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Geochemical Characterization Data Package for the Vadose Zone in the Single-Shell Tank Waste Management Areas at the Hanford Site

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Summary

This data package summarizes laboratory characterization data from Phase 1 of the *Resource Conservation and Recovery Act of 1976[1]* (RCRA) Corrective Action Plan, which focused on contaminant occurrence and mobility in vadose zone sediments beneath the single-shell tank (SST) farms and the Integrated Disposal Facility at the U.S. Department of Energy's Hanford Site located in southeastern Washington State. Phase 1 activities focused on the contamination events that posed the greatest risk to human health and the environment. These characterization studies at the SST farms were performed in support of the Tank Farm Vadose Zone Program by Pacific Northwest National Laboratory researchers working on the Vadose Zone Characterization Project. This characterization work has the following four primary objectives:

- Identify the type, quantity, lateral location, and vertical extent of specific contaminants (e.g., uranium, ^{99}Tc, ^{137}Cs, and ^{60}Co) in the vadose zone sediments

- Understand the physical processes that affect the transport of contaminants in the sediments

- When practical, identify the source(s) of contamination found in the sediment samples

- When practical, determine if a link can be made between the observed vadose zone contamination and any known nearby groundwater contamination.

Vadose zone characterization studies have been completed for sediment samples from SST waste management areas (WMAs) A-AX, B-BX-BY, C, S-SX, T, TX-TY, and U. Results of these studies are contained in numerous reports summarized in this data package, and have generated much of the geochemistry data reported in the field investigation reports for Hanford Site SST WMAs. The focus of this data package is to summarize the most current geochemical characterization data (as of December 31, 2007) conducted on vadose zone sediments beneath the SST farms and the Integrated Disposal Facility at the Hanford Site. A review of the empirical K_d model, its applicability and limitations for use at the Hanford Site, is also presented as it provides a framework for discussing K_d values listed in the summaries of the characterization data for the various SST WMAs.

Much has been learned during these initial investigations. Results show that mobile contaminants, such as ^{99}Tc and nitrate, migrate much differently in the subsurface than previously believed by researchers. Conventional thinking was that after mobile contaminants entered the subsurface, they migrated in a nearly vertical path through the soil column. However, the vadose zone sediment characterization studies indicate that the geologic layering of the vadose zone sediments has an important impact on the direction and rate of migration of the waste liquids and dissolved contaminants. Fine-grained sediment lenses have been shown to cause significant horizontal spreading of leaked fluids within the vadose zone.

In the sediment column, the zone of caustic attack, due to the interactions of the sediments with the high pH tank waste, can be determined by measuring the pH of the sediment. Soil pH has therefore become one of the key parameters measured when looking for waste discharge locations in the vadose

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[1]*Resource Conservation and Recovery Act of 1976*. 1976. Public Law 94-580, as amended, 90 Stat. 2795, 42 USC 6901 et seq.

zone. Because tank waste is generally considered caustic (in excess of 1M free hydroxide), it is quite common to find elevated soil pHs (between 8.5 and 10) in the vadose zone adjacent to the point of waste release. However, because natural minerals present in the sediment act to neutralize the elevated pH tank waste, the area exhibiting elevated soil pH is considerably smaller than the footprint that has been impacted by more mobile constituents, such as nitrate or [99]Tc.

When waste solutions containing high concentrations of dissolved sodium contact the sediment, sodium replaces the calcium and magnesium on the ion-exchange sites, thus creating an ion-exchange front. In this scenario, a front of naturally occurring calcium and magnesium that has been removed from the sediment exchange sites precedes the tank waste plume containing the elevated sodium. Although the ion-exchange front will not necessarily define the total vertical impact of tank waste contamination, it can be used to target the most appropriate depths to detect mobile contaminants.

The results of 1:1 sediment/water extracts can be utilized to determine the concentrations of water-soluble inorganic constituents in sediment that is too dry to easily extract pore water from the sediments. The extracts are prepared by contacting sediment with an amount of de-ionized water so that the ratio of water to dry sediment is exactly 1:1. After 24 hours of contact time, the solution extract is analyzed for numerous parameters and constituents, including pH, electrical conductivity, alkalinity, cations and trace metals, radionuclides, and anions. By correcting for dilution produced by adding deionized water to the sediment, an estimate of the actual composition of the native pore water in the vadose zone sediments can be derived from the composition of the extract solution.

As mentioned previously, this data package is a compilation of information gathered during Phase 1 of the RCRA Corrective Action Plan. Phase 2, which is just now beginning, is focused on remediation of the tank farms in preparation of tank farm closure. Much of the information garnered over the last 10 years will be used to determine, design, and test appropriate remediation alternatives.

Acknowledgments

Acronyms and Abbreviations

bgs	below ground surface
CCU_l	lower Cold Creek unit
CCU_u	upper Cold Creek unit
CCUu/R	upper Cold Creek unit/Ringold Formation
CCU_l/R	lower Cold Creek unit/Ringold Formation
COI	contaminant of interest
DOE	U.S. Department of Energy
EDTA	ethylenediaminetetraacetate acid
H1	Hanford formation, unit H1
H2	Hanford formation, unit H2
H3	Hanford formation, unit H3
HEDTA	hydroxyethylethylenediaminetriacetate acid
HS	hot semiworks
IC	ion chromatography
ICP-MS	inductively-coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry; same as inductively-coupled plasma atomic emission spectroscopy (ICP-AES)
IDF	Integrated Disposal Facility
ILAW	immobilized low-activity waste
K_d	partition coefficient or distribution coefficient; terms commonly used interchangeably
MCL	maximum contaminant level
pH	negative logarithm of the hydrogen ion activity
PNL	Pacific Northwest Laboratory. In 1995, DOE formally changed the name of the Pacific Northwest Laboratory to the Pacific Northwest National Laboratory.
PNNL	Pacific Northwest National Laboratory
Q_{fg}	quaternary flood gravels
Q_{fs}	quaternary flood silt and sand
RCRA	*Resource Conservation and Recovery Act of 1976*
R_{wi}	Ringold Formation, member of Wooded Island
redox	reduction and oxidation
S&T	science and technology
SEM	scanning electron microscopy
SMM	supernatant mixing model
SST	single-shell tank
UPR	unplanned release
WMA	Waste Management Area
WSTRS	Waste Status and Transaction Record Summary
XRD	X-ray diffraction

Units of Measure

‰	parts per thousand (said as "permil")
δ	delta, used to express stable isotope ratios relative to a standard (e.g., $\delta^{18}O$, and $\delta^{34}S$) in units of per mil (parts per thousand or ‰)
barn	unit of cross-sectional area for a physical interaction. The cross section is the probability that an interaction will occur between a projectile particle, e.g., a neutron and a target particle, e.g., the nucleus of an atom.
Da	Dalton – an alternate name for the unified atomic mass unit (u or amu). The size of large molecules or small colloid particles is often expressed in kDa. Measurements are typically in kilodaltons (kDa).
ft	feet
g/(g/yr)	grams dissolved per gram of mineral per year
gal	gallon
kDa	kilodalton
kg	kilogram
L	liter
M	molarity, moles of solute per liter solution
m	molality, moles of solute per 1,000 g solvent
m	meter
mg	milligram
Mgal	megagallon
mm	millimeter
mS	milliSiemen
pCi	picocurie
ppb	parts per billion (equivalent to μg/kg)
ppm	parts per million (equivalent to mg/kg)
yr	year

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1.0   Introduction

This data package summarizes laboratory characterization data from Phase 1 of the *Resource Conservation and Recovery Act of 1976* (RCRA) Corrective Action Plan, which focused on contaminant occurrence and mobility in vadose zone sediments beneath the single-shell tank (SST) farms and the Integrated Disposal Facility (IDF) at the U.S. Department of Energy's Hanford Site located in southeastern Washington State. Phase 1 activities focused on the contamination events that posed the greatest risk to human health and the environment. The vadose zone sediment characterization studies were completed in support of the Tank Farm Vadose Zone Program by Pacific Northwest National Laboratory (PNNL) researchers working on the Vadose Zone Characterization Project. The goal of these studies was to understand the extent of contamination and the transport processes that affect the mobility of contaminants released from the SSTs. PNNL chemists, geologists, geochemists, hydrologists, and computer modelers performed detailed characterization of the properties and the associated contamination as a function of depth for sediments obtained from core and grab samples collected by the Tank Farm Vadose Zone Program.

The four primary objectives of the vadose zone sediment characterization studies were as follows:

1. Identify the type and quantity of contamination present and develop conceptual representations for the lateral location and vertical extent of specific contaminants (e.g., uranium, ^{99}Tc, ^{137}Cs, and ^{60}Co) in the sediments.

2. Understand the physical processes that affect the transport of contaminants in the vadose zone sediments.

3. When practical, identify the source(s) of the contamination found in the sediment samples.

4. When practical, determine if a link can be made between the vadose zone contamination observed and any known nearby groundwater contamination.

Data were obtained to assess the long-term environmental impact associated with residual vadose zone contamination. However, before an accurate assessment can be made, it is imperative to understand what type of contamination is present, as well as how much of it resides in the vadose zone. Knowledge of the location of contamination within the vadose zone is also important because different remediation options are available for shallow versus deep contamination. Furthermore, different physical and chemical processes (e.g., diffusion, sorption, and precipitation) can dramatically affect the mobility of contaminants; therefore, knowledge of the existing state of the contamination can provide valuable insight when estimating its current and future mobility in the vadose zone. For additional information, Cantrell et al. (2007) provides a detailed review of the physical and chemical processes that impact contaminant mobility in vadose zone sediments at the Hanford Site.

Since its inception in 1998, the PNNL Vadose Zone Characterization Project has evolved to better meet the four key research objectives listed above. The single largest adaptation of the project was the advent of a tiered approach to sample analysis (see Figure 1.1). The basic premise of the three-tiered approach is to acquire the largest amount of scientific information—through an incremental process—that can be used to best meet project objectives while conserving resources and limiting risk to workers. Another factor that must be considered when working with sediment samples is that sample mass is often

limited by the field techniques used to acquire sediment from beneath the tank farms. When only a few hundred grams of sample material are available, it is increasingly important to judiciously select the order in which the analyses will be performed.

Tiered Characterization Approach

Tier I

- Geologic Description of the Samples
- Digital Photography of Samples
- Sediment Moisture Content
- Sediment Carbon Content
- Gamma Energy Analysis
- Sediment-Water Extracts
- Acid Extractions of the Sediment
- ICP-MS Analysis of Extracts
- ICP-OES Analysis of Extracts
- IC Analysis of Extracts

Tier II

- Particle-Size Analysis
- Matric Potential Measurements
- Tritium Separations
- ^{90}Sr Separations
- Actinide Separations
- ^{129}I Extraction and Analysis
- Total Elemental Analysis
- Mineralogy

Tier III

- Batch Sorption/Leaching Tests
- Column Transport Tests
- Cation Exchange Capacity
- Specific Surface Area Measurements
- Selective Extractions
- Iron Oxide Extractions
- Solid Phase Characterization

IC = Ion chromatography.
ICP-MS = Inductively-coupled plasma mass spectrometry.
ICP-OES = Inductively coupled plasma optical emission spectrometry.

Figure 1.1. Tiered Approach to Sample Analysis and Characterization

In the tiered-analysis approach, the first tier of tests (Tier I) includes those analyses that provide the following:

1. Supply information paramount to identify contaminants present in the samples
2. Help determine the basic chemical properties of the sediments.

Additionally, several of the Tier I analyses are nondestructive, so these sediments can be used again in other tests. The concentration profiles of contaminants measured in the sediment as a function of sample depth and sediment geology are one of the most important results from Tier I testing. These concentration profiles provide a measure of the extent of migration and relative mobility of each detected contaminant along the borehole length.

Upon completion of the Tier I tests, the Tank Farm Vadose Zone Program then decides whether there is a need to extend the studies to include Tier II and III testing. Tier II testing is focused on better resolving the type and extent of contamination present in the samples. Tests employed during Tier II characterization activities include specialized sediment chemical-dissolution (i.e., extraction) and analytical techniques. Additionally, several of the tests focused on identifying differences in the physical properties of the sediments. Tier III testing is reserved for analyses and experiments that will provide detailed information on the type of contamination present (e.g., element oxidation state or its physical/ chemical state within the sample), as well as information on the transport properties of the contaminants. Detailed information about the specific tests performed during each tier of analysis is included in several reports (Lindenmeier et al. 2002, 2003; Serne et al. 2002a, 2002b, 2002c, 2002d, 2002e, 2004a, 2004b; Brown et al. 2005, 2006a, 2007a, 2007b) and procedures (EPA 1984, 2000a, 2000b, 2000c; ASA 1996; ASTM 1998; USGS 2001).

A second geochemical data package titled *Geochemical Processes Data Package for the Vadose Zone in the Single-Shell Tank Waste Management Areas at the Hanford Site* (Cantrell et al. 2007) summarizes the most current and relevant information regarding geochemical processes that impact contaminant transport at the Hanford Site in general, but with a focus on vadose zone sediments beneath the SST waste management areas (WMAs) and the IDF at the Hanford Site. Companion reports that review other subject matter areas relevant to contaminant transport within the vadose zone beneath the SST WMAs, the IDF, and groundwater were recently published. The specific subject areas include the geology of the SST WMAs (Reidel and Chamness 2007), groundwater flow and contamination beneath the SST WMAs (Horton 2007), groundwater recharge (Fayer and Keller 2007), and far-field hydrology (Khaleel et al. 2007). In addition to these reports, a document titled *A Site Wide Perspective on Uranium Geochemistry at the Hanford Site* (Zachara et al. 2007) has been recently published. This report presents a cohesive review of the in-ground inventory of uranium and its geochemical behavior in the subsurface of the Hanford Site.

The focus of this data package is to summarize the most current geochemical characterization data (as of December 31, 2007) conducted on vadose zone sediments beneath the SST farms and the IDF at the Hanford Site. These summaries are preceded by a review of the empirical K_d model, its applicability, and limitations for use at the Hanford Site. Also included is a discussion of available sources of Hanford Site-specific K_d values. This discussion of the K_d model and Hanford Site-specific values was included to provide a framework for discussing K_d values listed in the summaries of the characterization data for the various SST WMAs. Summaries of geochemical characterization data are organized according to the various SST WMAs. Summaries of characterization data are also included for the IDF and BC cribs due to the potential relevance of these data to understanding contaminant migration at the SST WMAs.

2.0 Empirical K_d Model for Representing Adsorption in Performance Assessments

The following discussion of the empirical K_d model, published previously in Cantrell et al. (2007), provides a framework for discussing K_d values listed for the various SST WMAs in Section 3.0. Adsorption to mineral surfaces is typically the single most important geochemical process affecting transport of contaminants in the vadose zone and aquifer sediments at the Hanford Site. The constant K_d value (distribution coefficient) approach is an empirical adsorption model and is commonly used to represent the adsorption process in performance assessments conducted for the Hanford Site. Cantrell et al. (2007) provide a review of adsorption processes for radionuclides and the various approaches for modeling adsorption. Key findings from Cantrell et al. (2007) are summarized below.

The simplest type of adsorption isotherm is a linear adsorption coefficient, K_d (in ml/g or m^3/kg) as seen in Equation (2.1):

$$S = K_d C \tag{2.1}$$

where S (g/g)   = concentration of solute adsorbed onto the solid phase
        C (g/ml) = concentration of the solute in solution.

A linear isotherm (or K_d) approach generally assumes that K_d is a constant property of an aquifer, and forms the basis of the general retardation factor (R_f) through the relationship in Equation (2.2) (Freeze and Cherry 1979):

$$R_f = 1 + (\rho/\theta)K_d = v_{gw}/v_c \tag{2.2}$$

where ρ = bulk density
        θ = porosity
        v_{gw} = groundwater velocity
        v_c = contaminant velocity in aquifer.

The lower the value of K_d, the lower the retardation factor, and the faster a species migrates through the subsurface. For a non-adsorbing species, $K_d = 0$, R_f reduces to 1, and the species migrates at the groundwater flow velocity.

2.1 Applicability of the Empirical K_d Model at the Hanford Site

The K_d value is a lumped parameter and, as a result, neglects many of the chemical complexities of the adsorption processes such as saturation of adsorption sites and aqueous complexation. Because there are a finite number of adsorption sites on the aquifer solid phases, adsorption will reach a practical upper limit as sorbate concentrations increase. This can lead to erroneous results when used to predict retardation of metal and radionuclide contaminants in systems with varying chemical conditions (Bethke and Brady 2000; EPA 1999). The K_d concept works best when applied to trace concentrations of uncharged, hydrophobic organic molecules. Application of this approach to inorganic contaminants is often problematic because the parameter can be very sensitive to aqueous chemical conditions such as pH, alkalinity, or concentrations of complexing ligands that may be encountered along a migration flow path

(Kohler et al. 1996; Davis et al. 1998, 2004; Bethke and Brady 2000; Kent et al. 2000; Altmann et al. 2001). For example, the K_d for U(VI) adsorption on ferrihydrite at pH 8 decreases by four orders of magnitude as the carbonate concentrations increase as a result of increases in partial pressure of carbon dioxide gas, pCO_2, from its value in air (0.032%) to 1% (Davis et al. 2004). This is an important variation to understand because the pCO_2 in aquifers commonly reaches values of 1% to 5%, while most K_d values have been determined in laboratory experiments equilibrated with or exposed to air.

For these reasons, the constant K_d model is best used to represent adsorption when contaminant concentrations are low relative to the adsorption capacity and the variability in mineralogy and hydrochemistry is minimal along the water flow path. The constant K_d model is not adequate for representing adsorption in situations where spacial variability in mineralogy and hydrochemistry is significant along the groundwater flow path.

Variable or compartmentalized K_d values can be used to deal with spatially variable mineralogy and hydrochemistry that result in significant variability in K_d values along the water flow path. In this approach, different K_d values are used for different spatial compartments. Each compartment is assumed to have an average representative mineralogy, hydrochemistry, and associated K_d value. In principal, this approach could also be used to deal with temporal variation as well. This approach was used to support Hanford assessments including a composite analysis of low-level waste disposal at the Hanford Site (Last et al. 2006; Kincaid et al. 2004), and is discussed in more detail in the following paragraph.

To select reliable K_d values for performance assessment modeling at the Hanford Site, an experienced geochemist with a detailed knowledge of adsorption, speciation chemistry and the K_d approach at Hanford should always be consulted. The combination of such geochemical knowledge and experience, along with detailed site-specific geochemical characterization data, is generally the only reliable method for selecting K_d values that will adequately approximate adsorption processes in modeling efforts with critical outcomes such as performance assessments.

