzed at the required frequency.

### **Target Compound Identification**

- M01 Incorrect identifications were made.
- M02 Qualitative criteria were not met.
- M03 Cross contamination occurred.
- M04 Confirmatory analysis was not performed.
- M05 No results were provided.
- M06 Analysis occurred outside 12 hr GC/MS window.
- M07 Professional judgment was used to qualify the data.
- M08 The %D between the two pesticide/PCB column checks was >25%.

### **Laboratory Control Samples (LCSs)**

- P01 LCS recovery was above upper control limit.
- P02 LCS recovery was below lower control limit.
- P03 LCS recovery was <50%.
- P04 No action was taken on the LCS data.
- P05 LCS was not analyzed at required frequency.
- P06 Radiological LCS recovery was <50% for aqueous samples; <40% for solid samples.
- P07 Radiological LCS recovery was >150% for aqueous samples; >160% for solid samples.
- P08 Professional judgment was used to qualify the data.

### **Field Duplicate**

- Q01 No action was taken on the basis of field duplicate RPDs.
- Q02 Radiological field duplicate normalized absolute difference (NAD) was outside the control limit.
- Q03 Duplicate sample results were >5x the CRDL.
- Q04 Duplicate sample results were <5x the CRDL.

### **Radiological Calibration**

- R01 Efficiency calibration criteria were not met.
- R02 Energy calibration criteria were not met.
- R03 Resolution calibration criteria were not met
- R04 Background determination criteria were not met.
- R05 Quench curve criteria were not met.
- R06 Absorption curve criteria were not met.
- R07 Plateau curve criteria were not met.
- R08 Professional judgment was used to qualify the data.

### **Radiological Calibration Verification**

- S01 Efficiency verification criteria were not met.
- S02 Energy verification criteria were not met.
- S03 Resolution verification criteria were not met
- S04 Background verification criteria were not met.
- S05 Cross-talk verification criteria were not met.
- S06 Professional judgment was used to qualify the data.

### **Radionuclide Quantitation**

- T01 Detection limits were not met.
- T02 Analytical uncertainties were not met and/or not reported.
- T03 Inappropriate aliquot sizes were used.
- T04 Professional judgment was used to qualify the data.
- T05 Analytical result is less than the associated MDA, but greater than the counting uncertainty.
- T06 Analytical result is less than both the associated counting uncertainty and MDA.
- T07 Negative analytical result where the absolute value exceeds 2x the associated MDA.

### **System Performance**

- V01 High background levels or a shift in the energy calibration were observed.
- V02 Extraneous peaks were observed.
- V03 Loss of resolution was observed.
- V04 Peak-tailing or peak splitting that may result in inaccurate quantitation were observed.
- V05 Professional judgment was used to qualify the data.

# DATA VALIDATION REPORT

Date:

November 14, 2003

To: <b>Steve Passig</b>	From: <b>Carol Johnson</b>
Laboratory: <b>Severn Trent – St. Louis</b>	SDG #: <b>F3I230107</b>

Attached you will find the results from the data validation technical review for the Westinghouse/Hematite samples and analyses that are associated with the above referenced laboratory and sample delivery group (SDG) number. These data points have been selected for data validation and the sample index on the following page specifically identifies the samples and analyses associated with this validation review.

The Westinghouse/Hematite validation technical review was performed in accordance with the *Contract Laboratory Program Data Validation Functional Guidelines for Evaluating Inorganic Analytical Data*, and the *Laboratory Data Validation Guidelines for Evaluating Radionuclide Analyses and Radiochemical Data Verification and Validation*. It was based on the information and documentation supplied by the associated laboratory. The analyses were evaluated against criteria established in the related analytical procedures and the Westinghouse/Hematite data quality requirements.

Attachment A to this report provides the Sample Data Summary Sheets for the samples associated with the above referenced request. These summary sheets identify the analytical values and the qualifiers for each sample and parameter. Attachment B outlines the validation qualifiers and reason codes used in the validation of the data.

Report Summary	
Total Number of Samples	7
Total Number of Data Points	24
Total Number of Rejected Data Points	0
Percent Completeness (approval to rejection ratio)	100.0%

# Sample Index

Date:

November 14, 2003

Laboratory:

Severn Trent – St. Louis

SDG #:

F3I230117

WESTINGHOUSE Sample ID	Target Analyses
BHKD5-01	Total Uranium, Conductivity, pH
BHKD5-19	Total Uranium, Conductivity, pH
BHKD5-27	Total Uranium, Conductivity, pH
BHKD3-08	Total Uranium, Conductivity, Ph
BHKD2-04	Total Uranium, Technetium-99, Conductivity, pH
BHKD2-13	Total Uranium, Technetium-99, Conductivity, pH
BHKD2-23	Total Uranium, Technetium-99, Conductivity, pH

**ANALYTICAL CATEGORY: Miscellaneous**

- Specific Conductance was determined by SW846 Method 9050; pH was determined by SW846 Method 9045A; and percent moisture was determined by MCAWW 160.3.

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & blanks
  - laboratory blanks (method, TCLP)
  - laboratory control samples
    - matrix spike samples
  - matrix duplicates
  - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- Holding Times for Conductivity were exceeded, resulting in the samples being qualified as estimated, *J*.

3. Additional comments:

- None

**ANALYTICAL CATEGORY: Radiochemical**

- Isotopic uranium was determined by alpha spectroscopy (NAS/DOE 3050/RP), and technetium was determined by Liquid scintillation counters (DOE TC-02-RC), and Total Uranium was determined by Laser Phosphorimetry Method ASTM 5174-91.

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & background
  - preparation blanks
  - laboratory control samples
  - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- Instrument Counting Error

Several samples have reported results that are less than the MDA and the uncertainty is greater than the result. The non-detect results for these samples were qualified *UJ*.

**Method Blank**

- Contamination with Technetium-99 and Isotopic Uranium was seen in the method blank. Method blanks are run to verify that contamination is being introduced during the run. Technetium-99 data associated with the method blank did not pass the Normalized Absolute Difference criteria. Samples were qualified as estimated, *J*.

**Laboratory Control Sample**

The percent recovery for Technetium-99 LCS, was above the upper control limit (UCL). Recoveries above the UCL could be the result of poor preparation or instrumentation problems, and may indicate a high bias to the data. Only positive sample results for qualified as estimated, *J*.

3. Additional comments:  
None

## **ATTACHMENT A**

**WESTINGHOUSE Sample Data Summary Sheets**

## ATTACHMENT B

### KEY TO THE WESTINGHOUSE DATA VALIDATION QUALIFIERS

QUALIFIERS	
=	Indicates that the data met all QA/QC requirements, and that the parameter has been positively identified and the associated concentration value is accurate.
U	Indicates that the data met all QA/QC requirements, and that the parameter was analyzed for but was not detected above the reported sample quantitation limit.
J	Indicates that the parameter was positively identified; the associated numerical value is the approximate concentration of the parameter in the sample.
UJ	Indicates that the parameter was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
N	The analysis indicates the presence of a parameter for which there is presumptive evidence to make a "tentative identification."
R	Indicates that the sample results for the parameter are rejected or unusable due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the parameter cannot be verified.