2.2 Sources of K_d Data for the Hanford Site

The most complete and current source of K_d values measured on Hanford Site sediments has been compiled by Cantrell et al. (2003). In addition to the measured K_d values, other significant experimental parameters and solution and sediment characterization data associated with these measurements are included in the compilation. These data can be useful when attempting to select appropriate K_d values for a particular set of hydrochemical and mineralogical conditions. The importance of matching the experimental conditions used to measure K_d with the specific set of conditions for which the K_d value is to be applied was emphasized in the compilation.

In addition to the K_d data compilation published as a PNNL report (Cantrell et al. 2003), an electronic database is also available. This electronic database is the most up-to-date source of K_d data available for the Hanford Site. The database is periodically updated when new data become available. It can be accessed by Hanford Site employees through the Hanford Virtual Library.

The compilation of Hanford K_d data was used to develop a set of compartmentalized K_d values for input to the 2004 Composite Analysis, a Hanford Site-wide performance assessment (Last et al. 2006). These values are also provided in Appendix B of Cantrell et al. (2007). Because only a limited amount of site-specific characterization data were available for the large number of sites with diverse characteristics

and disposal histories, it was necessary to develop a generic Hanford Site-wide set of K_d values that would be applicable over a range of waste chemistry/source categories and impact zones.

For the 2004 Hanford Composite Analysis, six waste stream designations were used (Last et al. 2006). The first four waste stream designations (Very Acidic, High Salt/Very Basic, Chelate/High Salt, and Low Salt/Near Neutral) were assigned a specific composition (Table 2.1) to better justify the selection of the K_d values assigned to these waste streams. Specific waste stream compositions for the two IDF wastes (Vitrified Waste and Cementitious Waste) were not provided because the IDF waste form leach rates will be highly dynamic and a function of time, position in the disposal system, and other variables that are not yet known. Because of these factors, a specific composition for these waste streams is not provided in Table 2.1; instead, a generic composition was developed (Krupka et al. 2004). In addition to the waste stream composition designations, each of these waste stream designations was further compartmentalized into four impact zones. The four impact zone designations were high impact, intermediate impact, intermediate-gravel, and groundwater. Zones in which the organic concentration, pH, or salt concentration in the fluid may have significantly affected the K_d value were designated as high impact. Zones in which the acidic or basic nature of the wastes was expected to have been largely neutralized by reaction with the natural sediment were designated intermediate impact. Zones with minimal impact were designated to have the same K_d values as those applicable to uncontaminated Hanford Site groundwater. In addition to these three impact zones, another zone was designated as intermediate-gravel. The intermediate-gravel was assumed to be the same as the intermediate zone except that the sediment contained 90% gravel with little or no adsorption capacity. This is an important designation because the majority of the K_d values tabulated in Cantrell et al. (2003) were measured on Hanford Site sediments that were sieved to contain only particles that were less than 2 mm in size. Hanford Site sediments often contain large fractions of gravel and larger size material, and this gravel and larger size fraction generally has minimal adsorption capacity. The impact of gravel content is discussed in greater detail in Section 2.4.

Table 2.1. Waste Stream Designation and Assumed Compositions for Determination of K_d Values

Waste Stream	Composition
Very Acidic	1.0 M HNO_3
High Salt/Very Basic	2 M NaOH, 4 M $NaNO_3$, 2 M $NaNO_2$
Chelates/High Salt	1.0 M $NaNO_3$, 0.05 M EDTA, pH 12
Low Salt/Near Neutral	Same as Hanford Site groundwater
IDF Vitrified Waste	High pH, high ionic strength
IDF Cementitious Waste	High pH, medium ionic strength
EDTA = Ethylenediaminetetraacetate acid. IDF = Integrated Disposal Facility.	

The K_d values that were compartmentalized in terms of waste chemistry/source categories and impact zones for the 2004 Composite Analysis (Last et al. 2006) are provided in Appendix B of the Geochemical Processes Data Package (Cantrell et al. 2007). The non-IDF K_d values were selected based upon critical review of the K_d values tabulated in Cantrell et al. (2003) and application of geochemical knowledge and experience of the authors. The IDF K_d values were selected in a similar fashion; however, the selections relied heavily upon the values in Krupka et al. (2004) and were revised to have the same format used for the non-IDF K_d values in Last et al. (2006) and Appendix B of Cantrell et al. (2007).

It should be emphasized that in some cases, the K_d estimates provided in Appendix B of the Geochemical Processes Data Package (Cantrell et al. 2007) had to be made based on limited data that were not necessarily commensurate with those of the waste chemistry/source category. In addition, these compartmentalized K_d values did not account for future changes in chemical conditions that could occur and significantly change the K_d values. Finally, these compartmentalized K_d values should be considered as generic Hanford Site K_d values that should be used only in the absence of site-specific data.

Estimates of K_d values that cover a broader range of contaminants of interest (COI) were made for the Hanford Site IDF performance assessment in Krupka et al. (2004). Four K_d values were provided for various geochemical zones and include a reasonably conservative K_d value, a best estimate (or most probable) K_d value, and upper and lower K_d limits. The geochemical zones for which K_d estimates were made included Zone 1a – Near Field/Vitrified Waste; Zone 1b – Near Field/Cementitious Secondary Waste; Zone 2a – Chemically Impacted Far Field in Sand Sequence; Zone 2b – Far Field in Sand Sequence with Natural Recharge; Zone 3a – Chemically Impacted Far Field in Gravel Sequence; Zones 3b and 4 – Far Field Gravel Sequence; and Zone 5 – Unconfined Far-Field Aquifer. For the Zone 1b – Near Field/Cementitious Secondary Waste Zone, K_d value estimates are provide for three temporal environments: young concrete (pH ~ 12.5), moderately aged concrete (pH ~ 10.5), and aged concrete (pH ~ 8.5). Tables containing these K_d values are provided in Appendix C of the Geochemical Processes Data Package (Cantrell et al. 2007).

Recently, Serne (2007) published a compilation of K_d values for agricultural and surface soils for use in Hanford Site use scenarios (farm, residential, and Columbia River shoreline) that could exist today or potentially exist in the future when portions of the Hanford Site are released for farming, residential, and recreational use after DOE defense waste cleanup activities are completed. Best value and ranges of K_d values were provided. The values recommended in this work are shown in Appendix D of the Geochemical Processes Data Package (Cantrell et al. 2007), along with those of Napier and Snyder (2002). These K_d value estimates are intended to be used to estimate the fate and transport of contaminants and their availability for plant and animal uptake in selected non-groundwater scenarios included in Hanford Site environmental impact statements, risk assessments, and specific facility performance assessments.

2.3 Reversibility – Desorption K_d Values

In most modeling approaches, the K_d values are assumed to be at equilibrium and completely reversible. This is not always the case. For example, desorption K_d values are frequently higher than adsorption K_d values (for discussions, see Barney 1984; EPA 1999; and Um et al. 2004). This apparent hysteresis in adsorption versus desorption can result from a number of phenomena, both chemical and physical. For example, aging of the sediment after adsorption of a contaminant can potentially result in chemical alterations that could slow the release of adsorbed contaminants or encapsulate the contaminant. Mineralogical phase changes on or within the sediment, with or without reduction and oxidation (redox) changes, or subsequent precipitation of mineral phases onto the surfaces of sediment are examples of chemical alterations that could lead to these effects. Physical processes can also cause an apparent irreversibility of adsorption. For example, over time, contaminants can slowly diffuse through micro-pores within sediments grains to reach adsorption sites that were not initially accessible. This can result in a slow increase in K_d values over time and desorption K_d values that appear to be greater than adsorption values. In studies of Cs^+ adsorption onto Hanford Site sediments, it has been shown that 30% to 40% of adsorbed Cs^+ is poorly exchangeable because of intra-particle diffusion and grain armoring by

secondary precipitates (Liu et al. 2003, 2004a). Studies of uranium adsorption-desorption on Hanford Site sediments also demonstrate a lack of complete reversibility (Zachara et al. 2005; Bond et al. 2005; Dong et al. 2005).

2.4　Impact of Gravel Content

The impact of gravel content on K_d values is commonly ignored in performance assessments conducted at the Hanford Site. As previously indicated in Section 2.2, K_d measurements are generally conducted on Hanford Site sediment material that is <2 mm in size. For materials that contain significant amounts of gravel, K_d values are typically lower than those determined with <2-mm size material because the surface area and corresponding quantity of adsorption sites is much lower (Kaplan et al. 2000). At the Hanford Site, sediments often contain high-gravel (>2 mm to 76 mm) content facies, especially near the Columbia River. As a result, it is necessary to make corrections to K_d values determined with <2-mm-size material. For high K_d contaminants (cesium, strontium, and plutonium), Equation (2.3) is recommended (see Appendix A in Kaplan and Serne 2000).

$$K_d(gc) = (1-f)\ K_d(<2\ mm) + (f)0.23\ K_d(<2\ mm) \tag{2.3}$$

$$= K_d(gc) = (1 - 0.77f)\ K_d(<2\ mm)$$

where　　　　$K_d(gc)$　=　gravel corrected K_d value
　　　　　　　　f　=　weight fraction gravel
　　　　$K_d(<2mm)$　=　K_d value determined using <2-mm material.

For low K_d contaminants, Equation (2.4) is recommended:

$$K_d(gc) = (1-f)\ K_d(<2mm) \tag{2.4}$$

2.5　Impact of Moisture Content

The moisture dependency of K_d values has been evaluated in several studies (Lindenmeier et al. 1995; Kaplan et al. 1996; Gamerdinger et al. 1998, 2001). The findings of these studies suggest there is a slight decrease in K_d values for U(VI) and other contaminants as the moisture content of the system decreases. Four of the five sediments tested showed this trend. The sediment that did not show this trend had only two K_d data points: one from a saturated system, and the other from an unsaturated system (Kaplan et al. 1996). This decrease in K_d value for U(VI) as percent saturation decreased may be attributed to the fact that, as the degree of saturation decreases, solutes lose physical access to some of the exchange sites. With more contact time between the vadose zone sediments and pore water, diffusion processes may allow the contaminants to reach these adsorption sites that are hidden in dead-end pore spaces. An alternative explanation is that higher ionic-strength fluid exists in the double layer of partially saturated sediments, leading to weaker sorption. This latter explanation is less likely because the double layer around particle surfaces reaches only nanometers into the water, whereas the uniform film thickness of pore fluid around unsaturated Hanford Site sediments is estimated to be several micrometers. For most performance assessments, including the 2005 Integrated Disposal Facility Performance Assessment (Krupka et al. 2004), the K_d dependency on moisture content is ignored and K_d values measured using typical saturated tests were used.

3.0 Geochemistry of Contaminant Migration Through the Vadose Zone at Hanford – Site Specific Characterization Studies and K_d Estimates

This section contains summary reviews of the Phase 1 RCRA Corrective Action Plan laboratory characterization studies completed by PNNL's Vadose Zone Characterization Project at each of the SST WMAs at the Hanford Site. Each of these review sections is followed by a discussion of estimated K_d values appropriate for that WMA. Whenever possible, these K_d value estimates were based upon results of characterization studies conducted at individual WMAs. To formulate sorption-desorption parameters for key contaminants (to be used to predict future migration of contaminants), a method similar to that used in Last et al. (2006) was used in which the vadose zone sediment and their pore water geochemical environments around waste sites were broken into zones identified as high, intermediate, and no impact (background or groundwater) by the waste fluids that entered the sediments.

The K_d value estimates are provided in terms of best estimates and minimum and maximum values for each COI. The COIs for which K_d values were estimated are generally constituents that have large inventories, long half-lives for those that are radioactive, and/or move rapidly through sediments and groundwater and therefore have high intrinsic potential for risk impacts. The COIs include key contaminants of concern for tank waste through the groundwater pathway (^{99}Tc, ^{129}I, uranium, nitrate, chromium, and mercury) and inadvertent intruder scenario (^{90}Sr, ^{126}Sn, ^{137}Cs, uranium, ^{237}Np, $^{239/240}$Pu, and ^{241}Am) (Mann et al. 2005, Vol. 1, Chapter 17). The radionuclides ^{125}Sb, ^{60}Co and $^{152/154}$Eu were included because they were identified by spectral gamma logging in WMA B-BX-BY (DOE-GJO 1998). The radionuclide ^{79}Se was indicated to be a potential contaminant of concern in Mann et al. (2001). The rationale for the K_d value estimates is provided for each contaminant in Appendix A tables. At most of the WMAs that have been characterized, a region of elevated pH indicative of caustic fluid interaction with the native sediments was found. This region where sediments have elevated pH values (above 8.5) is defined here as the high impact zone. For all tank farms that have been characterized by vadose zone sediment sampling, a region with high salinity indicative of concentrated fluid release from the tanks was observed. This region of high salinity was used to define the intermediate impact zone. A salinity of ~3 to 5 times the background pore water ionic strength was used to represent high salinity or the intermediate impact zone. Beyond these two impact zones, sediments were assumed not to be significantly impacted by reactions with waste fluids such that the pore waters would interact with the sediments in a similar fashion as uncontaminated (natural) fluids. The "no impact" zone sediments and their pore waters can however, include contaminants at low concentrations, which can adsorb and desorb and compete with naturally present species for sediment surface adsorption sites. This situation is the condition for which the K_d construct is appropriately used.

3.1 Waste Management Area A-AX

In 2003, it was determined that two RCRA monitoring wells in WMA A-AX, 299-E24-19 and 299-E25-46, failed due to corrosion of the stainless-steel casing over a length of the wells. Complete casing corrosion occurred between 84.31 and 84.64 m below ground surface (bgs) in well 299-E24-19 and from 83.64 to 84.92 m bgs in well 299-E25-46. To determine the cause of this rapid corrosion, a detailed study was conducted on vadose zone sediment samples collected in the vicinity of WMA A-AX

from depths comparable to those where the rapid corrosion occurred (Brown et al. 2005). A map of locations for wells, tanks, and inactive facilities at WMA A-AX is provided in Figure 3.1.
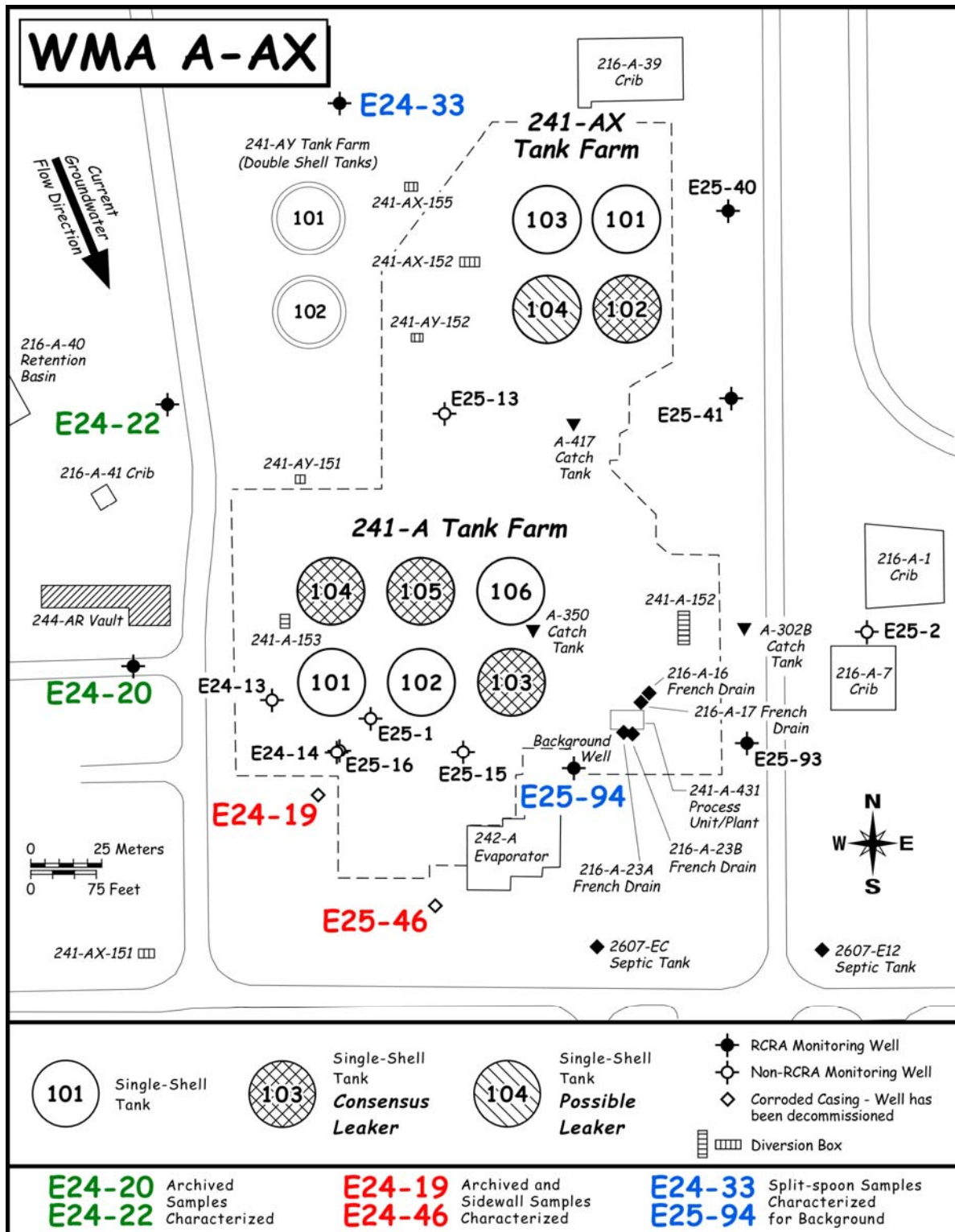
Figure 3.1. Location of Wells, Tanks, and Inactive Facilities at Waste Management Area A-AX

3.1.1 Brief Description of Geology

The following summary is based on the detailed description of geologic and statigraphic relationships beneath the A, AX, and C Tank Farms and adjoining areas of the 200 East Area provided in Reidel and Chamness (2007). Their description was based on a compilation of historical information (Brown 1959; Price and Fecht 1976a, 1976b, 1976f; Tallman et al. 1979; Lindsey et al. 1992; Jones et al. 1998; Williams et al. 2000) and some new interpretations allowed by new borehole emplacement and research conducted in calendar year 2003 (Williams and Narbutovskih 2003, 2004). The most recent detailed description of the A, AX, and C Tank Farms is that in Wood et al. (2003), and most of the discussion presented in Reidel and Chamness (2007) was built on that report. A summary table of the statigraphic terminology and thicknesses of units beneath the A, AX, and C Tank Farms from Reidel and Chamness (2007) is provided in Table 3.1. This table and the supporting text in this section and all the other geology summaries in Section 3.0 were taken essentially verbatim from Reidel and Chamness (2007).