## Data Validation Reason Codes

### Holding Times

- A01 Extraction holding times were exceeded.
- A02 Extraction holding times were grossly exceeded.
- A03 Analysis holding times were exceeded.
- A04 Analysis holding times were grossly exceeded.
- A05 Samples were not preserved properly.
- A06 Professional judgment was used to qualify the data.

### GC/MS Tuning

- B01 Mass calibration was in error, even after applying expanded criteria.
- B02 Mass calibration was not performed every 12 hours.
- B03 Mass calibration did not meet ion abundance.
- B04 Professional judgment was used to qualify the data.

### Initial/Continuing Calibration – Organics

- C01 Initial calibration RRF was <0.05.
- C02 Initial calibration RSD was >30%.
- C03 Initial calibration sequence was not followed as required.
- C04 Continuing calibration RRF was <0.05.
- C05 Continuing calibration %D was >25%.
- C06 Continuing calibration was not performed at the required frequency.
- C07 Resolution criteria were not met.
- C08 RPD criteria were not met.
- C09 RSD criteria were not met.
- C10 Retention time of compounds was outside windows.
- C11 Compounds were not adequately resolved.
- C12 Breakdown of endrin or DDT was >20%.
- C13 Combined breakdown of endrin/DDT was >30%.
- C14 Professional judgment was used to qualify the data.

### Blanks

- F01 Sample data were qualified as a result of the method blank.
- F02 Sample data were qualified as a result of the field blank.
- F03 Sample data were qualified as a result of the equipment rinsate.
- F04 Sample data were qualified as a result of the trip blank.
- F05 Gross contamination exists.
- F06 Concentration of the contaminant was detected at a level below the CRQL.
- F07 Concentration of the contaminant was detected at a level less than the action limit, but greater than the CRQL.
- F08 Concentration of the contaminant was detected at a level that exceeds the action level.
- F09 No laboratory blanks were analyzed.
- F10 Blank had a negative value >2x's the IDL.
- F11 Blanks were not analyzed at required frequency.
- F12 Professional judgment was used to qualify the data.

**Surrogate/Radiological Chemical Recovery**

- G01 Surrogate/radiological chemical recovery was above the upper control limit.
- G02 Surrogate/radiological chemical recovery was below the lower control limit.
- G03 Surrogate recovery was <10%.
- G04 Surrogate/radiological chemical recovery was zero.
- G05 Surrogate/radiological chemical recovery was not present.
- G06 Professional judgment was used to qualify the data.
- G07 Radiological chemical recovery was <20%.
- G08 Radiological chemical recovery was >150%.

**Matrix Spike/Matrix Spike Duplicate**

- H01 MS/MSD recovery was above the upper control limit.
- H02 MS/MSD recovery was below the lower control limit.
- H03 MS/MSD recovery was <10%.
- H04 MS/MSD pairs exceed the RPD limit.
- H05 No action was taken on MS/MSD results.
- H06 Professional judgment was used to qualify the data.
- H07 Radiological MS/MSD recovery was <20%.
- H08 Radiological MS/MSD recovery was >160%.
- H09 Radiological MS/MSD samples were not analyzed at the required frequency.

**Laboratory Duplicate**

- J01 Duplicate RPD/normalized absolute difference (NAD) was outside the control limit.
- J02 Duplicate sample results were >5x the CRDL.
- J03 Duplicate sample results were <5x the CRDL.
- J04 Professional judgment was used to qualify the data.
- J05 Duplicate was not analyzed at the required frequency.

#### **Target Compound Identification**

- M01 Incorrect identifications were made.
- M02 Qualitative criteria were not met.
- M03 Cross contamination occurred.
- M04 Confirmatory analysis was not performed.
- M05 No results were provided.
- M06 Analysis occurred outside 12 hr GC/MS window.
- M07 Professional judgment was used to qualify the data.
- M08 The %D between the two pesticide/PCB column checks was >25%.

#### **Laboratory Control Samples (LCSs)**

- P01 LCS recovery was above upper control limit.
- P02 LCS recovery was below lower control limit.
- P03 LCS recovery was <50%.
- P04 No action was taken on the LCS data.
- P05 LCS was not analyzed at required frequency.
- P06 Radiological LCS recovery was <50% for aqueous samples; <40% for solid samples.
- P07 Radiological LCS recovery was >150% for aqueous samples; >160% for solid samples.
- P08 Professional judgment was used to qualify the data.

#### **Field Duplicate**

- Q01 No action was taken on the basis of field duplicate RPDs.
- Q02 Radiological field duplicate normalized absolute difference (NAD) was outside the control limit.
- Q03 Duplicate sample results were >5x the CRDL.
- Q04 Duplicate sample results were <5x the CRDL.

#### **Radiological Calibration**

- R01 Efficiency calibration criteria were not met.
- R02 Energy calibration criteria were not met.
- R03 Resolution calibration criteria were not met
- R04 Background determination criteria were not met.
- R05 Quench curve criteria were not met.
- R06 Absorption curve criteria were not met.
- R07 Plateau curve criteria were not met.
- R08 Professional judgment was used to qualify the data.

#### **Radiological Calibration Verification**

- S01 Efficiency verification criteria were not met.
- S02 Energy verification criteria were not met.
- S03 Resolution verification criteria were not met
- S04 Background verification criteria were not met.
- S05 Cross-talk verification criteria were not met.
- S06 Professional judgment was used to qualify the data.

### **Radionuclide Quantitation**

- T01 Detection limits were not met.
- T02 Analytical uncertainties were not met and/or not reported.
- T03 Inappropriate aliquot sizes were used.
- T04 Professional judgment was used to qualify the data.
- T05 Analytical result is less than the associated MDA, but greater than the counting uncertainty.
- T06 Analytical result is less than both the associated counting uncertainty and MDA.
- T07 Negative analytical result where the absolute value exceeds 2x the associated MDA.

### **System Performance**

- V01 High background levels or a shift in the energy calibration were observed.
- V02 Extraneous peaks were observed.
- V03 Loss of resolution was observed.
- V04 Peak-tailing or peak splitting that may result in inaccurate quantitation were observed.
- V05 Professional judgment was used to qualify the data.

## DATA VALIDATION REPORT

Date:

November 14, 2003

<b>To:</b> Steve Passig	<b>From:</b> Carol Johnson
<b>Laboratory:</b> Severn Trent – St. Louis	<b>SDG #:</b> F3I230110

Attached you will find the results from the data validation technical review for the Westinghouse/Hematite samples and analyses that are associated with the above referenced laboratory and sample delivery group (SDG) number. These data points have been selected for data validation and the sample index on the following page specifically identifies the samples and analyses associated with this validation review.