Because the geologic stratigraphy provides the framework that controls the flow of pore water and contaminants, understanding the stratigraphy is important to predicting the fate of the contaminants released into the vadose zone. At WMA A-AX, the sediments from ground surface to the water table (~79 to 92 m bgs) are predominately gravel, except the 30- to 65-m thick Hanford H2 unit composed of sand, with its upper surface between 30 to 40 m bgs of the WMA. In very localized regions below the WMA, there is also a thin silt-dominated strata, the upper Cold Creek unit (CCU_u) (0 to 6-m thick) found below the Hanford formation and right above or at the water table when the silt unit is present. In general, because the geologic strata at WMA A-AX is approximately $\geq 50\%$ gravel and $\leq 50\%$ sand, contaminants are expected to migrate deeper for a given volume of liquid released to the vadose zone than for some other WMAs that contain much less gravel and more sand and silt strata. This generalization ignores the large influence of thin, fine-grained lenses often found in the Hanford formation sediments that are usually only identified by near-continuous core sampling or geophysical logging (neutron moisture and spectral gamma). Because nearly continuous borehole samples are not available within the WMA fence line at locations suspected of being contaminated by tank-related fluids, estimates of K_d values for key contaminants discussed in Section 3.1.3 are largely based on expert opinion of the authors. The only actual measurements of contaminants in vadose zone sediments from near WMA A-AX are discussed in Section 3.1.2.

3.1.2 Investigation of Accelerated Casing Corrosion in Two Wells at Waste Management Area A-AX

The WMA A-AX accelerated casing corrosion report (Brown et al. 2005) contains all the geochemical and selected physical characterization data collected on archived vadose zone sediment recovered during the early 1990s installation of four RCRA monitoring wells (299-E24-19, 299-E24-20, 299-E24-22, and 299-E25-46), sidewall core samples collected during the decommissioning (in 2004) of wells 299-E24-19 and 299-E25-46, split-spoon core samples collected during the installation (in 2004) of two RCRA monitoring wells (299-E24-33 and 299-E25-94), a sample of Wyoming bentonite, and a perched water sample collected during the installation of well 299-E24-33. All these wells were assumed to have been drilled in uncontaminated vadose zone sediments surrounding the WMA fence line. Laboratory tests were conducted to characterize the sediment and to identify water-leachable constituents. Testing consisted primarily of 1:1 sediment/water extractions, which were used to calculate the elemental

Table 3.1. Stratigraphic Terminology and Unit Thickness for Waste Management Areas A-AX and C (from Reidel and Chamness 2007)

Stratigraphic Symbol	Formation	Facies/ Subunit	Description	A-AX Thickness	C Thickness
Backfill	NA	Backfill – Anthropogenic	Gravel-dominated consisting of poorly to moderately sorted cobbles, pebbles, and coarse to medium sand with some silt derived from coarse-grained Hanford formation (H1 unit) excavated around tanks (Price and Fecht 1976a, 1976b, 1976f; Wood et al. 2003); occasional layers of sand to silty sand occur near the base of the backfill sequence.	10 m	10 m
H1	Hanford formation	Unit H1 – (Gravel-dominated facies association). Cataclysmic flood deposits (high-energy)	Gravel-dominated flood sequence; composed of mostly poorly sorted, basaltic, sandy gravel to silty sandy gravel. Equivalent to the upper gravel sequence discussed by Last et al. (1989), the Q_{fg} documented by Reidel and Fecht (1994), coarse-grained sequence (H1 unit) of Wood et al. (2003) and gravel facies of unit H1 of Lindsey et al. (2001a, 2001b), and gravel-dominated facies association of DOE-RL (2002).	20 – 30 m	10 – 30 m
H2	Hanford formation	Unit H2 – (Sand-dominated facies association). Cataclysmic flood deposits (moderate energy)	Sand-dominated flood sequence; composed of mostly horizontal to tabular cross-bedded sand to gravelly sand. Some sand beds capped with thin layers of silty sand to sandy silt. Equivalent to Fine-Grained Sequence (H2 unit) of Wood et al. (2003) and unit H2 of Lindsey et al. (2001b), the sandy sequence of Last et al. (1989) and Lindsey et al. (1992), to Q_{fs} documented by Reidel and Fecht (1994), and sand-dominated facies association of DOE-RL (2002).	30 – 65 m	45 – >70 m
H3	Hanford formation	Unit H3 – (Gravel-dominated facies association). Cataclysmic flood deposits (high-energy)	Gravel-dominated flood sequence; composed of open framework gravel and poorly sorted, basaltic, sandy gravel to silty sandy gravel. Equivalent to the lower coarse-grained unit of the Hanford formation of Last et al. (1989), to the lower gravel sequence of Lindsey et al. (1992), and to the Hanford formation, H3 sequence of Lindsey et al. (1994).	0 – 20 m	0
CCU$_u$/R	Undifferentiated Cold Creek unit and Ringold Formation	Upper subunit	Silty sequence; locally thick layer of silt overlying the gravelly sediments of the lower subunit. Silt facies is light olive-brown to tan colored, massive, well-sorted, fine, calcareous silt to sand with pedogenic traces (i.e., root casts).	0 – 6 m	0
CCU$_l$/R	Undifferentiated Cold Creek unit and Ringold Formation	Lower subunit	Lower gravel sequence equivalent to pre-Missoula gravels; sandy gravel to gravelly sand beneath the silt-dominated facies and above the top of basalt. Occurs as muddy, sandy gravel to sandy gravel. Moderate to uncemented with some caliche fragments.	0 – >15 m	0 – 25 m

Table 3.1. (contd)

Stratigraphic Symbol	Formation	Facies/ Subunit	Description	A-AX	C
				Thickness	Thickness
R_{wi}	Ringold	R_{wi} unit – Ancestral Columbia River System braided-stream deposits	Coarse-grained Ringold Formation sequence, consisting of mostly moderately sorted, quartzitic sandy gravel to silty sandy gravel. Equivalent to middle Ringold Formation unit (DOE 1988) and the Ringold Formation unit E gravels (Wood et al. 2003, Lindsey et al. 2001a).	Probably not present	Probably not present

CCUu/R	=	Upper Cold Creek unit/Ringold Formation.
CCU$_l$/R	=	Lower Cold Creek unit/Ringold Formation.
H1	=	Hanford formation, unit H1; equivalent to upper sand-dominated.
H2	=	Hanford formation, unit H2; equivalent to middle sand-dominated.
H3	=	Hanford formation, unit H3; equivalent to lower sand-dominated.
NA	=	Not applicable.
Q$_{fg}$	=	Quaternary flood gravels.
Q$_{fs}$	=	Quaternary flood silt and sand.
R$_{wi}$	=	Ringold Formation, member of Wooded Island.

concentrations of water soluble constituents in the sediment and to estimate in situ pore-water chloride concentrations. Additionally, 8 M nitric-acid extractions and x-ray diffraction (XRD) analyses of the solids were used to provide a measure of the total leachable constituents in the sediments and to search for the formation of new crystalline phases that may have formed during the corrosion process, respectively.

The archived sediment samples collected during installation of the four RCRA monitoring wells (299-E24-19, 299-E24-20, 299-E24-22, and 299-E25-46) were examined to provide baseline (natural background) characterization data for the study. Analysis of these samples did not result in the identification of any constituents at concentrations that greatly exceed those typically measured in native Hanford Site sediments. Because the primary focus of the study by Brown et al. (2005) was the investigation of well casing failure, special emphasis was placed on determining the chloride content of all the samples. The 11 archived samples tested from the RCRA monitoring wells had calculated pore-water chloride concentrations ranging from 28 to almost 600 mg/L. However, due to sample preservation problems, the measured moisture content of the samples was artificially low by a factor of 10x or more and resulted in an overestimation of the true pore-water chloride concentration. Therefore, it is unlikely that any of the archived sediment samples tested could generate pore waters with a sufficient chloride content to initiate corrosion of the well casing. Under typical Hanford Site conditions, the dissolved chloride threshold for initiating corrosion of stainless-steel is estimated to be 100 mg/L (Brown et al. 2005).

The perched water sample collected during the recent installation of RCRA groundwater monitoring well 299-E24-33 was used as a baseline for the current vadose zone geochemical conditions in WMA A-AX. Detailed analysis of this sample indicated that it was composed of the typical major Hanford Site groundwater constituents (calcium, magnesium, and sulfate), with a dissolved chloride concentration of 49.5 mg/L. These results further support the assessment that the archived sediment samples lost moisture during storage and therefore are not suitable for estimating the true pore-water concentrations of chemical constituents.

Twelve split-spoon core samples, collected during the recent installation of RCRA monitoring wells 299-E24-33 and 299-E25-94, were characterized to further assess the current vadose zone geochemical

conditions in WMA A-AX. Again, analyses of these samples showed that only normal Hanford Site sediment constituents were present. Further, the common constituents were present at concentrations typically observed in uncontaminated vadose zone sediments. Two of the cores, which contained coarse-grained material (271-S and 272.5) from well 299-E25-94 had calculated pore-water chloride concentrations of 113 and 114 mg/L, respectively. Although the dissolved chloride concentrations in both of these samples exceed the 100 mg/L threshold value for type 304L stainless-steel, it is doubtful that concentrations at these levels could lead to the advanced corrosion found in wells 299-E24-19 and 299-E25-46 (Brown et al. 2005).

The sample of Enviroplug® #8 high-swelling Wyoming bentonite was characterized for its potential to generate pore waters of sufficient chlorinity to lead to accelerated corrosion of type 304L stainless steel.[2] Overall, the bentonite sample had considerably higher water extractable concentrations of sodium, chloride, fluoride, sulfate, and alkalinity than the water extracts of the vadose sediments studied. Inter-pretation of the laboratory data by Brown et al. (2005) indicated that the Wyoming bentonite was capable of generating localized vadose zone pore water with chloride concentrations in excess of 700 mg/L. However, the vadose zone at the Hanford Site is primarily composed of coarse-grained sands with an in situ volumetric moisture content ranging from 5 to 12%. Therefore, it is doubtful enough moisture will be available throughout the majority of the vadose zone to sufficiently wet the bentonite and leach chloride from the bentonite. Consequently, Brown et al. (2005) concluded Wyoming bentonite material should be suitable as an annulus filling agent in all low-moisture zones and those regions that lack the potential to accumulate perched water.

Characterization and analysis of the sidewall core samples collected from the zone of corrosion during decommissioning of corroded wells 299-E24-19 and 299-E25-46 resulted in several key findings that significantly affected the outcome of the casing corrosion study. All of the sidewall core samples generated water extract solutions with an acidic pH (1.8-2.5), which was likely the cause of the breakdown/corrosion of the well casing. Additionally, the sidewall core samples from well 299-E24-19 were elevated with respect to water extractable sodium, while the sidewall core samples from well 299-E25-46 contained significantly elevated concentrations of water extractable nitrate. Because both sodium and nitrate are common components in Hanford Site waste streams, the water extract samples were further analyzed for ^{99}Tc. Surprisingly, the sidewall core samples from both failed wells contained measurable quantities of ^{99}Tc (ranging from 0.984 to 21.9 pCi/g) at depths of ~84 m bgs. These findings appear to demonstrate that the vadose zone chemistry in the vicinity of the two failed wells has been affected by a Hanford Site waste stream that has not been identified at this time. Because no previous researcher has determined a plausible source for the apparent waste fluids that corroded the two casings, this corrosion event has not been currently factored into the discussion on selection of impact zones for WMA A-AX (described below).

The sidewall core samples from well 299-E24-19, which were comprised of a mixture of bentonite and silt sediment, had an average pore-water chloride concentration of 376 mg/L. The sidewall core samples collected from well 299-E25-46 had calculated pore water chloride concentrations ranging from 1,200 to more than 10,000 mg/L. Clearly, the sidewall core samples tested were capable of generating pore waters with sufficient chloride concentrations to cause corrosion of the stainless-steel well casing (Brown et al. 2005). Furthermore, analysis of the sidewall core samples yielded a clear relationship between chloride concentration and extent of well casing corrosion. The sidewall core samples

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[2] Enviroplug is a registered trademark of Enviroplug Limited.

containing the greatest amount of chloride, 3,000 µg/g of sediment, came from the well that experienced the longest length of casing failure (1.28 m in well 299-E25-46 between the depths of 83.6 and 84.9 m bgs). All the sidewall core samples tested from both decommissioned wells contained more chloride than the Wyoming bentonite test material. However, as previously noted, the Wyoming bentonite material tested was that which was commercially available at the time of this study, and therefore does not necessarily represent the bentonite material used during the installation of these wells. Because chloride was present as a trace constituent in all of the sidewall core samples (less than 0.4 wt.%), it is possible that it could have been introduced to the system as a contaminant in the bentonite backfill material. Therefore, it is likely that chloride leached from the bentonite material and/or chloride carried by/as a constituent of the liquid waste stream caused the advanced well casing corrosion found at wells 299-E24-19 and 299-E25-46 via crevice corrosion and stress corrosion cracking.

3.1.3 Estimated K_d Values for Key Contaminants at Waste Management Area A-AX

Aside from the investigation of the two corroded casings at the RCRA monitoring wells 299-E24-19 and 299-E25-46, no vadose zone sediment sampling has been completed inside WMA A-AX. The following generalizations can be made for the WMA A-AX vadose zone. The chemical composition of the fluids released from tank A-103 (Table 3.2) had a very high salt content, predominately sodium, aluminum, hydroxide, nitrate, nitrite, and carbonate. Because the tank A-103 fluid composition has very high salinity, is quite caustic, and the first 30 to 40 m under the tank appear to be dominated by gravel, K_d values for most contaminants were estimated to be zero in this highly impacted zone. Below the high impact zone at tank A-103 and below the other three tanks that leaked fluid at WMA A-AX, recommended K_d values for the intermediate impact zone for key contaminant of concern are shown in

Table 3.2. Chemical Composition (mol/L) of the Tank Fluids Released in Waste Management Area A-AX (from Corbin et al. 2005)

Waste Type[a]	Concentration (mol/L)				
	A1SltCk	AR	B	P1	P2
Na^+	13.5	1.35	0.62	0.72	1.17
Ca^{2+}	0.004	0.0037	0.0037	0.0037	0.0037
K^+	0.084	0.008	0.003	0.003	0.006
Sr^{2+}	5.00E-07	5.00E-07	5.00E-07	5.00E-07	5.00E-07
NH_4^+	0.09	0.018	3.70E-05	0.008	0.031
Cr	0.055	0.017	0.002	0.008	0.008
Mn	5.60E-04	1.80E-04	0	0	0
Fe	0.0019	0.0019	0.0019	0.0018	0.0018
Ni	0.0018	0.0018	0.0018	0.0018	0.0018
Bi	2.20E-04	2.20E-06	0	0	0
NO_3^-	3.5	0.3	0.26	0.175	0.12
NO_2^-	2.72	0.478	0.022	0.277	0.615
CO_3^{2-}	0.582	0.14	0.004	0.004	0.004
PO_4^{3-}	0.063	0.022	0	0	0
SO_4^{2-}	0.124	0.074	0.017	0.044	0.124
Cl^-	0.29	0.019	0.013	0.014	0.026
F^-	0.094	4.40E-04	0	0	0
OH^-	2.97	0.089	0.182	0.184	0.185
$Al(OH)_4^-$	1.75	0.022	0.077	0	0
Organics	0.3	0	0	0	0
(a) See Corbin et al. (2005) for definitions.					

Table 3.3. The rationale used to select the K_d values in all the K_d tables in Section 3.0, such as Table 3.3 and 3.4, is provided in Appendix A. Outside and beyond these two impact zones, vadose and aquifer sediments at this WMA are assumed to have sorption K_d values similar to uncontaminated sediments in the region. Table 3.4 lists K_d values for uncontaminated sediments (no impact) (taken mostly from Last et al. [2006] when available) for various lithologies for all WMAs. The K_d values for gravel-dominated sediments should be modified according to Equations (2.3) and (2.4) in Section 2.4. For example, the K_d value for a low adsorbing contaminant on a sediment sample with 60% gravel would be 0.4 times the K_d value for sand (<2 mm). This gravel correction convention requires that the user know or estimate the wt% of gravel present in the strata for which K_d values are being sought.

Table 3.3. K_d Values for Key Contaminants for Sand and Silt Sediments Impacted by Waste

	Sand-Size Sediments						Silt Size-Sediments					
	High Impact			Intermediate Impact			High Impact			Intermediate Impact		
	Best	Min	Max	Best	Min	Max	Best	Min	Max	Best	Min	Max
Chemicals												
F$^-$	0	0	0	0	0	1	0	0	0	0.05	0	1
Cr(VI)	0.05	0	3	0	0	3	0.1	0	3	0	0	10
Hg(II)	0	0	0	0	0	0	0	0	0	0	0	0
NO$_3^-$, NO$_2^-$	0	0	0	0	0	0.1	0	0	0	0	0	0.1
Pb(II)	3	0	10	10	3	100	0	0	30	30	10	300
U(VI) – all isotopes	0.1	0	1	0.8	0.2	4	0.3	0	3	2.5	0.6	15
Radionuclides												
^{241}Am(III)	3	0	50	600	200	2000	10	0	150	600	200	2000
^{14}C	5	0	50	1	0	100	5	0	50	1	0	100
^{60}Co(II,III)	0	0	10	0	0	10	0	0	30	0	0	30
^{137}Cs	1	0	10	100	10	1000	1	0	30	100	30	3000
Eu – all isotopes	1	0	10	10	3	100	3	0	30	30	10	300
^{3}H	0	0	0	0	0	0	0	0	0	0	0	0
^{129}I	0	0	0.2	0.2	0	2	0	0	0	0.2	0	2
^{63}Ni	0	0	10	3	1	20	0	0	30	10	3	60
^{237}Np(V)	0	0	5	10	2	30	0	0	15	10	2	50
Pu – all isotopes	3	0	50	600	200	2000	5	0	150	600	200	2000
^{226}Ra	1	0.2	20	10	5	20	3	0.6	60	10	5	60
^{79}Se(VI,IV)	0	0	3	0.1	0	3	0	0	3	0.3	0	10
^{126}Sn(IV)	0	0	10	0.5	0	20	0	0	30	1.5	0	60
^{90}Sr	1	0.2	20	10	5	20	3	0.6	60	10	5	60
^{99}Tc(VII)	0	0	0.2	0	0	1	0	0	0.2	0	0	5
For gravel-size sediments, modify sand-size K_d values using Equations (2.3) and (2.4) in Section 2.4. See Appendix A for references and selection rationale.												

Table 3.4. K_d Values for Sand, Silt and Carbonate Dominated Sediments for Fluids Not Impacted by Waste (~Natural Pore Waters/Groundwater)

	Sand-Size Sediments			Silt-Size Sediments			Carbonate-Dominated Sediments		
	No Impact			No Impact			No Impact		
	Best	Min	Max	Best	Min	Max	Best	Min	Max
Chemicals									
F$^-$	0.1	0	3	0.2	0	3	0	0	1
Cr(VI)	0	0	0.3	0	0	0.6	0	0	0.3
Hg(II)	150	72	673	150	118	1900	150	72	673
NO$_3^-$, NO$_2^-$	0	0	0	0	0	0	0	0	0
Pb(II)	50	10	500	100	30	2000	50	10	500
U(VI) – all isotopes	0.8	0.2	4	1.5	0.2	20	4	3	20
Radionuclides									
^{241}Am(III)	300	60	2000	300	200	4000	150	60	2000
^{14}C	5	0	100	5	0	100	15	5	250
^{60}Co(II,III)	10	0	2000	10	0	2000	15	3	2000
^{137}Cs	2000	200	10000	2000	600	10000	2000	200	10000
Eu(III) – all isotopes	300	60	2000	300	200	4000	150	60	2000
^{3}H	0	0	0	0	0	0	0	0	0
^{129}I – as iodide	0.2	0	2	0.2	0	5	0.2	0	2
^{63}Ni	300	50	2500	300	50	2500	300	50	2500
^{237}Np(V)	10	2	30	20	5	60	10	2	30
Pu – all isotopes	600	200	2000	600	200	4000	300	200	2000
^{226}Ra(II)	20	10	50	40	20	200	40	20	200
^{79}Se(VI,IV)	5	3	10	5	3	30	5	3	30
^{126}Sn(IV)	50	50	250	100	50	250	50	50	250
^{90}Sr	20	10	50	40	20	200	40	20	200
^{99}Tc(VII)	0	0	0.1	0	0	0.2	0	0	0.2

For gravel-size sediments, modify sand-size K_d values using Equations (2.3) and (2.4) in Section 2.4.
See Appendix A for references and selection rationale.

3.2   Waste Management Area B-BX-BY

Characterization studies were completed on sediment samples from five boreholes within or near WMA B-BX-BY. These include 299-E33-45 (Serne et al. 2002c), 299-E33-46 (Serne et al. 2002a), 299-E33-338 (Lindenmeier et al. 2003), and C3103 and C3104 (Lindenmeier et al. 2002). Brown et al. (2007c) also completed geochemical studies of several direct-push samples[3] recovered from boreholes surrounding tanks 241-B-110 and 241-BX-102 and related waste transfer lines and diversion boxes to provide evidence for the transit of a contaminant plume through the sediment column at WMA B-BX-BY. Some contaminated vadose zone sediment samples from crib B-7A and trench B-38 were also charac-terized. Figure 3.2 provides a map of WMA B-BX-BY showing the locations of the WMA facilities, RCRA wells, and locations where vadose zone samples were obtained.

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[3] Direct-push samples are collected using a closed-end boring technique in which small-diameter casing (2.5-in. outside diameter) is driven using a hydraulic hammer mounted to a backhoe.
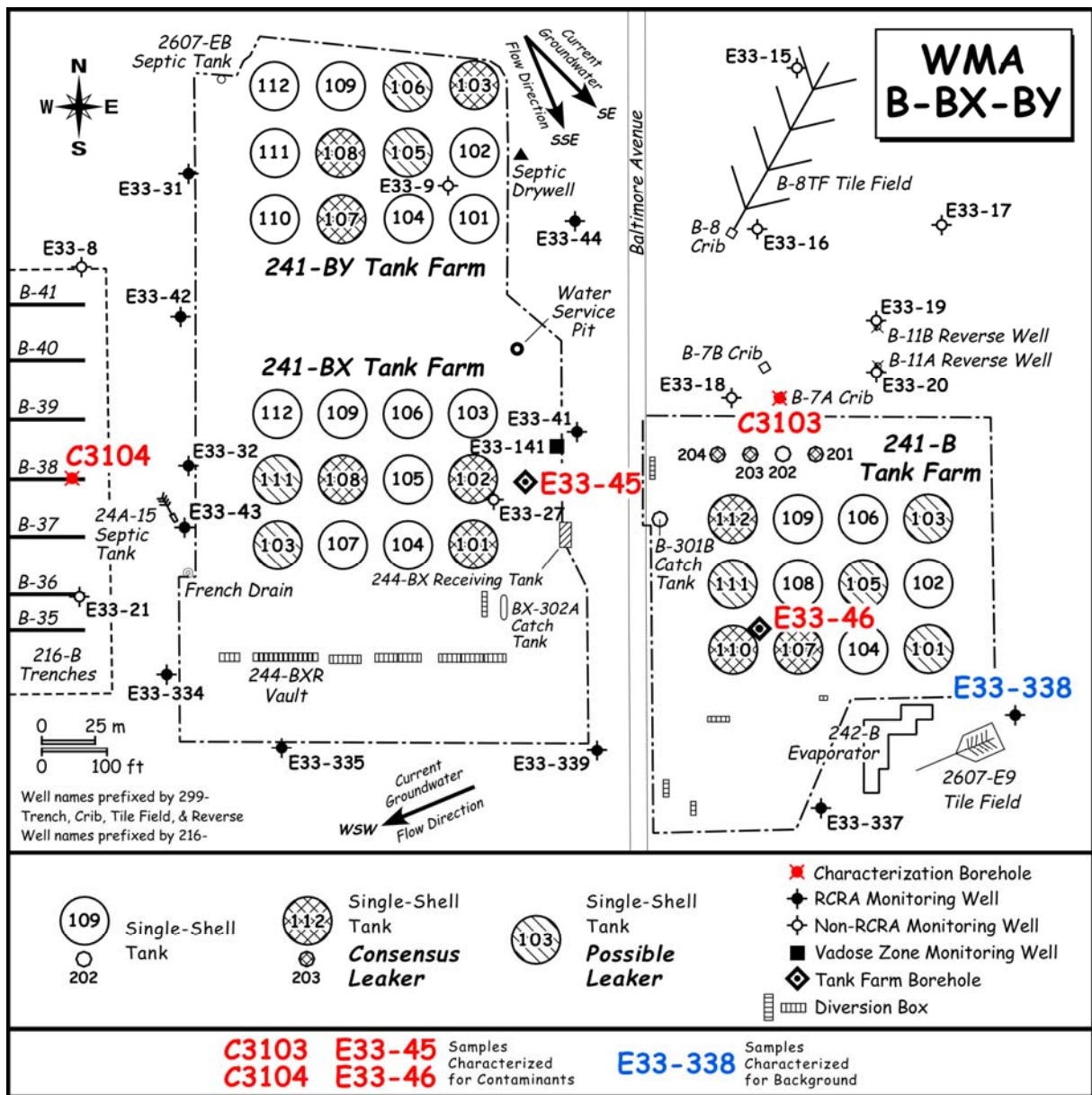
Figure 3.2. Location of Facilities, Wells and Boreholes in Waste Management Area B-BX-BY

Section 3.2.1 presents a brief summary description of the geology at WMA B-BX-BY. This is followed by summaries of the results and interpretation of the analyses conducted for each of the boreholes. These include, when possible, a description of the conceptual geologic model; vertical extent of contamination; controlling geochemical processes; and an assessment of the possible sources of contamination in the deep vadose zone, perched water, and groundwater. The final section includes K_d values (actual or assumed) needed as input parameters for performance assessment modeling.

3.2.1   Brief Description of Geology of the Waste Management Area B-BX-BY

The geology of the WMA B-BX-BY and vicinity is well understood as a result of several decades of site characterization activities. The main source of geologic data for the WMA is borehole information.

WMA B-BX-BY geology has been described in numerous reports (Price and Fecht 1976c, 1976d, 1976e; Tallman et al. 1979; Last et al. 1989; Connelly et al. 1992a; DOE-GJO 1997; Wood et al. 2000; Lindsey et al. 2001a). A detailed description of the geology is provided in Reidel and Chamness (2007). A summary table of the stratigraphic terminology and thicknesses of units beneath the B, BX, and BY Tank Farms is provided in Table 3.5. Conceptual models of the geology have also been developed for three of the characterization boreholes: 299-E33-338 (Lindenmeier et al. 2003), 299-E33-45 (Serne et al. 2002c), and 299-E33-46 (Serne et al. 2002a).

3.2.2 Geochemical Characterization in Borehole 299-E33-45

Results of geologic, geochemical, and selected physical characterization studies completed on vadose zone sediment recovered from borehole 299-E33-45 (installed northeast of tank BX-102) are presented in Serne et al. (2002c). Their report also presents an interpretation of the results in the context of the sediment lithologies, the vertical extent of contamination, the migration potential of the contaminants, and the likely sources of contamination in the vadose zone, perched water, and groundwater east of the BX Tank Farm. Some of the most significant parameters measured are presented as a function of depth in Figure 3.3. These include parameters that can have a significant influence on contaminant mobility and can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and indicators of hydrologic control (lithology, statigraphy, and moisture content). Note that in this and all subsequent figures, ^{238}U (determined by ICP-MS) is taken to be equal to total uranium.

Interpretation of the results identified ion exchange and precipitation as important mechanisms influencing the distribution of contaminants within that portion of the vadose zone affected by tank liquor. Significant indications of caustic alteration of the sediment mineralogy or porosity were not observed, but slightly elevated pH values (8.9 to 9.5) between the depths of 24 to 43 m bgs were observed. XRD measurements indicated no evidence of significant mineral alteration or precipitation of measurable amounts of new crystalline minerals resulting from the interaction of the tank liquor with the sediment. However, no samples were studied by scanning electron microscopy (SEM), a more sensitive characterization method for searching for faint evidence of caustic attack. The water extract testing showed elevated aluminum and iron and other constituents were present in the zone of elevated pH that suggests waste fluid-sediment interactions occurred and that precipitation of amorphous solids likely toke place as pH was neutralized to lower values.

The contaminated sediment analyses did not firmly identify the tank BX-102 overfill event as the source of the contamination in the groundwater east of the BX Tank Farm; however, the sediment characterization, including elevated concentrations of radionuclides (^{238}U, ^{99}Tc, etc.) and sulfate and nitrate from the metals tank waste solution does show that fluids from the overfill event are present in the vadose zone sediments to a depth of 52 m bgs at borehole 299-E33-45.

The near horizontally bedded, northeasterly dipping sediment likely caused horizontal flow of the migrating contaminants (Serne et al. 2002c). At borehole 299-E33-45, there are several fine-grained lenses within the Hanford H2 unit at 23, 37, and 51 m bgs that likely caused some horizontal spreading of the migrating fluids. The 6.4-m thick upper CCU$_u$, composed of fine-grained silt/clay, is also an important vertical flow boundary as evidenced by a perched water zone between 67 and 71 m bgs.

Table 3.5. Geologic Stratigraphy at Waste Management Area B-BX-BY (from Reidel and Chamness 2007)

Stratigraphic Symbol	Formation	Facies/Subunit	Description	Thickness[a]
Backfill	NA	Backfill – Anthropogenic	Gravel-dominated consisting of poorly to moderately sorted cobbles, pebbles, and coarse to medium sand with some silt derived from coarse-grained Hanford formation (H1 unit) excavated around tanks (Price and Fecht 1976c, 1976d, 1976e; Wood et al. 2000); occasional layers of sand to silty sand occur near the base of the backfill sequence.	12 m
H1	Hanford formation	Unit H1 – (Gravel-dominated facies association). Cataclysmic flood deposits (high-energy)	Gravel-dominated flood sequence; composed of mostly poorly-sorted, basaltic, sandy gravel to silty sandy gravel. Equivalent to the upper gravel sequence discussed by Last et al. (1989), the Q_{fg} documented by Reidel and Fecht (1994), Hanford Gravel Unit A of Johnson et al. (1999), coarse-grained sequence (H1 unit) of Wood et al. (2000) and gravel facies of unit H1 of Lindsey et al. (2001a), and gravel-dominated facies association of DOE-RL (2002).	Up to 20 m
H2		Unit H2 – (Sand-dominated facies association). Cataclysmic flood deposits (moderate energy)	Sand-dominated flood sequence; composed of mostly horizontal to tabular cross-bedded sand to gravelly sand. Some sand beds capped with thin layers of silty sand to sandy silt. Equivalent to Hanford Sands of Johnson et al. (1999), Fine-Grained Sequence (H2 unit) of Wood et al. (2000) and unit H2 of Lindsey et al. (2001a), the sandy sequence of Last et al. (1989) and Lindsey et al. (1992), and to Q_{fs} documented by Reidel and Fecht (1994), and sand-dominated facies association of DOE-RL (2002).	30 – 60 m
Hf/CCU$_u$	Undifferentiated Hanford formation/ Cold Creek unit	Upper Post-Ringold Formation eolian and/or overbank alluvial deposits	Silty sequence; consisting of interstratified well-sorted silt. Uncemented but may be moderately to strongly calcareous from detrital $CaCO_3$. Equivalent to the "early Palouse soil" (Tallman et al. 1979, DOE 1988, DOE-GJO 1997) and the Hf/PP deposits of Wood et al. (2000). Also equivalent to the upper Plio-Pleistocene unit in Lindsey et al. (2001a) and the fine-grained, laminated to massive lithofacies of the Cold Creek unit DOE-RL (2002).	0 – 10 m
Hf/CCU$_l$		Lower gravel resulting from eroded Ringold or post-Ringold Formation fluvial deposits	Gravelly sequence; consisting of open framework gravel and sandy gravel to gravelly sand; may be equivalent to pre-Missoula gravels in part and/or to H3 gravel facies of the Hanford formation where the fine facies is not present. It is possible some of these gravels are remnants of Ringold Formation unit A gravels.	10 – 30 m

(a) Multiply by 3.281 to convert meters to feet.
$CaCO_3$ = Calcium carbonate.
CCU$_l$ = Lower Cold Creek unit.
CCU$_u$ = Upper Cold Creek unit.
Hf/CCU = Hanford formation/Cold Creek unit.
NA = Not applicable.
Q_{fg} = Quaternary flood gravels.
Q_{fs} = Quaternary flood silt and sand.

Figure 3.3. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole 299-E33-45 Located in Waste Management Area B-BX-BY (Serne et al. 2002c)

3.13

Key findings of the detailed characterization of borehole 299-E33-45 vadose zone sediments are indicated below. The pore water electrical conductivity indicates a plume with two lobes distributed along the vertical axis. The shallow lobe, between 24.1 and 36.6 m bgs, resides within the middle-sand sequence in the Hanford H2 unit. The shallow lobe appears to pond on top of the fine-grained paleosol at 36.6 m bgs. A second and more concentrated lobe resides between 45.7 and 52.7 m bgs with the most concentrated fluid occurring between 45.7 m (149 ft) and 48.8 m (160 ft) bgs (within the Hanford H2 unit), and perhaps ponding on the fine-grained wet zone (i.e., 50.90 m [167 ft] to 51.755 m [169.8 ft] bgs) at the bottom of the Hanford H2 unit. Thus, the leading edge of the tank overfill plume appears to reside at approximately 51.8 m bgs, which is well above the water table at 77.7 m (254 ft) bgs.

High-nitrate concentrations in borehole 299-E33-45 sediment start at the contact between the Hanford H1 and H2 units at 10.4 m bgs and extend down into the fine-grained CCU_u and perhaps extend all the way to the water table at 77.7 m bgs. The bulk of the water-extractable nitrate is bounded by two thin fine-grained lenses in the H2 middle-sand sequence unit. The upper boundary is the fine-grained lens at 36.6 m bgs and lower boundary is the fine-grained 0.76 m thick lens that forms the bottom of the Hanford H2 unit at 50.9 to 51.8 m bgs. Nitrate concentrations reach 6,150 mg/L or ~0.1M at 47.6 m bgs. However, there also appears to be somewhat elevated nitrate throughout the Hanford H3 unit at a fairly constant pore water concentration of 600 ± 200 mg/L. The nitrate in the CCU_u pore water is slightly higher than the nitrate in the Hanford H3 unit. There is a decrease in pore water nitrate in the lower Cold Creek unit (CCU_l) down to the capillary fringe zone where nitrate increases to values similar to those found in the groundwater. The nitrate data suggest that tank BX-102 overfill fluids might have reached the groundwater. However, an alternate source of nitrate within and below the CCU_u could be the nearby cribs and trenches after allowing for horizontal transport within the perched water zone.

The first appearance of significantly elevated ^{238}U occurs at 22.4 m bgs in the Hanford H2 unit sediment just above the first thin lens (0.30-m thick at 22.7 m bgs). From about 27.4 m to ~33.8 m bgs, there is little indication that significantly elevated concentrations of uranium are present. Between 33.8 and 36.6 m bgs, the uranium content in the sediment averages about 100 ppm compared to a natural background uranium concentration of a few ppm. In the thin lens at 36.6 bgs, which may be a paleosol, the uranium concentration is very high (up to 1,649 ppm in the finest-grained material from this sample). Below 36.6 m bgs down to 44.2 m bgs, the uranium content in the sediment is quite high (reaching values between 200 and 500 ppm). Between 44.2 and 51.0 m bgs, in the lower portion of the Hanford H2 unit middle-sand sequence, there are slightly elevated uranium concentrations (between 50 and 200 ppm). Within the fine-grained lens between 50.9 and 51.8 m bgs, the uranium concentration increases again to values between 200 and 400 ppm. In the deeper Hanford H3 unit lower-sand sequence and the Cold Creek unit sediments, there is no significant indication of elevated uranium in the sediments.