The Westinghouse/Hematite validation technical review was performed in accordance with the *Contract Laboratory Program Data Validation Functional Guidelines for Evaluating Inorganic Analytical Data*, and the *Laboratory Data Validation Guidelines for Evaluating Radionuclide Analyses and Radiochemical Data Verification and Validation*. It was based on the information and documentation supplied by the associated laboratory. The analyses were evaluated against criteria established in the related analytical procedures and the Westinghouse/Hematite data quality requirements.

Attachment A to this report provides the Sample Data Summary Sheets for the samples associated with the above referenced request. These summary sheets identify the analytical values and the qualifiers for each sample and parameter. Attachment B outlines the validation qualifiers and reason codes used in the validation of the data.

Report Summary	
Total Number of Samples	7
Total Number of Data Points	24
Total Number of Rejected Data Points	0
Percent Completeness (approval to rejection ratio)	100.0%

# Sample Index

*Date:*

**November 14, 2003**

*Laboratory:*

**Severn Trent – St. Louis**

*SDG #:*

**F3I230110**

<b>WESTINGHOUSE Sample ID</b>	<b>Target Analyses</b>
BHKD5-01	Total Uranium, Conductivity, pH
BHKD5-19	Total Uranium, Conductivity, pH
BHKD5-27	Total Uranium, Conductivity, pH
BHKD3-08	Total Uranium, Conductivity, Ph
BHKD2-04	Total Uranium, Technetium-99, Conductivity, pH
BHKD2-13	Total Uranium, Technetium-99, Conductivity, pH
BHKD2-23	Total Uranium, Technetium-99, Conductivity, pH

**ANALYTICAL CATEGORY: Miscellaneous**

- Specific Conductance was determined by SW846 Method 9050; pH was determined by SW846 Method 9045A; and percent moisture was determined by MCAWW 160.3.

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & blanks
  - laboratory blanks (method, TCLP)
  - laboratory control samples
    - matrix spike samples
  - matrix duplicates
    - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- Holding Times for Conductivity were exceeded, resulting in the samples being qualified as estimated, *J*.

3. Additional comments:

- None

**ANALYTICAL CATEGORY: Radiochemical**

- Isotopic uranium was determined by alpha spectroscopy (NAS/DOE 3050/RP), and technetium was determined by Liquid scintillation counters (DOE TC-02-RC), and Total Uranium was determined by Laser Phosphorimetry Method ASTM 5174-91.

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & background
  - preparation blanks
  - laboratory control samples
    - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- Instrument Counting Error

Several samples have reported results that are less than the MDA and the uncertainty is greater than the result. The non-detect results for these samples were qualified *UJ*.

Method Blank

- Contamination with Technetium-99 and Isotopic Uranium was seen in the method blank. Method blanks are run to verify that contamination is being introduced during the run. Technetium-99 data associated with the method blank did not pass the Normalized Absolute Difference criteria. Samples were qualified as estimated, *J*.

Laboratory Control Sample

The percent recovery for Technetium-99 LCS, was above the upper control limit (UCL). Recoveries above the UCL could be the result of poor preparation or instrumentation problems, and may indicate a high bias to the data. Only positive sample results for qualified as estimated, *J*.

3. Additional comments:

None

**ATTACHMENT A**

**WESTINGHOUSE Sample Data Summary Sheets**

## ATTACHMENT B

### KEY TO THE WESTINGHOUSE DATA VALIDATION QUALIFIERS

QUALIFIERS	
=	Indicates that the data met all QA/QC requirements, and that the parameter has been positively identified and the associated concentration value is accurate.
U	Indicates that the data met all QA/QC requirements, and that the parameter was analyzed for but was not detected above the reported sample quantitation limit.
J	Indicates that the parameter was positively identified; the associated numerical value is the approximate concentration of the parameter in the sample.
UJ	Indicates that the parameter was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
N	The analysis indicates the presence of a parameter for which there is presumptive evidence to make a "tentative identification."
R	Indicates that the sample results for the parameter are rejected or unusable due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the parameter cannot be verified.

## Data Validation Reason Codes

### Holding Times

- A01 Extraction holding times were exceeded.
- A02 Extraction holding times were grossly exceeded.
- A03 Analysis holding times were exceeded.
- A04 Analysis holding times were grossly exceeded.
- A05 Samples were not preserved properly.
- A06 Professional judgment was used to qualify the data.

### GC/MS Tuning

- B01 Mass calibration was in error, even after applying expanded criteria.
- B02 Mass calibration was not performed every 12 hours.
- B03 Mass calibration did not meet ion abundance.
- B04 Professional judgment was used to qualify the data.

### Initial/Continuing Calibration – Organics

- C01 Initial calibration RRF was <0.05.
- C02 Initial calibration RSD was >30%.
- C03 Initial calibration sequence was not followed as required.
- C04 Continuing calibration RRF was <0.05.
- C05 Continuing calibration %D was >25%.
- C06 Continuing calibration was not performed at the required frequency.
- C07 Resolution criteria were not met.
- C08 RPD criteria were not met.
- C09 RSD criteria were not met.
- C10 Retention time of compounds was outside windows.
- C11 Compounds were not adequately resolved.
- C12 Breakdown of endrin or DDT was >20%.
- C13 Combined breakdown of endrin/DDT was >30%.
- C14 Professional judgment was used to qualify the data.

### Blanks

- F01 Sample data were qualified as a result of the method blank.
- F02 Sample data were qualified as a result of the field blank.
- F03 Sample data were qualified as a result of the equipment rinsate.
- F04 Sample data were qualified as a result of the trip blank.
- F05 Gross contamination exists.
- F06 Concentration of the contaminant was detected at a level below the CRQL.
- F07 Concentration of the contaminant was detected at a level less than the action limit, but greater than the CRQL.
- F08 Concentration of the contaminant was detected at a level that exceeds the action level.
- F09 No laboratory blanks were analyzed.
- F10 Blank had a negative value >2x's the IDL.
- F11 Blanks were not analyzed at required frequency.
- F12 Professional judgment was used to qualify the data.

#### **Surrogate/Radiological Chemical Recovery**

- G01 Surrogate/radiological chemical recovery was above the upper control limit.
- G02 Surrogate/radiological chemical recovery was below the lower control limit.
- G03 Surrogate recovery was <10%.
- G04 Surrogate/radiological chemical recovery was zero.
- G05 Surrogate/radiological chemical recovery was not present.
- G06 Professional judgment was used to qualify the data.
- G07 Radiological chemical recovery was <20%.
- G08 Radiological chemical recovery was >150%.

#### **Matrix Spike/Matrix Spike Duplicate**

- H01 MS/MSD recovery was above the upper control limit.
- H02 MS/MSD recovery was below the lower control limit.
- H03 MS/MSD recovery was <10%.
- H04 MS/MSD pairs exceed the RPD limit.
- H05 No action was taken on MS/MSD results.
- H06 Professional judgment was used to qualify the data.
- H07 Radiological MS/MSD recovery was <20%.
- H08 Radiological MS/MSD recovery was >160%.
- H09 Radiological MS/MSD samples were not analyzed at the required frequency.