The other major contaminant in the tank overfill fluid is ^{99}Tc. Elevated concentrations of ^{99}Tc are found in the vadose zone between 36.6 and 50.9 m bgs (within the middle-sand sequence of the Hanford H2 unit). There appears to be a second less-concentrated plume of ^{99}Tc within the contact between the Hanford H3 unit and the CCU_u unit (i.e., 67.1 to 71.6 m bgs). Both the acid-extractable and water-extractable data from Serne et al. (2002c) support this conclusion. There is very good agreement between the ^{99}Tc concentrations found in the actual pore water and the dilution-corrected sediment-water extracts in all regions and lithologies. Further, the ^{99}Tc concentration in the perched water also agrees with the nearby dilution-corrected water extracts. There are obvious elevated concentrations of ^{99}Tc in the CCU_u but not the CCU_l unit down to the water table. It is also possible that the ^{99}Tc in the perched water and groundwater in the vicinity of borehole 299-E33-45 did not come from the overfilling of tank BX-102.

Other possible sources are cribs that are located to the north (BY cribs) and northeast (B-7 and B-8 cribs), the B Tank Farm directly east, or possibly the B trenches west of the 299-E33-45 borehole.

The analyses of water-extractable cations suggest that ion-exchange dominates the major constituent pore water-sediment interactions in the borehole sediments where tank fluid passed by or currently exists. The leading edge of the tank-leak plume is enriched in alkaline earth cations that were displaced from the native sediment exchange sites. The interaction of uranium present in the 1951 tank overfill fluids with the vadose zone sediments appears to include a combination of surface adsorption and discrete solid phase precipitation-dissolution reactions with precipitation of uranium being the more important of these two processes. Zachara and co-investigators studied the occurrence of uranium at the microscopic scale in contaminated sediments from borehole 299-E33-45 (Catalano et al. 2004, Liu et al. 2004b, McKinley et al. 2006). Detailed characterization studies by McKinley et al. (2006) found that uranium had precipitated in the U(VI) oxidation state as 1-3 µm clusters of sodium boltwoodite [ideally $Na(UO_2)SiO_3OH \bullet 1.5H_2O$] in microfractures within the granitic clasts in the sediments. Their results suggest that some of the released uranium is effectively immobilized within these microfractures under the geochemical and hydrologic conditions of the presently unsaturated vadose zone. More details of these mechanistic studies are discussed in the Science and Technology Project contributions found in Appendix D of the *Field Investigation Report for Waste Management Area B-BX-BY* (RPP 2002).

Based on a comparison of the depth of migration of various contaminants and the percentages that are water leachable, Serne et al. (2002c) concluded that uranium had migrated more slowly than ^{99}Tc and nitrate. The ^{99}Tc desorption K_d data are consistently near zero, meaning that the ^{99}Tc is not interacting with the sediment. Although only a small fraction of uranium (10 to 30%) is water leachable in 1:1 sediment/water extracts over a few days, the uranium desorption K_d values are still quite low (<3 mL/g) in the entire zone where the bulk of the tank fluid is currently thought to reside.

In summary, the moisture content, pH, electrical conductivity, and the sodium, tritium, and uranium profiles in the sediment from borehole 299-E33-45 do not suggest that the leading edge of the plume has penetrated below 51.8 m bgs. In general, the majority of the ratios of constituents found in the pore water in the Hanford formation sediments from borehole 299-E33-45 are closer to those from the 1951 metals waste solution that escaped tank BX-102 during a cascading accident than to the other possible source, such as the 1970s BX-101 junction box leaks (Serne et al. 2002c). The profiles (but not the ratios to other contaminants) of two constituents considered to be mobile, ^{99}Tc and nitrate, suggest that the leading edge of the plume may have penetrated all the way to groundwater. However, the ratios also suggest that there may be other sources for the concentrations of these two mobile contaminants in the deep vadose zone. The perched water is a likely driving force to move fluids from other sources into the borehole environs. The ^{99}Tc-nitrate ratio for the perched water at 69.2 m bgs is ~1.8 pCi/mg and for the groundwater at 78.9 m bgs is 43 pCi/mg. These data indicate there may be a source of water, containing nitrate but not technetium, which is feeding the perched water zone. But this unknown water source has not changed the ratio in the surrounding sediments, nor diluted the groundwater that is found only 6.4 m deeper. The deep vadose sediment and pore water, perched water, and groundwater data at borehole 299-E33-45 do not present a clear picture on what might be occurring in the Cold Creek unit.

Another unresolved issue is the depth of penetration of uranium from the 1951 tank overfill fluids. Based on the zone with elevated total uranium content in the vadose zone sediments, Serne et al. (2002c) concluded that Hanford Site-derived uranium had not migrated below the fine-grained lens separating the

Hanford formation H2 unit from the H3 unit (~51.8 m bgs). However, the water extract data for the borehole sediments indicate that Hanford Site-derived uranium might have penetrated the entire Hanford formation down to the CCU$_u$ at ~67 m bgs.

3.2.3   Geochemical Characterization: Borehole 299-E33-46

Results of geologic, geochemical, and selected physical characterization analyses completed on vadose zone sediment recovered from borehole 299-E33-46 (installed ~4.6 m northeast of tank B-110) were presented in Serne et al. (2002a). Serne et al. (2002a) also interprets the data in the context of sediment lithologies, vertical extent of contamination, migration potential of the contaminants, and the likely source of contamination in the vadose zone and groundwater east of the B Tank Farm. Some of the most significant parameters measured are presented in Figure 3.4 as a function of depth. These include parameters that can have a significant influence on contaminant mobility and can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and indicators of hydrologic control (lithology, statigraphy, and moisture content).

The analyses identified ion exchange and precipitation reactions as two primary mechanisms that influence the distribution of contaminants within that portion of the vadose zone affected by tank waste fluid. Significant indications of caustic alteration of the sediment mineralogy or porosity were not observed, but slightly elevated pH values (8.8 to 9.5) between the depths of 15.8 m and 25.3 m bgs were found. XRD measurements indicate no evidence of mineral alteration or precipitation resulting from the interaction of the tank liquor with the sediment. However, no SEM analyses of samples were performed that might suggest that there is faint evidence of caustic attack.

It is concluded from the characterization of the 299-E33-46 borehole sediments that fluids from the transfer-line leak event are present in the vadose zone at borehole 299-E33-46 to a depth of 51.8 m bgs, within the Hanford H2 sand unit. Below this depth, the concentration of nitrate still appears to be slightly elevated above natural background levels. There is also elevated ^{99}Tc between 67.7 and 68.9 m bgs in the CCU$_u$. However, it could not be confirmed that this contamination traveled vertically downward through the entire vadose zone at this location. It may have migrated horizontally from other sources. Additionally, analyses did not confirm that the source of contamination in groundwater below and to the east of B Tank Farm is from the 1971 transfer-line leak at tank B-110.

The near horizontally bedded, northeasterly dipping sediment likely caused lateral flow of the migrating contaminants (Serne et al. 2002a). At borehole 299-E33-46, there are several fine-grained lens within the Hanford H2 unit at 25.9, 51.2, and 56.7 m bgs that likely cause some horizontal spreading of percolating fluids. The 3.9-m thick CCU$_u$ is also an important horizontal flow conduit between 65.5-69.4 m bgs.

The pore-water electrical conductivity shows a plume with two lobes distributed one above the other. The shallower but more concentrated lobe, between 15.4 and 25.9 m bgs, resides within the middle-sand sequence in the Hanford H2 unit. The shallow lobe appears to pond on top of the fine-grained lens at 25.9 m bgs. The slightly less-concentrated lobe resides between 27.6 and 42.7 m bgs within the Hanford H2 unit. Thus, the leading edge of the transfer-line leak plume appears to reside well above the water table, which is at 78.0 m bgs.
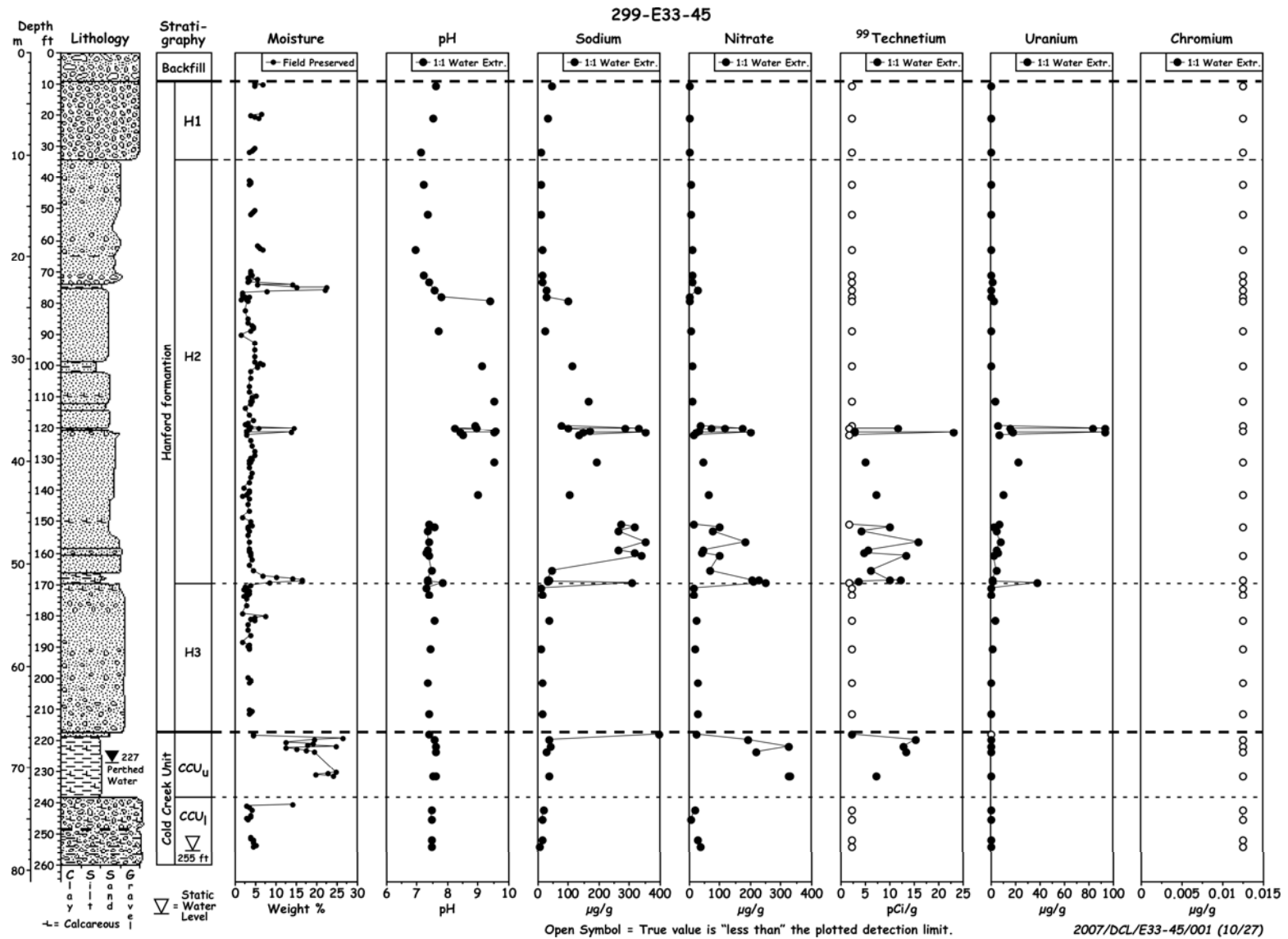
Figure 3.4. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole 299-E33-46 Located in Waste Management Area B-BX-BY (Serne et al. 2002a)

Elevated nitrate concentrations in 299-E33-46 borehole sediment start at 15.4 m bgs, but the more concentrated zone resides between 26.8 and 51.2 m bgs within the Hanford H2 unit. This more concentrated nitrate plume appears to stop at the fine-grained thin lens at 51.2 m bgs. The peak vadose zone pore-water nitrate concentration is 1,500 mg/L at 40.8 m bgs. The deeper units, Hanford H3 and CCU_u, have pore waters that contain 100 to 200 and 130 mg/L nitrate, respectively. These values appear to be slightly elevated above natural background values. Even the coarse-grained CCU_l that includes the water table has pore-water nitrate concentrations near 50 mg/L, indicating slightly elevated nitrate concentrations penetrate the entire vadose zone at this borehole. However, an alternate source of nitrate within and below the CCU_u could be waste solutions originating from nearby cribs and trenches that was transported horizontally within the very moist fine-grained sediments of the CCU_u until fractures in the CCL_l were encountered that allowed further vertical migration.

Within the Hanford H2 unit, the pore-water concentrations of fluoride and bicarbonate are also elevated above natural background levels down to a depth of about 36.6 m bgs. The pore-water cation distributions show the ion-exchange front wherein the Na^+ in the tank fluids pushes the naturally occurring divalent cations (Ca^{2+}, Mg^{2+}, and Sr^{2+}) deeper into the sediments and out in front of the plume. The most concentrated portion of the vadose zone plume has a pore-water chemical composition that is 0.15M [3,450 mg/L] sodium and 0.13 M [7,930 mg/L] bicarbonate, 0.01 M [190 mg/L] fluoride, 0.007 M sulfate [690 mg/L], and 0.003 M [190 mg/L] nitrate. This composition is not as saline as contaminated pore waters below tank BX-102 or under WMA S-SX.

The only detectable radionuclides in the vadose zone sediments from borehole 299-E33-46 are ^{90}Sr, ^{99}Tc and a faint trace of water-leachable uranium.[4] Strontium-90 is considered to be the primary radionuclide released from the tank B-110 transfer line and is concentrated in the sediment between 19 and 28 m bgs at concentrations between 1,000 and 11,250 pCi/g. Strontium-90 in the sediments is not readily water leachable yielding an in situ desorption K_d value of >100 ml/g. All ^{99}Tc concentrations in the shallow depths are at or below the detection limit. Thus, it is difficult to determine if the ^{99}Tc profile at 299-E33-46 can be traced from below the tank all the way to the groundwater. The two more concentrated peaks of ^{99}Tc are found in the deep Hanford H3 unit and in the CCU_u. It is likely that the ^{99}Tc found at the deeper depths is from horizontal migration of fluids containing ^{99}Tc from other sources carried to depth by active disposal of large quantities of contaminated water or by some other driving force such as domestic water line leaks or localized recharge from topographic lows where snow melt has been found to concentrate.

PNNL's Hanford Site Science and Technology (S&T) Program completed specialized mineralogical analyses as part of laboratory studies to determine the geochemical reactions controlling the sorption and speciation of ^{90}Sr (McKinley et al. 2007) in sediment samples from borehole 299-E33-46. Based on laboratory studies where this sediment was equilibrated with varying concentrations of dissolved Na^+ and Ca^{2+}, McKinley et al. (2007) applied a cation exchange model to successfully predict the desorption data. The model included binary exchange reactions for Sr^{2+}, Mg^{2+}, Ca^{2+}, and Na^+ and an equilibrium dissolution/precipitation reaction for calcite. Analyses of the contaminated sediment using digital

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[4] Water-leachable uranium is a very sensitive method of discerning whether uranium derived from the Hanford Site is present because natural uranium is not readily extracted with water at a 1:1 ratio of sediment to water. The amount of uranium leached in the water extract of selected sediments from borehole 299-E33-46 was too large to have been natural uranium in the sediments.

autoradiography identified smectite formed from weathering of interstitial glass in basaltic lithic fragments present in the Hanford formation sands as the exchanger phase containing ^{90}Sr.

In summary, the moisture content, pH, electrical conductivity, sodium, and ^{90}Sr profiles do not suggest that the leading edge of the plume has penetrated below 51.8 m bgs. The profiles of two mobile constituents, ^{99}Tc and nitrate, suggest that the leading edge of the plume may have penetrated all the way to groundwater. However, there may be other sources of these two mobile contaminants in the deep vadose zone. The CCU_u sediments, which contain a perched water table at several nearby wells, likely promote the lateral migration of fluids from other sources into the borehole environs.

3.2.4　　Geochemical Characterization: Borehole 299-E33-338

Results of geologic, geochemical, and selected physical characterization studies completed on vadose zone sediment recovered from borehole 299-E33-338 installed near WMA B-BX-BY are provided in Lindenmeier et al. (2003). Lindenmeier et al. (2003) also interpreted the data in the context of sediment lithologies and the chemical composition of natural background vadose zone pore water proximal to the B Tank Farm. Some of the most significant parameters measured are presented in Figure 3.5 as a function of depth. These include parameters that can have a significant influence on contaminant mobility and can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and indicators of hydrologic control (lithology, statigraphy, and moisture content).

The conceptual model of the vadose zone associated with the 299 E33-338 borehole involves five distinct stratigraphic units beginning with the Hanford formation H1 unit from the groundsurface to a depth of approximately 15.7 m described as a sandy gravel to gravelly sand sequence. This is followed by the Hanford formation H2 unit extending to a depth of approximately 57.9 m that is a sequence consisting of sand-dominated facies, with multiple graded beds of horizontal to tabular cross-bedded sand to slightly gravelly sand. These graded beds are sometimes capped with thin layers of silty sand to silt. The last unit associated with the cataclysmic flood deposits is the Hanford H3 formation unit that extends to a depth of approximately 64.8 m. It is a gravelly sand to slightly gravelly sand sequence. Just below the Hanford H3 unit is the CCU_u, extending to a depth of approximately 67.8 m. This unit is a silt-dominated sequence consisting of interstratified well sorted silt and fine sand. The last unit characterized from this borehole was the CCU_l extending to a depth of approximately 82.6 m; however, sampling ended at approximately 73.1 m. This unit is differentiated from the CCU_u by its sandy gravel to gravelly sand sequence consisting predominantly of unconsolidated basalt-rich sand and gravel.

Sediment samples from the various stratigraphic units were analyzed and characterized in the laboratory using the following analyses and methods: mass water content, soil suction, particle-size distribution, calcium carbonate and organic carbon content, bulk chemical composition, mineralogy, water leach (1:1 sediment/water extractions), and acid leach (8M nitric acid extractions).

Physical properties, such as particle-size distribution and water content, varied according to lithology as expected. In general, areas of elevated water content (~ >5%) were typically associated with regions of fine grained sediments. Most notable are those regions involving lithological facies at which water contents equal or exceed 10%. Three major peaks are noted at 15.7, 52.9, and 67.1 m bgs with water contents of 13.0, 14.3, and 26.0%, respectively. Along with water content, soil suction measurements
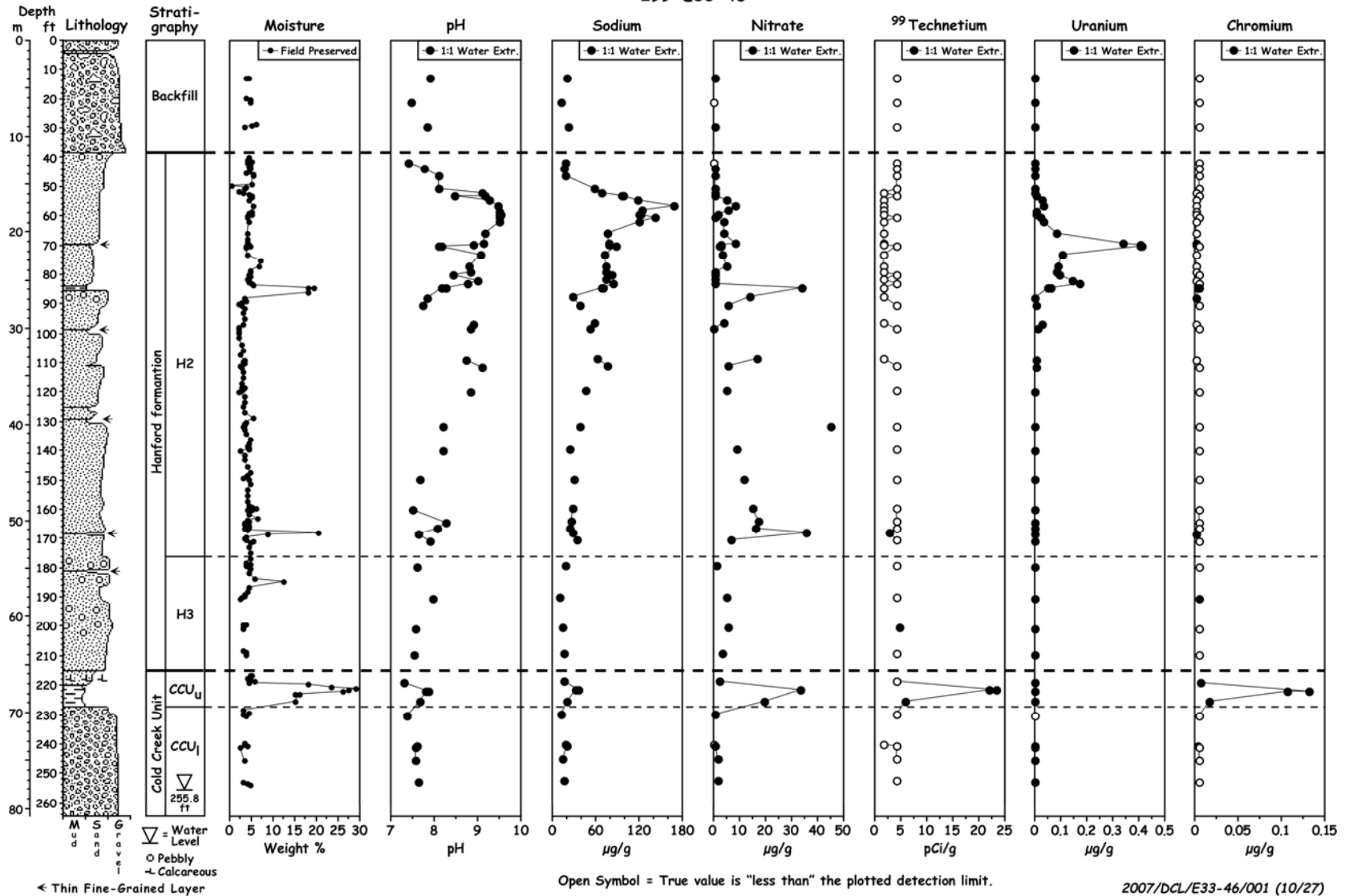
Figure 3.5. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole 299-E33-338 Located in Waste Management Area B-BX-BY (Lindenmeier et al. 2003)

were made on most of the core liner and grab samples from the borehole using a filter paper method. Three major peaks were noted at approximately 14, 64, and 73 m bgs with suction measurements of approximately 1.3, 1.5, and 2.2 Mpa. The matric potential profile indicates that wetting from surface recharge has not reached the water table.

Inorganic carbon results reported in terms of calcium carbonate were found to be within the range of 0.5 to 2.0 wt.%, and are consistent with results reported elsewhere (e.g., Serne et al. 2002a, 2002b, 2002c, 2002d, 2002e, 2002f). The low values for organic carbon (0.01 to 0.14%) are within the ranges generally reported for sediment at the Hanford Site. The method used to measure the organic carbon relies on subtracting the measured concentration of inorganic carbon from the measured concentration of total carbon in the sample. For such low carbon values, this method is not very accurate.

Sediment samples were analyzed for the concentrations of major and trace elements in the bulk solid using a lithium metaborate/tetraborate procedure to fuse the sample to readily soluble form, and subsequent analysis of the dissolved fused solid by inductively coupled plasma – optical emission spectrometry (ICP-OES) and inductively-coupled plasma – mass spectrometry (ICP-MS) methods. Overall results showed very little difference in the primary element concentrations for any of the bulk sediment samples as a function of depth or lithology.

The water chemistry analysis for samples collected between 5 and 73 m bgs using the 1:1 soil/water extract method shows no strong trends as a function of depth, and there is little, if any, indication of tank waste interaction with vadose zone soils at this location. Primary characteristics include the following:

- The pH for the 1:1 sediment/water extract varied from 6.97 to 7.74, and in general increased with depth to an average value of 7.4.

- There were small increases in pH at the contact between the Hanford H2 and H3 units and the top and bottom of the Plio-Pleistocene mud unit.

- Pore water electrical conductivity varied from 0.88 to 4.3 mS/cm with an average of 2.4 mS/cm.

- Electrical conductivity values were high in the Hanford H2 unit at approximately 49 m bgs and in the deepest sample characterized in the CCU_l.

The shapes of the major cation profiles (sodium, potassium, calcium, magnesium, and strontium) in terms of calculated pore-water concentration versus depth are very similar with slight peaks in the deep portion of the Hanford H2 unit at approximately 49 m bgs, at the top of the CCU_u, and in the deepest sample characterized in the CCU_l. All three of these samples had very low water contents and thus the dilution factor was high. The apparent high pore-water concentrations likely represent some dissolution of salts from the sediment that are multiplied by a large dilution factor, and thus suggest more saline pore water than surrounding sediments with higher water content.

Unlike the major cation profiles, the major anion profiles (fluoride, chloride, nitrate, bicarbonate, phosphate, and sulfate) in terms of calculated pore-water concentration versus depth showed no consistent depths where all anions peaked. The wetter samples do consistently show low calculated pore-water anion concentrations suggesting that the dilution factor is again controlling the apparent concentrations. That is, all the sediments likely dissolve some salts that are not truly in the pore water, so that the dilution correction makes it appear that the pore-water anion concentrations are higher in the drier sediments.

3.2.5 Geochemical Characterization: Boreholes C3103 and C3104

Lindenmeier et al. (2002) present a summary of the geologic, geochemical, and selected physical characterization data collected on vadose zone sediment recovered from borehole C3103 (B7A crib), a few sediment samples from C3104 (trench 216-B-38), and supplemental data provided from borehole C3104 reported by Bechtel Hanford Inc. in *Borehole Summary Report for Boreholes C3101, C3341, C3342, C3343, and C3344, in the 216-B-38 Trench and 216-B-7A Crib, 200-TW-2 Tank Waste Group Operable Unit* (Todd and Trice 2002). Some of the most significant parameters measured in borehole C3103 are presented in Figure 3.6 as a function of depth. These include parameters that can have a significant influence on contaminant mobility and can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and indicators of hydrologic control (lithology, statigraphy, and moisture content).

The geochemical characterization work completed on sediments from borehole C3103 was less extensive than for samples collected from boreholes 299-E33-45 and 299-E33-46. Analyses that were conducted include measurement of moisture content, and analyses of 1:1 sediment/water extracts for pH, electrical conductivity, major cations and anions, trace metals, and gamma energy analysis.

The results of these analyses indicate that reactions between wastewater and the sediment column appears to result in the reduction of tank fluid pH by reaction with lower pH soil water, in situ displacement of ambient divalent soil cations with high concentrations of sodium present in the wastewater, precipitation of uranium, and essentially complete sorption of ^{137}Cs just below the crib bottom.

Best estimates of typical wastewater fluid suggest that a pH between 10 and 11 was likely. The observation of an elevated zone between pH 8.5 and 9 just below the crib bottom indicates partial neutralization of the infiltrating wastewater by reaction with sediment minerals and sediment water whose ambient pH values are between 7.0 and 7.5 in this area. The location of a high concentration of ^{137}Cs at 9.08×10^4 pCi/g from a grab sample analysis is estimated to be between 7 and 11 m bgs. This value is consistent with the 6.73×10^4 to 1.53×10^5 pCi/g ^{137}Cs concentration range for this depth as reported in DOE-RL (2002). Further down the soil column (18.3 m), the concentration of ^{137}Cs is less than background indicating a rapid and essentially complete sorption of this contaminant within the soil-water system. Uranium appears to have migrated down as far as 27.4 m bgs. Conversely, other more mobile constituents appear to have migrated down to groundwater as indicated by elevated concentrations of nitrate and sulfate in almost all samples. The ^{99}Tc profile was generated based on values that were less than the detection limit and no pore water corrected technetium values were determined above the range of 1.1×10^4 to 3.3×10^4 pCi/L.

The results from the analyses of samples from borehole C3104 are consistent with the results of those from borehole C3103 in that no detectable ^{99}Tc appeared to be associated with high nitrate levels.

3.2.6 Characterization Results of Direct-Push Vadose Zone Sediments from the B and BX Tank Farms

Brown et al. (2007c) conducted geochemical studies to provide evidence for the transit of a plume of caustic-waste solution through the sediment column at the Hanford 241-B and -BX Tank Farms. Six vadose-zone cone-penetrometer (direct-push) boreholes were emplaced in the vicinity of the 241-B-BX
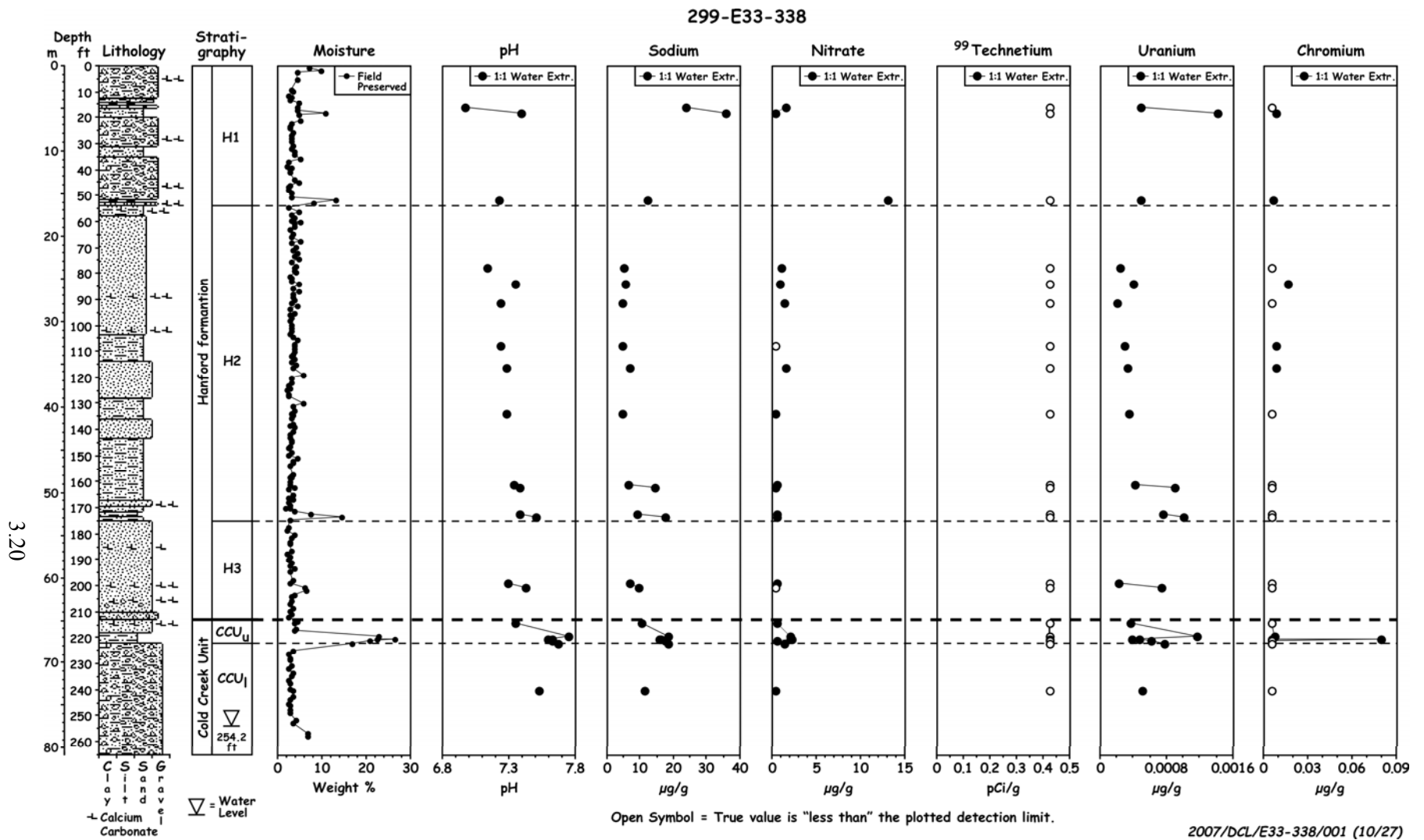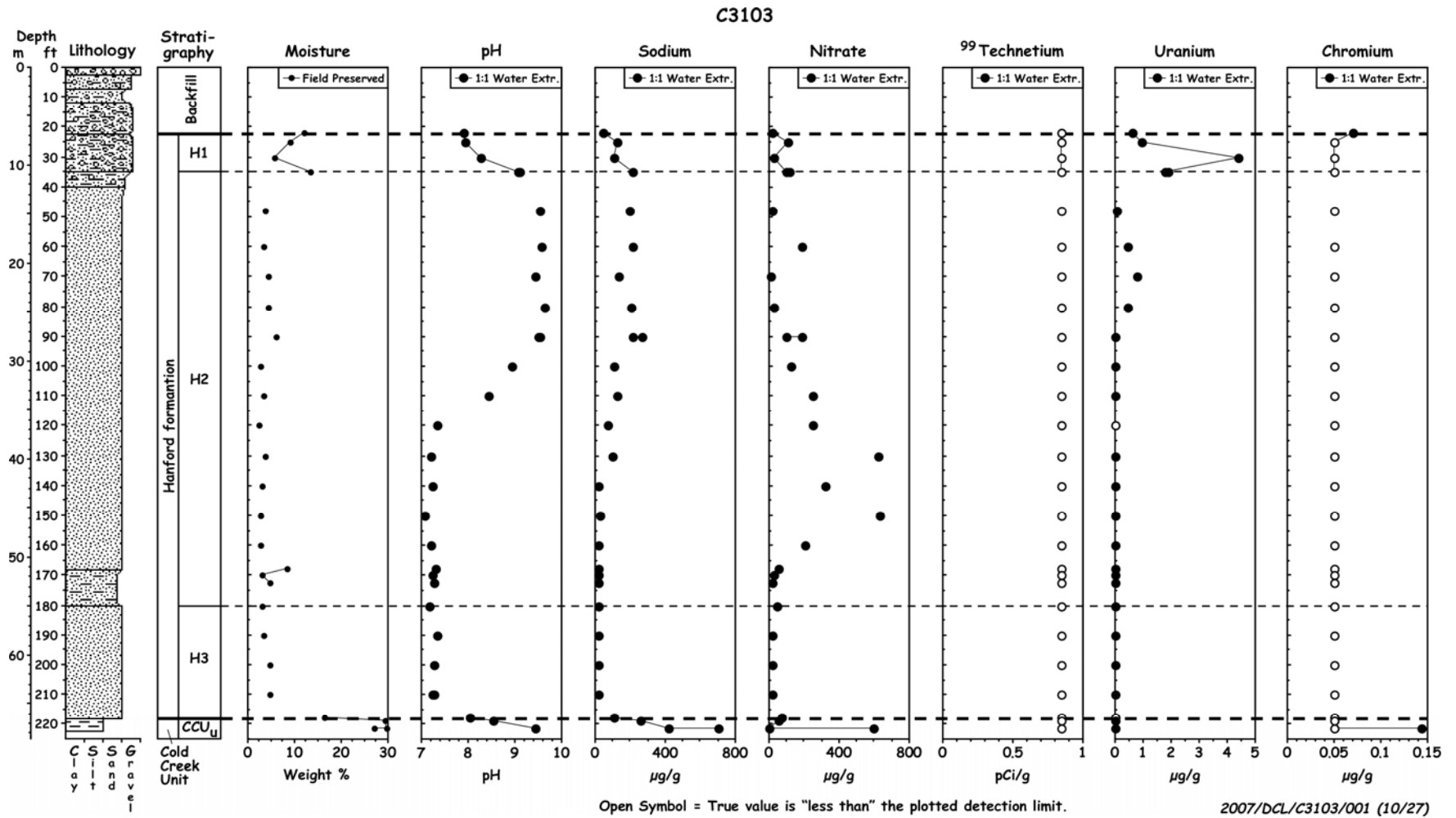
Figure 3.6. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole C3103 located in Waste Management Area B-BX-BY (Lindenmeier et al. 2002)

Tank Farms for geologic/geochemical sampling. Three of the holes were emplaced within B Tank Farm (Figure 3.7), and the other three were drilled within BX Tank Farm (Figure 3.8). Direct-push samples recovered from boreholes surrounding tanks 241-B-110 and 241-BX-102 and related waste transfer lines and diversion boxes included sediments typical of those previously recovered from other localities on the Hanford Site. The Hanford formation sediments are dominantly quartzo-feldspathic sands strewn with lithic fragments, displaying a range of particle-size distributions and sorting characteristics. Some moderately well-sorted, fine-grained lithologies are interpreted as lenticular bodies irregularly dispersed in coarser-grained, more poorly sorted sediments.