#### **Laboratory Duplicate**

- J01 Duplicate RPD/normalized absolute difference (NAD) was outside the control limit.
- J02 Duplicate sample results were >5x the CRDL.
- J03 Duplicate sample results were <5x the CRDL.
- J04 Professional judgment was used to qualify the data.
- J05 Duplicate was not analyzed at the required frequency.

### **Target Compound Identification**

- M01 Incorrect identifications were made.
- M02 Qualitative criteria were not met.
- M03 Cross contamination occurred.
- M04 Confirmatory analysis was not performed.
- M05 No results were provided.
- M06 Analysis occurred outside 12 hr GC/MS window.
- M07 Professional judgment was used to qualify the data.
- M08 The %D between the two pesticide/PCB column checks was >25%.

### **Laboratory Control Samples (LCSs)**

- P01 LCS recovery was above upper control limit.
- P02 LCS recovery was below lower control limit.
- P03 LCS recovery was <50%.
- P04 No action was taken on the LCS data.
- P05 LCS was not analyzed at required frequency.
- P06 Radiological LCS recovery was <50% for aqueous samples; <40% for solid samples.
- P07 Radiological LCS recovery was >150% for aqueous samples; >160% for solid samples.
- P08 Professional judgment was used to qualify the data.

### **Field Duplicate**

- Q01 No action was taken on the basis of field duplicate RPDs.
- Q02 Radiological field duplicate normalized absolute difference (NAD) was outside the control limit.
- Q03 Duplicate sample results were >5x the CRDL.
- Q04 Duplicate sample results were <5x the CRDL.

### **Radiological Calibration**

- R01 Efficiency calibration criteria were not met.
- R02 Energy calibration criteria were not met.
- R03 Resolution calibration criteria were not met
- R04 Background determination criteria were not met.
- R05 Quench curve criteria were not met.
- R06 Absorption curve criteria were not met.
- R07 Plateau curve criteria were not met.
- R08 Professional judgment was used to qualify the data.

### **Radiological Calibration Verification**

- S01 Efficiency verification criteria were not met.
- S02 Energy verification criteria were not met.
- S03 Resolution verification criteria were not met
- S04 Background verification criteria were not met.
- S05 Cross-talk verification criteria were not met.
- S06 Professional judgment was used to qualify the data.

### **Radionuclide Quantitation**

- T01 Detection limits were not met.
- T02 Analytical uncertainties were not met and/or not reported.
- T03 Inappropriate aliquot sizes were used.
- T04 Professional judgment was used to qualify the data.
- T05 Analytical result is less than the associated MDA, but greater than the counting uncertainty.
- T06 Analytical result is less than both the associated counting uncertainty and MDA.
- T07 Negative analytical result where the absolute value exceeds 2x the associated MDA.

### **System Performance**

- V01 High background levels or a shift in the energy calibration were observed.
- V02 Extraneous peaks were observed.
- V03 Loss of resolution was observed.
- V04 Peak-tailing or peak splitting that may result in inaccurate quantitation were observed.
- V05 Professional judgment was used to qualify the data.

## DATA VALIDATION REPORT

Date:

November 14, 2003

To: Steve Passig	From: Carol Johnson
Laboratory: Severn Trent – St. Louis	SDG #: F3I230117

Attached you will find the results from the data validation technical review for the Westinghouse/Hematite samples and analyses that are associated with the above referenced laboratory and sample delivery group (SDG) number. These data points have been selected for data validation and the sample index on the following page specifically identifies the samples and analyses associated with this validation review.

The Westinghouse/Hematite validation technical review was performed in accordance with the *Contract Laboratory Program Data Validation Functional Guidelines for Evaluating Inorganic Analytical Data*, and the *Laboratory Data Validation Guidelines for Evaluating Radionuclide Analyses and Radiochemical Data Verification and Validation*. It was based on the information and documentation supplied by the associated laboratory. The analyses were evaluated against criteria established in the related analytical procedures and the Westinghouse/Hematite data quality requirements.

Attachment A to this report provides the Sample Data Summary Sheets for the samples associated with the above referenced request. These summary sheets identify the analytical values and the qualifiers for each sample and parameter. Attachment B outlines the validation qualifiers and reason codes used in the validation of the data.

Report Summary	
Total Number of Samples	11
Total Number of Data Points	65
Total Number of Rejected Data Points	0
Percent Completeness (approval to rejection ratio)	100.0%

## Sample Index

Date:

November 14, 2003

Laboratory:

Severn Trent - St. Louis

SDG #:

F3I230117

WESTINGHOUSE Sample ID	Target Analyses
BHKD2-04	Isotopic Uranium, Total Uranium, Technetium-99, Conductivity, pH
BHKD2-13	Isotopic Uranium, Total Uranium, Technetium-99, Conductivity, pH
BHKD2-23	Isotopic Uranium, Total Uranium, Technetium-99, Conductivity, pH
BHKD3-08	Isotopic Uranium, Total Uranium, Technetium-99, Conductivity, pH, Percent Moisture
BHKD5-01	Total Uranium, Conductivity, pH, Percent Moisture
BHKD5-19	Isotopic Uranium, Total Uranium, Technetium-99, Conductivity, pH, Percent Moisture
BHKD5-27	Isotopic Uranium, Total Uranium, Technetium-99, Conductivity, pH, Percent Moisture
BHKD5-01	Isotopic Uranium, Technetium-99
BHKD5-19	Isotopic Uranium, Technetium-99, Percent Moisture
BHKD5-27	Isotopic Uranium, Technetium-99, Percent Moisture
BHKD3-08	Isotopic Uranium, Technetium-99, Percent Moisture

**ANALYTICAL CATEGORY: Miscellaneous**

- Specific Conductance was determined by SW846 Method 9050; pH was determined by SW846 Method 9045A; and percent moisture was determined by MCAWW 160.3.

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & blanks
  - laboratory blanks (method, TCLP)
  - laboratory control samples
    - matrix spike samples
  - matrix duplicates
    - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- None.

3. Additional comments:

- None

**ANALYTICAL CATEGORY: Radiochemical**

- Isotopic uranium was determined by alpha spectroscopy (NAS/DOE 3050/RP), and technetium was determined by Liquid scintillation counters (DOE TC-02-RC), and Total Uranium was determined by Laser Phosphorimetry Method ASTM 5174-91.

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & background
  - preparation blanks
  - laboratory control samples
  - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- Instrument Counting Error

Several samples have reported results that are less than the MDA and the uncertainty is greater than the result. The non-detect results for these samples were qualified *UJ*.

Method Blank

- Contamination with Technetium-99 and Isotopic Uranium was seen in the method blank. Method blanks are run to verify that contamination is being introduced during the run. Technetium-99 data associated with the method blank did not pass the Normalized Absolute Difference criteria. Samples were qualified as estimated, *J*.
- Laboratory Control Sample

The percent recovery for Technetium-99 LCS, was above the upper control limit (UCL). Recoveries above the UCL could be the result of poor preparation or instrumentation problems, and may indicate a high bias to the data. Only positive sample results for qualified as estimated, *J*.