Some of the most significant parameters measured in the B and BX Tank Farms' direct-push samples are presented in Figure 3.9 as a function of depth. These include parameters that can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and moisture content. Tier I tests conducted on the samples revealed an inverse correlation between moisture content and sediment-size fraction, as shown in Figure 3.9 (i.e., there is greater moisture content in finer-grained specimens). The Tier I tests also showed that the pore water solutions were likely sodium-rich, moderately saline, and possessed higher pH values than background samples. These data are characteristic of sediments that have encountered sodium-rich, saline, caustic-waste solutions, as at other suspect contamination sites at the Hanford Site (Brown et al. 2006a; Serne et al. 2002a, 2002b, 2002c, 2002e). Analyses of solutions from 1:1 water extracts indicate the total cation and anion concentrations have a relatively good charge balance, indicating that most of the geochemical species have been accounted for in the solution analyses. The water extract data also indicate unusually high concentrations of aluminum, iron, and phosphorus at concentrations up to 2.36 μg/g, 5.73 μg/g, and 7.21 μg/g, respectively. The relatively high concentrations of aluminum and iron (both of these elements are typically not present at quantifiable concentrations in non-contaminated sediments) may be the result of dissolution of secondary amorphous phases that precipitated after a reactive plume partially dissolved aluminum- and iron-bearing phases as it migrated through the sediment column. However, the presence of elevated concentrations of phosphorous may be the signature of wastes derived from the bismuth phosphate separation process. In these sediments, mobile contaminants such as ^{99}Tc are present at either low concentrations or are below the analytical detection limit. However, the mobile contaminants were expected to be present mainly along a narrow plume front, and if this front had passed the depths that were sampled, the retention of these contaminants in the direct-push samples would be minor. Therefore, the lack of mobile contaminants in these sediments indicates that the primary plume front has migrated beyond the depth interrogated by the direct push sampling campaign. Additionally, ^{238}U was detected in nearly all direct-push sediment specimens (by acid extract experiments) at concentrations above the natural crustal average, and the presence of several anthropogenic radioisotopes (such as ^{60}Co, ^{137}Cs, ^{154}Eu, and ^{155}Eu) were also detected by gamma emission analysis. Detection of these contaminants are direct confirmation of sediment contamination.

As described in Brown et al. (2007c), researchers selected a pair of lithologies from a single borehole they anticipated would reveal details of the mechanism for radionuclide binding in these sediments, and subjected the lithologics to a series of Tier II tests. These samples, coarse- and fine-grained specimens subdivided from a single lithologic entity, were labeled B1JWW6C fine and coarse. The occurrence of fine- and coarse-grained materials provided a good opportunity to probe the controls that mineralogy, sediment-size fraction, and hydraulic properties exert on the distribution of radionuclide elements. To determine the total concentration of uranium in the sediments, the two samples were completely dissolved
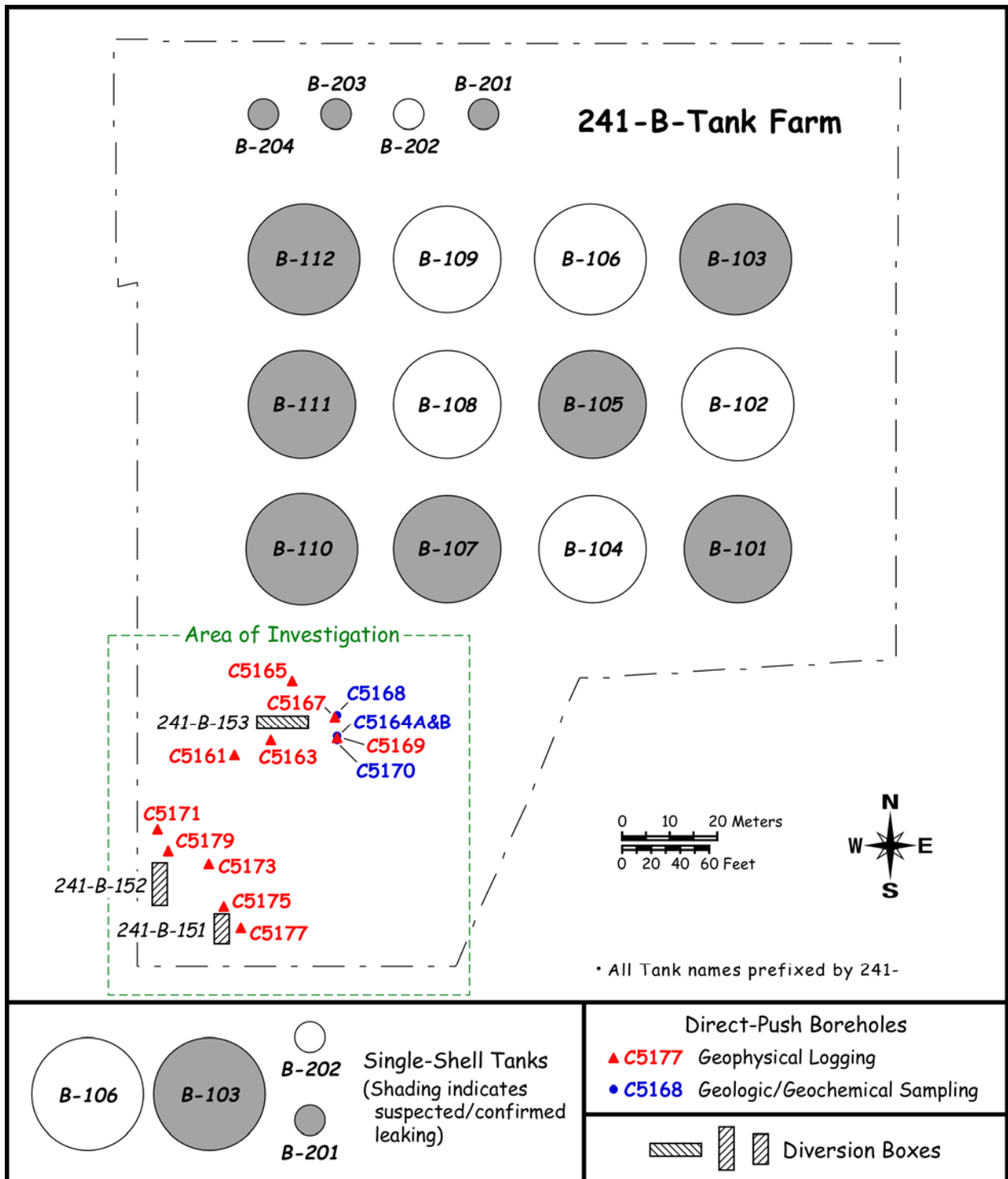
Figure 3.7. Locations of New Direct-Push Boreholes in Vicinity of the 241-B Tank Farm
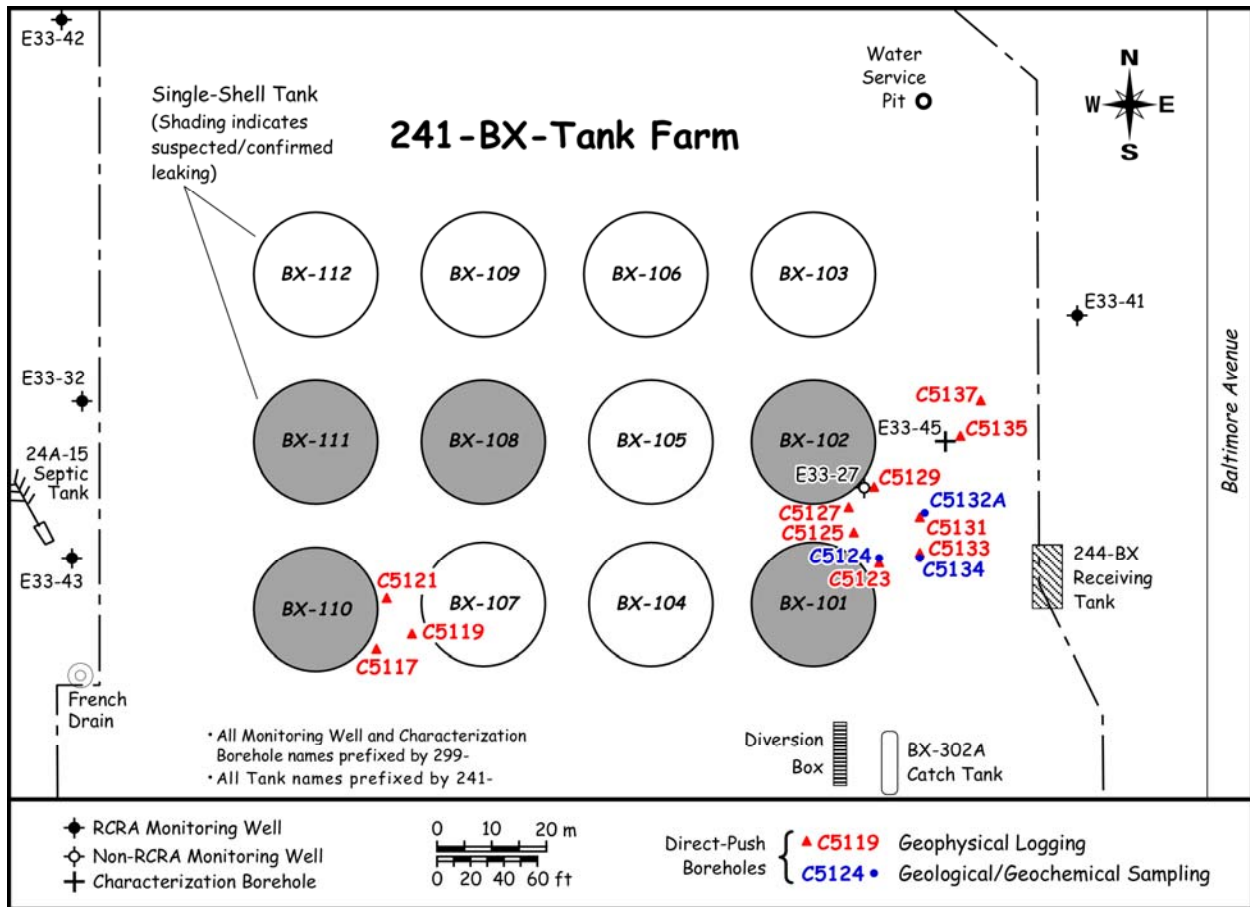
Figure 3.8. Locations of New Direct-Push Boreholes in Vicinity of the 241-BX Tank Farm

using an microwave-assisted acid digestion procedure. The fine-grained sample contained nearly four times the concentration of uranium as the coarse-grained sample (390 versus 108 μg/g uranium). Additional tests were performed on the coarse-grained sample that was subdivided by dry sieving into its various size fractions. These analyses revealed that most of the uranium resides in the finer-size fractions. It is not yet evident, however, if this preference for the finer-particle fraction is a reflection of mineralogical, hydraulic, or kinetic factors.

Tests were carried out to distinguish between mobile and immobile (sequestered) uranium. The first test consisted of exposing the sediment to a bicarbonate-carbonate leach solution. The solution was designed to remove weakly sorbing uranium from mineral grains by forming strong uranyl-carbonate aqueous complexes without liberating uranium by dissolving solid reservoirs that sequester uranium. The second test consisted of equilibrating the uranium-contaminated sediment with a synthetic groundwater solution, and then spiking the solution with a uranium isotope that can easily be distinguished analytically from common uranium. The dopant in this case was ^{233}U, which can be conveniently detected using liquid scintillation counting. This test rests on the supposition that weakly sorbed common uranium (from contamination) can exchange with the doped ^{233}U such that the uptake of both isotopes can be quantified. Therefore, the extent of uptake of ^{233}U correlates with the amount of mobile uranium in the system.
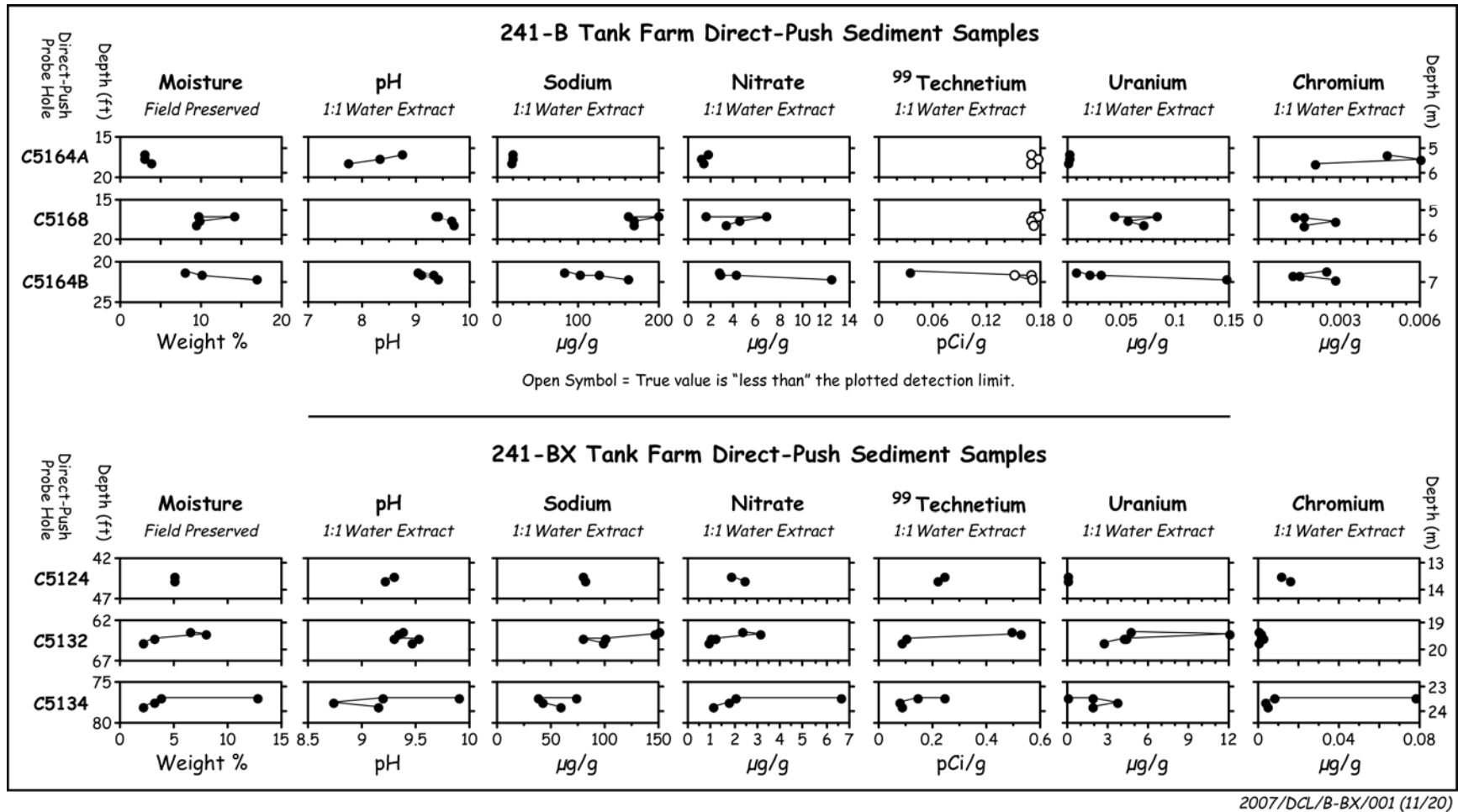
Figure 3.9. Moisture Content and Significant Geochemical Parameters Measured in Direct-Push Sediment Samples Collected from the B and BX Tank Farms (Brown et al. 2007c)

From both the Tier I and Tier II tests, Brown et al. (2007c) calculated estimated K_d values for uranium on the B1JWW6C fine- and coarse-sediment samples. Based on the concentration of uranium recovered in the bicarbonate-carbonate solution and the concentration of uranium from the 1:1 water extract solution, they obtained K_d values of 983 and 1.56 mL/g for the fine- and coarse-grained specimens, respectively. These values are numerically similar to the K_d values of 927 and 1.27 mL/g determined from the acid extract and 1:1 water extract data for the fine- and coarse-grained specimens, respectively. The concentrations of uranium determined from the isotope exchange experiments are lower than those obtained by the acid or bicarbonate-carbonate extracts, so the resulting K_d values are smaller (832 and 1.19 mL/g for the fine- and coarse-grained, respectively), yet are similar to the other K_d values. The K_d values determined by the bicarbonate-carbonate and the isotope exchange experiments differ by less than 10% relative and thus indistinguishable statistically (Brown et al. 2007c). The quantities of mobile uranium in the coarse- and fine-grained sediments are, by the two test methods, similar and make up 51 to 67% and 63 to 75% of the total uranium, respectively. These data indicate that a sizeable fraction of uranium is sequestered in a phase that is resistant to dissolution.

Brown et al. (2007c) used micro-X-ray fluorescence (μ-XRF) and micro-X-ray absorption near-edge spectroscopy (μ-XANES) to identify the uranium-sequestering phase in fine- and coarse-grained sediment specimens from B1JWW6C. Small areas (400 × 400 μm) within each specimen were analyzed, and element distribution maps from μ-XRF showed a strong correlation between the spatial proximity of uranium and calcium. Evaluation by μ-XANES of the oxidation state of uranium in these spots indicated that the majority of uranium is in the hexavalent state [U(VI)]. These data support the supposition that the uranium sequestering phase is the calcium uranyl silicate uranophane $[Ca(UO_2)_2(SiO_3OH)_2(H_2O)_5]$. Results from further analysis using time-resolved laser induced fluorescence were consistent with the spectrum of uranophane in both the fine- and coarse-grained samples.

Results reported by Brown et al. (2007c) indicate that the B and BX Tank Farm sediments further delineate the extent of contamination from wastes that escaped either from storage or during transit between waste storage tanks. It is likely the plume front migrated down past the level of sampling from the direct-push boreholes, so a detailed analysis of the total amount of contaminants released to the subsurface could not be made from this study. However, their study (Brown et al. 2007c) shows an unusual amount of mobile uranium is present in the finer-grained fractions that are interspersed through-out the Hanford formation, and provides a vital link to understanding the migration of contaminants that encounter different lithologies possessing different hydraulic qualities. Modeling the migration of contaminants and the movement of pore waters may thus depend on understanding the effects of capillary barriers that form as a result of the layering of fine- and coarse-grained sediments.

3.2.7 Estimated K_d Values for Key Contaminants at Waste Management Area B-BX-BY

The calculated chemical compositions of the various waste streams which were released to the vadose zone from these 12 tanks shown in Figure 3.2 are listed in Table 3.6. The waste composition of B-107 is a mixture of waste streams P1, CWP1, and CWP2 such that the overall composition is a sodium-nitrate-aluminate-hydroxide waste stream with an ionic strength of approximately 1 to 1.5 M.