3. Additional comments:  
None

# **ATTACHMENT A**

**WESTINGHOUSE Sample Data Summary Sheets**

# ATTACHMENT B

## KEY TO THE WESTINGHOUSE DATA VALIDATION QUALIFIERS

QUALIFIERS	
=	Indicates that the data met all QA/QC requirements, and that the parameter has been positively identified and the associated concentration value is accurate.
U	Indicates that the data met all QA/QC requirements, and that the parameter was analyzed for but was not detected above the reported sample quantitation limit.
J	Indicates that the parameter was positively identified; the associated numerical value is the approximate concentration of the parameter in the sample.
UJ	Indicates that the parameter was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
N	The analysis indicates the presence of a parameter for which there is presumptive evidence to make a "tentative identification."
R	Indicates that the sample results for the parameter are rejected or unusable due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the parameter cannot be verified.

## Data Validation Reason Codes

### Holding Times

- A01 Extraction holding times were exceeded.
- A02 Extraction holding times were grossly exceeded.
- A03 Analysis holding times were exceeded.
- A04 Analysis holding times were grossly exceeded.
- A05 Samples were not preserved properly.
- A06 Professional judgment was used to qualify the data.

### GC/MS Tuning

- B01 Mass calibration was in error, even after applying expanded criteria.
- B02 Mass calibration was not performed every 12 hours.
- B03 Mass calibration did not meet ion abundance.
- B04 Professional judgment was used to qualify the data.

### Initial/Continuing Calibration – Organics

- C01 Initial calibration RRF was <0.05.
- C02 Initial calibration RSD was >30%.
- C03 Initial calibration sequence was not followed as required.
- C04 Continuing calibration RRF was <0.05.
- C05 Continuing calibration %D was >25%.
- C06 Continuing calibration was not performed at the required frequency.
- C07 Resolution criteria were not met.
- C08 RPD criteria were not met.
- C09 RSD criteria were not met.
- C10 Retention time of compounds was outside windows.
- C11 Compounds were not adequately resolved.
- C12 Breakdown of endrin or DDT was >20%.
- C13 Combined breakdown of endrin/DDT was >30%.
- C14 Professional judgment was used to qualify the data.

### Blanks

- F01 Sample data were qualified as a result of the method blank.
- F02 Sample data were qualified as a result of the field blank.
- F03 Sample data were qualified as a result of the equipment rinsate.
- F04 Sample data were qualified as a result of the trip blank.
- F05 Gross contamination exists.
- F06 Concentration of the contaminant was detected at a level below the CRQL.
- F07 Concentration of the contaminant was detected at a level less than the action limit, but greater than the CRQL.
- F08 Concentration of the contaminant was detected at a level that exceeds the action level.
- F09 No laboratory blanks were analyzed.
- F10 Blank had a negative value >2x's the IDL.
- F11 Blanks were not analyzed at required frequency.
- F12 Professional judgment was used to qualify the data.

### **Surrogate/Radiological Chemical Recovery**

- G01 Surrogate/radiological chemical recovery was above the upper control limit.
- G02 Surrogate/radiological chemical recovery was below the lower control limit.
- G03 Surrogate recovery was <10%.
- G04 Surrogate/radiological chemical recovery was zero.
- G05 Surrogate/radiological chemical recovery was not present.
- G06 Professional judgment was used to qualify the data.
- G07 Radiological chemical recovery was <20%.
- G08 Radiological chemical recovery was >150%.

### **Matrix Spike/Matrix Spike Duplicate**

- H01 MS/MSD recovery was above the upper control limit.
- H02 MS/MSD recovery was below the lower control limit.
- H03 MS/MSD recovery was <10%.
- H04 MS/MSD pairs exceed the RPD limit.
- H05 No action was taken on MS/MSD results.
- H06 Professional judgment was used to qualify the data.
- H07 Radiological MS/MSD recovery was <20%.
- H08 Radiological MS/MSD recovery was >160%.
- H09 Radiological MS/MSD samples were not analyzed at the required frequency.

### **Laboratory Duplicate**

- J01 Duplicate RPD/normalized absolute difference (NAD) was outside the control limit.
- J02 Duplicate sample results were >5x the CRDL.
- J03 Duplicate sample results were <5x the CRDL.
- J04 Professional judgment was used to qualify the data.
- J05 Duplicate was not analyzed at the required frequency.

### **Target Compound Identification**

- M01 Incorrect identifications were made.
- M02 Qualitative criteria were not met.
- M03 Cross contamination occurred.
- M04 Confirmatory analysis was not performed.
- M05 No results were provided.
- M06 Analysis occurred outside 12 hr GC/MS window.
- M07 Professional judgment was used to qualify the data.
- M08 The %D between the two pesticide/PCB column checks was >25%.

### **Laboratory Control Samples (LCSs)**

- P01 LCS recovery was above upper control limit.
- P02 LCS recovery was below lower control limit.
- P03 LCS recovery was <50%.
- P04 No action was taken on the LCS data.
- P05 LCS was not analyzed at required frequency.
- P06 Radiological LCS recovery was <50% for aqueous samples; <40% for solid samples.
- P07 Radiological LCS recovery was >150% for aqueous samples; >160% for solid samples.
- P08 Professional judgment was used to qualify the data.

### **Field Duplicate**

- Q01 No action was taken on the basis of field duplicate RPDs.
- Q02 Radiological field duplicate normalized absolute difference (NAD) was outside the control limit.
- Q03 Duplicate sample results were >5x the CRDL.
- Q04 Duplicate sample results were <5x the CRDL.

### **Radiological Calibration**

- R01 Efficiency calibration criteria were not met.
- R02 Energy calibration criteria were not met.
- R03 Resolution calibration criteria were not met
- R04 Background determination criteria were not met.
- R05 Quench curve criteria were not met.
- R06 Absorption curve criteria were not met.
- R07 Plateau curve criteria were not met.
- R08 Professional judgment was used to qualify the data.

### **Radiological Calibration Verification**

- S01 Efficiency verification criteria were not met.
- S02 Energy verification criteria were not met.
- S03 Resolution verification criteria were not met
- S04 Background verification criteria were not met.
- S05 Cross-talk verification criteria were not met.
- S06 Professional judgment was used to qualify the data.

### **Radionuclide Quantitation**

- T01 Detection limits were not met.
- T02 Analytical uncertainties were not met and/or not reported.
- T03 Inappropriate aliquot sizes were used.
- T04 Professional judgment was used to qualify the data.
- T05 Analytical result is less than the associated MDA, but greater than the counting uncertainty.
- T06 Analytical result is less than both the associated counting uncertainty and MDA.
- T07 Negative analytical result where the absolute value exceeds 2x the associated MDA.

### **System Performance**

- V01 High background levels or a shift in the energy calibration were observed.
- V02 Extraneous peaks were observed.
- V03 Loss of resolution was observed.
- V04 Peak-tailing or peak splitting that may result in inaccurate quantitation were observed.
- V05 Professional judgment was used to qualify the data.

## DATA VALIDATION REPORT

Date:

November 17, 2003

<b>To:</b> Steve Passig	<b>From:</b> Carol Johnson
<b>Laboratory:</b> Severn Trent – St. Louis	<b>SDG #:</b> F3J140125

Attached you will find the results from the data validation technical review for the Westinghouse/Hematite samples and analyses that are associated with the above referenced laboratory and sample delivery group (SDG) number. These data points have been selected for data validation and the sample index on the following page specifically identifies the samples and analyses associated with this validation review.

The Westinghouse/Hematite validation technical review was performed in accordance with the *Contract Laboratory Program Data Validation Functional Guidelines for Evaluating Inorganic Analytical Data*, and the *Laboratory Data Validation Guidelines for Evaluating Radionuclide Analyses and Radiochemical Data Verification and Validation*. It was based on the information and documentation supplied by the associated laboratory. The analyses were evaluated against criteria established in the related analytical procedures and the Westinghouse/Hematite data quality requirements.

Attachment A to this report provides the Sample Data Summary Sheets for the samples associated with the above referenced request. These summary sheets identify the analytical values and the qualifiers for each sample and parameter. Attachment B outlines the validation qualifiers and reason codes used in the validation of the data.

Report Summary	
Total Number of Samples	11
Total Number of Data Points	24
Total Number of Rejected Data Points	0
Percent Completeness (approval to rejection ratio)	100.0%

# Sample Index

Date:

November 17, 2003

Laboratory:

Severn Trent - St. Louis

SDG #:

F3J140125

WESTINGHOUSE Sample ID	Target Analyses
BHKD4-14	Total Uranium, Technetium-99, pH
BHKD6-01	Total Uranium, Technetium-99, pH
BHKD1-04	Total Uranium, pH
BHKD1-23	Total Uranium, pH
BHKD1-28	Total Uranium, pH
BHKD3-16	Total Uranium, pH
BHKD3-23	Total Uranium, pH
BHKD4-02	Total Uranium, pH
BHKD4-24	Total Uranium, pH
BHKD6-11	Total Uranium, pH
BHKD6-26	Total Uranium, pH

**ANALYTICAL CATEGORY: Miscellaneous**

- pH was determined by SW846 Method 9045A.
- 1. The following items (as applicable) have been addressed during the validation review:
  - sample custody, integrity & preservation
  - sample handling & preparation
  - holding times
  - instrument calibration & performance
  - dilution factors
  - detection limits
  - laboratory background & carry-over
  - overall appearance of the data
  - Quality Control:
    - calibration checks & blanks
    - laboratory blanks (method, TCLP)
    - laboratory control samples
      - matrix spike samples
    - matrix duplicates
    - field blanks (if available)
    - field duplicates (if available)
- 2. The above items were found to be acceptable, except as follows:
  - none
- 3. Additional comments:
  - none

**ANALYTICAL CATEGORY: Radiochemical**

- Total Uranium was determined by Laser Phosphorimetry Method ASTM 5174-91, Technetium was determined by Liquid scintillation counters (DOE TC-02-RC).
1. The following items (as applicable) have been addressed during the validation review:
    - sample custody, integrity & preservation
    - sample handling & preparation
    - holding times
    - instrument calibration & performance
    - dilution factors
    - detection limits
    - laboratory background & carry-over
    - overall appearance of the data
    - Quality Control:
      - calibration checks & background
      - preparation blanks
      - laboratory control samples
      - field blanks (if available)
      - field duplicates (if available)
  2. The above items were found to be acceptable, except as follows:

None
  3. Additional comments:

None

# **ATTACHMENT A**

## **WESTINGHOUSE Sample Data Summary Sheets**

## ATTACHMENT B

### KEY TO THE WESTINGHOUSE DATA VALIDATION QUALIFIERS

QUALIFIERS	
=	Indicates that the data met all QA/QC requirements, and that the parameter has been positively identified and the associated concentration value is accurate.
U	Indicates that the data met all QA/QC requirements, and that the parameter was analyzed for but was not detected above the reported sample quantitation limit.
J	Indicates that the parameter was positively identified; the associated numerical value is the approximate concentration of the parameter in the sample.
UJ	Indicates that the parameter was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
N	The analysis indicates the presence of a parameter for which there is presumptive evidence to make a "tentative identification."
R	Indicates that the sample results for the parameter are rejected or unusable due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the parameter cannot be verified.

## Data Validation Reason Codes

### Holding Times

- A01 Extraction holding times were exceeded.
- A02 Extraction holding times were grossly exceeded.
- A03 Analysis holding times were exceeded.
- A04 Analysis holding times were grossly exceeded.
- A05 Samples were not preserved properly.
- A06 Professional judgment was used to qualify the data.

### GC/MS Tuning

- B01 Mass calibration was in error, even after applying expanded criteria.
- B02 Mass calibration was not performed every 12 hours.
- B03 Mass calibration did not meet ion abundance.
- B04 Professional judgment was used to qualify the data.

### Initial/Continuing Calibration – Organics

- C01 Initial calibration RRF was  $<0.05$ .
- C02 Initial calibration RSD was  $>30\%$ .
- C03 Initial calibration sequence was not followed as required.
- C04 Continuing calibration RRF was  $<0.05$ .
- C05 Continuing calibration %D was  $>25\%$ .
- C06 Continuing calibration was not performed at the required frequency.
- C07 Resolution criteria were not met.
- C08 RPD criteria were not met.
- C09 RSD criteria were not met.
- C10 Retention time of compounds was outside windows.
- C11 Compounds were not adequately resolved.
- C12 Breakdown of endrin or DDT was  $>20\%$ .
- C13 Combined breakdown of endrin/DDT was  $>30\%$ .
- C14 Professional judgment was used to qualify the data.

### Blanks

- F01 Sample data were qualified as a result of the method blank.
- F02 Sample data were qualified as a result of the field blank.
- F03 Sample data were qualified as a result of the equipment rinsate.
- F04 Sample data were qualified as a result of the trip blank.
- F05 Gross contamination exists.
- F06 Concentration of the contaminant was detected at a level below the CRQL.
- F07 Concentration of the contaminant was detected at a level less than the action limit, but greater than the CRQL.
- F08 Concentration of the contaminant was detected at a level that exceeds the action level.
- F09 No laboratory blanks were analyzed.
- F10 Blank had a negative value  $>2x$ 's the IDL.
- F11 Blanks were not analyzed at required frequency.
- F12 Professional judgment was used to qualify the data.

#### **Surrogate/Radiological Chemical Recovery**

- G01 Surrogate/radiological chemical recovery was above the upper control limit.
- G02 Surrogate/radiological chemical recovery was below the lower control limit.
- G03 Surrogate recovery was <10%.
- G04 Surrogate/radiological chemical recovery was zero.
- G05 Surrogate/radiological chemical recovery was not present.
- G06 Professional judgment was used to qualify the data.
- G07 Radiological chemical recovery was <20%.
- G08 Radiological chemical recovery was >150%.

#### **Matrix Spike/Matrix Spike Duplicate**

- H01 MS/MSD recovery was above the upper control limit.
- H02 MS/MSD recovery was below the lower control limit.
- H03 MS/MSD recovery was <10%.
- H04 MS/MSD pairs exceed the RPD limit.
- H05 No action was taken on MS/MSD results.
- H06 Professional judgment was used to qualify the data.
- H07 Radiological MS/MSD recovery was <20%.
- H08 Radiological MS/MSD recovery was >160%.
- H09 Radiological MS/MSD samples were not analyzed at the required frequency.

#### **Laboratory Duplicate**

- J01 Duplicate RPD/normalized absolute difference (NAD) was outside the control limit.
- J02 Duplicate sample results were >5x the CRDL.
- J03 Duplicate sample results were <5x the CRDL.
- J04 Professional judgment was used to qualify the data.
- J05 Duplicate was not analyzed at the required frequency.

### **Target Compound Identification**

- M01 Incorrect identifications were made.
- M02 Qualitative criteria were not met.
- M03 Cross contamination occurred.
- M04 Confirmatory analysis was not performed.
- M05 No results were provided.
- M06 Analysis occurred outside 12 hr GC/MS window.
- M07 Professional judgment was used to qualify the data.
- M08 The %D between the two pesticide/PCB column checks was >25%.

### **Laboratory Control Samples (LCSs)**

- P01 LCS recovery was above upper control limit.
- P02 LCS recovery was below lower control limit.
- P03 LCS recovery was <50%.
- P04 No action was taken on the LCS data.
- P05 LCS was not analyzed at required frequency.
- P06 Radiological LCS recovery was <50% for aqueous samples; <40% for solid samples.
- P07 Radiological LCS recovery was >150% for aqueous samples; >160% for solid samples.
- P08 Professional judgment was used to qualify the data.

### **Field Duplicate**

- Q01 No action was taken on the basis of field duplicate RPDs.
- Q02 Radiological field duplicate normalized absolute difference (NAD) was outside the control limit.
- Q03 Duplicate sample results were >5x the CRDL.
- Q04 Duplicate sample results were <5x the CRDL.

### **Radiological Calibration**

- R01 Efficiency calibration criteria were not met.
- R02 Energy calibration criteria were not met.
- R03 Resolution calibration criteria were not met.
- R04 Background determination criteria were not met.
- R05 Quench curve criteria were not met.
- R06 Absorption curve criteria were not met.
- R07 Plateau curve criteria were not met.
- R08 Professional judgment was used to qualify the data.

### **Radiological Calibration Verification**

- S01 Efficiency verification criteria were not met.
- S02 Energy verification criteria were not met.
- S03 Resolution verification criteria were not met.
- S04 Background verification criteria were not met.
- S05 Cross-talk verification criteria were not met.
- S06 Professional judgment was used to qualify the data.

### **Radionuclide Quantitation**

- T01 Detection limits were not met.
- T02 Analytical uncertainties were not met and/or not reported.
- T03 Inappropriate aliquot sizes were used.
- T04 Professional judgment was used to qualify the data.
- T05 Analytical result is less than the associated MDA, but greater than the counting uncertainty.
- T06 Analytical result is less than both the associated counting uncertainty and MDA.
- T07 Negative analytical result where the absolute value exceeds 2x the associated MDA.

### **System Performance**

- V01 High background levels or a shift in the energy calibration were observed.
- V02 Extraneous peaks were observed.
- V03 Loss of resolution was observed.
- V04 Peak-tailing or peak splitting that may result in inaccurate quantitation were observed.
- V05 Professional judgment was used to qualify the data.

## DATA VALIDATION REPORT

Date:

November 17, 2003

To: <b>Steve Passig</b>	From: <b>Carol Johnson</b>
Laboratory: <b>Severn Trent – St. Louis</b>	SDG #: <b>F3J140132</b>

Attached you will find the results from the data validation technical review for the Westinghouse/Hematite samples and analyses that are associated with the above referenced laboratory and sample delivery group (SDG) number. These data points have been selected for data validation and the sample index on the following page specifically identifies the samples and analyses associated with this validation review.

The Westinghouse/Hematite validation technical review was performed in accordance with the *Contract Laboratory Program Data Validation Functional Guidelines for Evaluating Inorganic Analytical Data*, and the *Laboratory Data Validation Guidelines for Evaluating Radionuclide Analyses and Radiochemical Data Verification and Validation*. It was based on the information and documentation supplied by the associated laboratory. The analyses were evaluated against criteria established in the related analytical procedures and the Westinghouse/Hematite data quality requirements.

Attachment A to this report provides the Sample Data Summary Sheets for the samples associated with the above referenced request. These summary sheets identify the analytical values and the qualifiers for each sample and parameter. Attachment B outlines the validation qualifiers and reason codes used in the validation of the data.

Report Summary	
Total Number of Samples	11
Total Number of Data Points	24
Total Number of Rejected Data Points	0
Percent Completeness (approval to rejection ratio)	100.0%

# Sample Index

Date:

November 17, 2003

Laboratory:

Severn Trent - St. Louis

SDG #:

F3J140132

WESTINGHOUSE Sample ID	Target Analyses
BHKD4-14	Total Uranium, Technetium-99, pH
BHKD6-01	Total Uranium, Technetium-99, pH
BHKD1-04	Total Uranium, pH
BHKD1-23	Total Uranium, pH
BHKD1-28	Total Uranium, pH
BHKD3-16	Total Uranium, pH
BHKD3-23	Total Uranium, pH
BHKD4-02	Total Uranium, pH
BHKD4-24	Total Uranium, pH
BHKD6-11	Total Uranium, pH
BHKD6-26	Total Uranium, pH

**ANALYTICAL CATEGORY: Miscellaneous**

- pH was determined by SW846 Method 9045A.

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & blanks
  - laboratory blanks (method, TCLP)
  - laboratory control samples
    - matrix spike samples
  - matrix duplicates
    - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

- none

3. Additional comments:

- none

**ANALYTICAL CATEGORY: Radiochemical**

- Total Uranium was determined by Laser Phosphorimetry Method ASTM 5174-91 Technetium was determined by Liquid scintillation counters (DOE TC-02-RC)

1. The following items (as applicable) have been addressed during the validation review:

- sample custody, integrity & preservation
- sample handling & preparation
- holding times
- instrument calibration & performance
- dilution factors
- detection limits
- laboratory background & carry-over
- overall appearance of the data
- Quality Control:
  - calibration checks & background
  - preparation blanks
  - laboratory control samples
  - field blanks (if available)
  - field duplicates (if available)

2. The above items were found to be acceptable, except as follows:

None

3. Additional comments:

None

**ATTACHMENT A**

**WESTINGHOUSE Sample Data Summary Sheets**

# ATTACHMENT B

## KEY TO THE WESTINGHOUSE DATA VALIDATION QUALIFIERS

QUALIFIERS	
=	Indicates that the data met all QA/QC requirements, and that the parameter has been positively identified and the associated concentration value is accurate.
U	Indicates that the data met all QA/QC requirements, and that the parameter was analyzed for but was not detected above the reported sample quantitation limit.
J	Indicates that the parameter was positively identified; the associated numerical value is the approximate concentration of the parameter in the sample.
UJ	Indicates that the parameter was not detected above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
N	The analysis indicates the presence of a parameter for which there is presumptive evidence to make a "tentative identification."
R	Indicates that the sample results for the parameter are rejected or unusable due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the parameter cannot be verified.

## Data Validation Reason Codes

### Holding Times

- A01 Extraction holding times were exceeded.
- A02 Extraction holding times were grossly exceeded.
- A03 Analysis holding times were exceeded.
- A04 Analysis holding times were grossly exceeded.
- A05 Samples were not preserved properly.
- A06 Professional judgment was used to qualify the data.

### GC/MS Tuning

- B01 Mass calibration was in error, even after applying expanded criteria.
- B02 Mass calibration was not performed every 12 hours.
- B03 Mass calibration did not meet ion abundance.
- B04 Professional judgment was used to qualify the data.

### Initial/Continuing Calibration – Organics

- C01 Initial calibration RRF was <0.05.
- C02 Initial calibration RSD was >30%.
- C03 Initial calibration sequence was not followed as required.
- C04 Continuing calibration RRF was <0.05.
- C05 Continuing calibration %D was >25%.
- C06 Continuing calibration was not performed at the required frequency.
- C07 Resolution criteria were not met.
- C08 RPD criteria were not met.
- C09 RSD criteria were not met.
- C10 Retention time of compounds was outside windows.
- C11 Compounds were not adequately resolved.
- C12 Breakdown of endrin or DDT was >20%.
- C13 Combined breakdown of endrin/DDT was >30%.
- C14 Professional judgment was used to qualify the data.

### Blanks

- F01 Sample data were qualified as a result of the method blank.
- F02 Sample data were qualified as a result of the field blank.
- F03 Sample data were qualified as a result of the equipment rinsate.
- F04 Sample data were qualified as a result of the trip blank.
- F05 Gross contamination exists.
- F06 Concentration of the contaminant was detected at a level below the CRQL.
- F07 Concentration of the contaminant was detected at a level less than the action limit, but greater than the CRQL.
- F08 Concentration of the contaminant was detected at a level that exceeds the action level.
- F09 No laboratory blanks were analyzed.
- F10 Blank had a negative value >2x's the IDL.
- F11 Blanks were not analyzed at required frequency.
- F12 Professional judgment was used to qualify the data.

#### **Surrogate/Radiological Chemical Recovery**

- G01 Surrogate/radiological chemical recovery was above the upper control limit.
- G02 Surrogate/radiological chemical recovery was below the lower control limit.
- G03 Surrogate recovery was <10%.
- G04 Surrogate/radiological chemical recovery was zero.
- G05 Surrogate/radiological chemical recovery was not present.
- G06 Professional judgment was used to qualify the data.
- G07 Radiological chemical recovery was <20%.
- G08 Radiological chemical recovery was >150%.

#### **Matrix Spike/Matrix Spike Duplicate**

- H01 MS/MSD recovery was above the upper control limit.
- H02 MS/MSD recovery was below the lower control limit.
- H03 MS/MSD recovery was <10%.
- H04 MS/MSD pairs exceed the RPD limit.
- H05 No action was taken on MS/MSD results.
- H06 Professional judgment was used to qualify the data.
- H07 Radiological MS/MSD recovery was <20%.
- H08 Radiological MS/MSD recovery was >160%.
- H09 Radiological MS/MSD samples were not analyzed at the required frequency.

#### **Laboratory Duplicate**

- J01 Duplicate RPD/normalized absolute difference (NAD) was outside the control limit.
- J02 Duplicate sample results were >5x the CRDL.
- J03 Duplicate sample results were <5x the CRDL.
- J04 Professional judgment was used to qualify the data.
- J05 Duplicate was not analyzed at the required frequency.

### **Target Compound Identification**

- M01 Incorrect identifications were made.
- M02 Qualitative criteria were not met.
- M03 Cross contamination occurred.
- M04 Confirmatory analysis was not performed.
- M05 No results were provided.
- M06 Analysis occurred outside 12 hr GC/MS window.
- M07 Professional judgment was used to qualify the data.
- M08 The %D between the two pesticide/PCB column checks was >25%.

### **Laboratory Control Samples (LCSs)**

- P01 LCS recovery was above upper control limit.
- P02 LCS recovery was below lower control limit.
- P03 LCS recovery was <50%.
- P04 No action was taken on the LCS data.
- P05 LCS was not analyzed at required frequency.
- P06 Radiological LCS recovery was <50% for aqueous samples; <40% for solid samples.
- P07 Radiological LCS recovery was >150% for aqueous samples; >160% for solid samples.
- P08 Professional judgment was used to qualify the data.

### **Field Duplicate**

- Q01 No action was taken on the basis of field duplicate RPDs.
- Q02 Radiological field duplicate normalized absolute difference (NAD) was outside the control limit.
- Q03 Duplicate sample results were >5x the CRDL.
- Q04 Duplicate sample results were <5x the CRDL.

### **Radiological Calibration**

- R01 Efficiency calibration criteria were not met.
- R02 Energy calibration criteria were not met.
- R03 Resolution calibration criteria were not met.
- R04 Background determination criteria were not met.
- R05 Quench curve criteria were not met.
- R06 Absorption curve criteria were not met.
- R07 Plateau curve criteria were not met.
- R08 Professional judgment was used to qualify the data.

### **Radiological Calibration Verification**

- S01 Efficiency verification criteria were not met.
- S02 Energy verification criteria were not met.
- S03 Resolution verification criteria were not met.
- S04 Background verification criteria were not met.
- S05 Cross-talk verification criteria were not met.
- S06 Professional judgment was used to qualify the data.

### **Radionuclide Quantitation**

- T01 Detection limits were not met.
- T02 Analytical uncertainties were not met and/or not reported.
- T03 Inappropriate aliquot sizes were used.
- T04 Professional judgment was used to qualify the data.
- T05 Analytical result is less than the associated MDA, but greater than the counting uncertainty.
- T06 Analytical result is less than both the associated counting uncertainty and MDA.
- T07 Negative analytical result where the absolute value exceeds 2x the associated MDA.

### **System Performance**

- V01 High background levels or a shift in the energy calibration were observed.
- V02 Extraneous peaks were observed.
- V03 Loss of resolution was observed.
- V04 Peak-tailing or peak splitting that may result in inaccurate quantitation were observed.
- V05 Professional judgment was used to qualify the data.