Table 3.6. Estimated Chemical Composition of Waste Streams Released from B-BX-BY Tanks (from Corbin et al. 2005)

Waste Type	Concentration (mol/L)									
	MW1	P1	P2	P2'	CWP1	CWP2	BL	CSR	224-1	BYSltCk
Na^+	1.91	0.72	1.17	9.35E-02	2.38	1.62	3.67	4.15	1.62	11.1
Ca^{2+}	0.0037	0.0037	0.0037	0.482	0.0037	0.0037	0.01	0.0038	0.0037	0.0038
K^+	7.74E-04	0.003	0.006	0.019	0.0015	0.0025	0.015	0.021	0.232	0.064
Sr^{2+}	6.33E-07	5.00E-07	5.00E-07	2.02E-04	1.33E-07	1.33E-07	1.50E-05	5.30E-07	1.60E-11	1.76E-06
NH_4^+	7.18E-05	0.008	0.031	0	9.10E-05	1.80E-05	6.55E-04	0.025	3.20E-14	0.054
Cr	0.0035	0.008	0.008	0	0.003	0.003	2.00E-07	0.032	0.007	0.055
Mn	0	0	0	1.13E-04	0	0	0	3.24E-04	5.60E-04	5.56E-04
Fe	0.0019	0.0018	0.0018	8.59E-04	0.0018	0.0018	0.017	0.0019	0.0018	0.0018
Ni	0.0018	0.0018	0.0018	0	0.0015	0.0015	0.01	0.0018	0.0016	0.0018
Bi	3.13E-04	0	0	0	0	0	0	5.10E-06	4.60E-04	1.62E-04
NO_3^-	0.186	0.175	0.12	9.45E-03	0.69	0.69	0.772	1.25	1.39	3.5
NO_2^-	0.017	0.277	0.615	0	0.8	0.28	0.117	0.86	0	2.53
CO_3^{2-}	0.624	0.004	0.004	1.263	0.004	0.004	0.271	0.184	0.0037	0.527
PO_4^{3-}	0.071	0	0	0	0	0	0.01	0.0065	0.033	0.062
SO_4^{2-}	0.124	0.044	0.124	0.108	0.009	0.007	0.044	0.094	0.003	0.124
Cl^-	0.0036	0.014	0.026	0.030	0.007	0.012	0.069	0.07	0.029	0.212
F^-	0	0	0	0.007	0	0	0	0.0016	0.271	0.106
OH^-	0.036	0.184	0.185	NA	0.019	0.019	0.043	0.994	0.079	1.28
$Al(OH)_4^-$	0	0	0	0	0.852	0.629	0.261	0.385	0	1.75
Organics	0	0	0	0	0	0	0.7	0.07	0	0.26

K_d value estimates for key contaminants in the high and intermediate impact zones of WMA B-BX-BY are shown in Table 3.7. Sediment outside this intermediate impact zone should exhibit sorption properties similar to uncontaminated sediments contacting uncontaminated pore waters and have K_d values as given in Appendix B of Cantrell et al. (2007).

3.3   Waste Management Area C

Two geochemical characterization studies have been conducted on vadose zone sediments collected from below the C Tank Farm (Brown et al. 2006a, 2007a). The first study was completed on sediments recovered from borehole C4297, installed adjacent to tank C-105, and sediment from borehole 299-E27-22 installed directly north of the C Tank Farm (Brown et al. 2006a). The results of the characterization work on borehole 299-E27-22 were intended to represent background (i.e., uncontam-inated) sediments against which to compare contaminated sediments during the C Tank Farm characteri-zation effort. Their results indicated that sediments from this borehole had been contaminated with an unknown non-radiological waste stream. As a result, it was recommended that data from borehole 299-E33-338 (Lindenmeier et al. 2003) be used for background data instead of the results for 299-E27-22.

The second study conducted on vadose zone sediments collected from below the C Tank Farm involved investigation of the C-152 transfer-line leak. This report (Brown et al. 2007a) contains all the geologic, geochemical, and selected physical characterization data compiled on vadose zone sediment recovered from direct-push samples collected around the site of an unplanned release (UPR), UPR-200-E-82, adjacent to the 241-C-152 Diversion Box located in WMA C.

For a brief description of the geology applicable to the C Tank Farm refer to Section 3.1.1 in the WMA A-AX section. A map of WMA C showing the locations of the WMA facilities, RCRA wells, and locations where vadose zone samples have been obtained is provided in Figure 3.10.

3.3.1   Geochemical Characterization: Boreholes C4297 and 299-E27-22

Sediments from borehole 299-E27-22 were characterized for their potential to be used as background (i.e., uncontaminated) sediments against which to compare contaminated sediments during the C Tank Farm characterization effort (Brown et al. 2006a). Analysis of sediment samples from this borehole, showed elevated concentrations of chloride, nitrate, sulfate, phosphate, magnesium, calcium, strontium, and sodium encountered at various depths within the borehole. Although no known spills have been recorded at this location, the data strongly suggest that the sediment has been contacted by a non-radiological waste stream.

After the core samples were opened, a geologic evaluation was conducted and core logs were generated for both boreholes (Brown et al. 2006a). Aliquots of sediment from the core samples were analyzed and characterized for moisture content, gamma-emitting radionuclides, 1:1 sediment/water extracts (which provide soil pH, electrical conductivity, cation, trace metal, and anion data), total carbon and inorganic carbon content, and 8 M nitric acid extracts (which provide a measure of the total leachable contaminant content from the sediment). Two key radioactive contaminants, ^{99}Tc and ^{238}U, along with other trace metals were determined in the acid and water extracts using ICP-MS.

Table 3.7. K_d Values for Impacted Sediments at Waste Management Area B-BX-BY (K_d units are mL/g)

	Sand-Size Sediments						Silt-Size Sediments					
	High Impact			Intermediate Impact			High Impact			Intermediate Impact		
	Best	Min	Max	Best	Min	Max	Best	Min	Max	Best	Min	Max
Chemicals												
F $^-$	0	0	0	0	0	1	0	0	0	0.05	0	1
Cr(VI)	0.05	0	3	0	0	3	0.1	0	3	0	0	10
Hg(II)	0	0	0	0	0	0	0	0	0	0	0	0
NO_3^-, NO_2^-	0	0	0	0	0	0.1	0	0	0	0	0	0.1
Pb	3	0	10	10	3	100	0	0	30	30	10	300
U(VI) – all isotopes	0.1	0	2	0.2	0.2	0.4	0.3	0	3	2.5	0.6	15
Radionuclides												
^{241}Am(III)	3	0	50	600	200	2000	10	0	150	600	200	2000
^{14}C(IV)	5	0	50	1	0	100	5	0	50	1	0	100
^{60}Co(II,III)	0	0	10	0	0	10	0	0	30	0	0	30
^{137}Cs	1	0	10	100	10	1000	1	0	30	100	30	3000
Eu – all isotopes	1	0	10	10	3	100	3	0	30	30	10	300
^{3}H	0	0	0	0	0	0	0	0	0	0	0	0
^{129}I	0	0	0.2	0.2	0	2	0	0	0	0.2	0	2
^{63}Ni	0	0	10	3	1	20	0	0	30	10	3	60
^{237}Np(V)	0	0	5	10	2	30	0	0	15	10	2	50
Pu – all isotopes	3	0	50	600	200	2000	5	0	150	600	200	2000
^{226}Ra	1	0.2	20	10	5	20	3	0.6	60	10	5	60
^{79}Se(VI,IV)	0	0	3	0.1	0	3	0	0	3	0.3	0	10
^{126}Sn(IV)	0	0	10	0.5	0	20	0	0	30	1.5	0	60
^{90}Sr	1	0.2	20	10	5	20	3	0.6	60	10	5	100
^{99}Tc(VII)	0	0	0.2	0	0	1	0	0	0.2	0	0	5

For gravel-size sediments, modify sand-size K_d values using Equations (2.3) and (2.4) in Section 2.4.
See Appendix A for references and selection rationale.
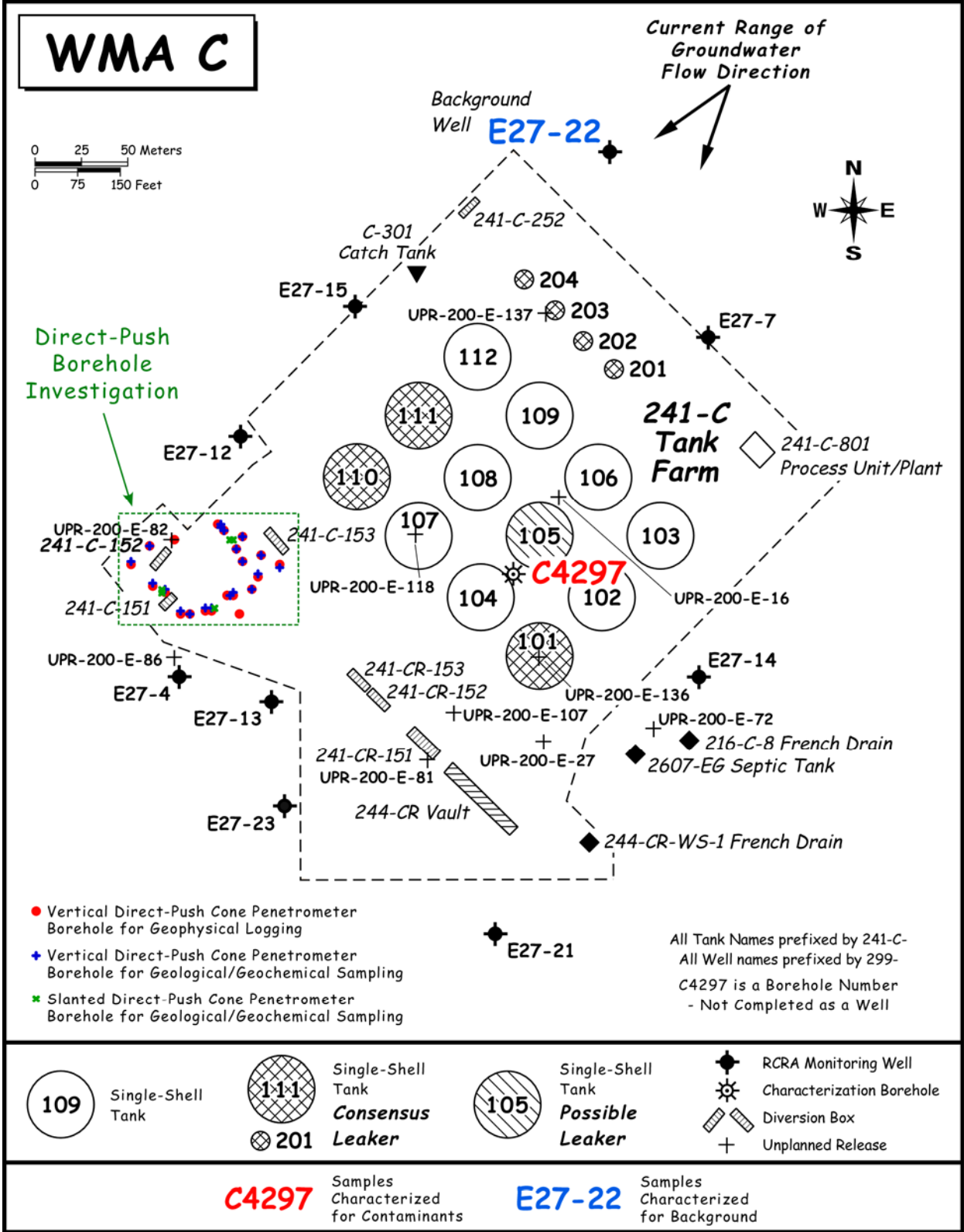
Figure 3.10. Location of Facilities, RCRA Wells, and Locations Where Vadose Zone Sediments Have Been Obtained at Waste Management Area C

Based on these laboratory analyses, Brown et al. (2006a) concluded that heterogeneities, including thin fine-grained lenses in the Hanford formation H1 and H2 units, likely cause anisotropic water flow at the C Tank Farm. Elevated moisture was found to correlate with each of the fine-grained thin lenses. Average moisture contents for the Hanford formation H1 and H2 units in borehole 299-E27-22 were approximately the same as the moisture contents from the same units in borehole 299-E33-338, as well as in contaminated borehole (C4297). This suggests that any leak that may have occurred in the vicinity of borehole C4297 was either small in total volume and/or occurred sufficiently long ago that residual vadose zone moisture has returned to background or natural conditions for each lithology. Fine-grained lens naturally retain more moisture without the occurrence of transient water additions.

Results for some of the most significant parameters measured from C4297 sediments are presented in Figure 3.11 as a function of depth. These include parameters that can have a significant influence on contaminant mobility and can serve as tank waste indicators (pH, sodium, and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and indicators of hydrologic control (lithology, statigraphy, and moisture content).

The pH profile for sediments from borehole C4297 showed elevated soil pH values (up to 9.53) from 12.4 to 15.6 m bgs indicating impact by alkaline tank fluids. The first sample with an elevated soil pH was collected at a depth that coincided with the bottom of tank C-105. Below 15.6 m, the soil pH values were less than 8.0. Based upon these results, Brown et al. (2006a) concluded that pH is not a sensitive parameter for evaluating the vertical extent of migration for mobile constituents in the vadose zone. However, the elevated pH zone is considered to be a good indicator of the zone where the caustic nature of the released fluids was neutralized by the native sediments.

The average pore-water corrected electrical conductivity (EC) of 8.68 mS/cm from borehole 299-E27-22 was more than a factor of three times greater than the average EC from borehole 299-E33-338 (2.63 mS/cm), which further indicates that sediments from 299-E27-22 have been compromised by a waste spill or leak. The EC depth profile for borehole C4297 showed elevated levels in the Hanford formation H1 unit over the same depth range that exhibited elevated soil pH (12.4 to 15.6 m bgs). The peak pore-water-corrected EC value determined in sediments from borehole C4297 occurred at 13.7 m bgs with a value of 20.5 mS/cm. Although elevated, this value was approximately four times more dilute than that determined for sediments collected near tank BX-102, and was more than 80 times more dilute than the peak value in contaminated sediment collected near tank SX-108 (slant borehole C3082 described in more detail in Section 4.7.5).

Elevated water-extractable sodium was measured in C4297 borehole sediments beginning at approximately 2.13 m bgs and extending to a depth of 21.6 m bgs. Brown et al. (2006a) suggested that these trends indicate a chemical reaction between alkaline tank fluids and native sediments resulting in a cation exchange front where calcium and magnesium are replaced by sodium as the dominant exchangeable cation.
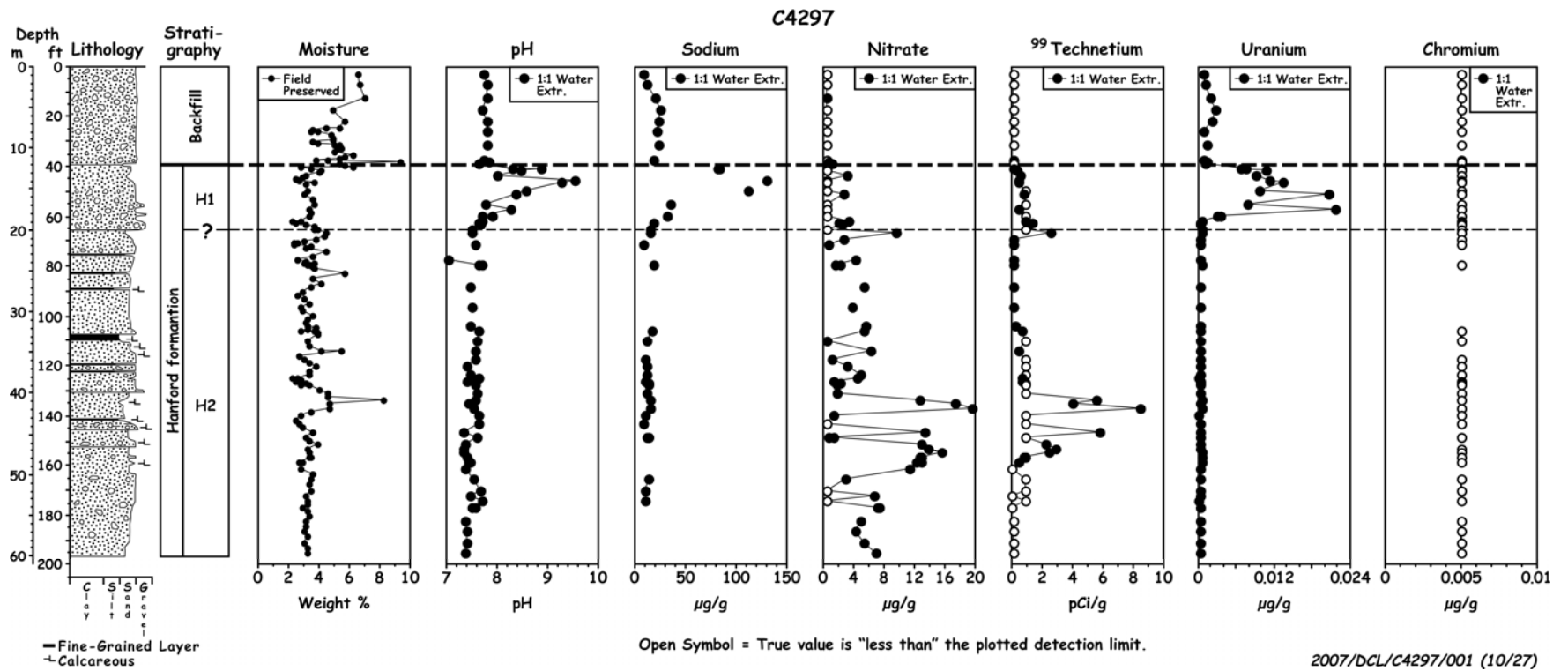
Figure 3.11. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole C4297 Located in Waste Management Area C (Brown et al. 2006a)

3.34

In the core and grab samples from borehole C4297, there was a bimodal distribution for the uranium concentration profile as a function of depth. A relatively small extractable uranium peak was measured in the 1:1 sediment/water extracts from 2.13 to 6.7 m bgs. The uranium present at this depth was likely associated with the ^{137}Cs activity measured at a shallow depth of 0.76 to 3.66 m bgs. The second peak of water-extractable uranium was observed at a depth corresponding to the bottom of tank C-105 (12.2 m bgs) and extended to a total depth of 18.3 m bgs. However, due to the high dissolved carbonate concentration in this zone (the pore water corrected carbonate concentration was as high as 13,300 mg/L), some of the water-extractable uranium was likely present as labile uranium released as a result of strong uranyl-carbonate complexation. The maximum water-extractable uranium concentration over this depth occurred at 17.4 m bgs with a peak value 0.0217 µg/g. Uranium-236 was not detected in these samples using ICP-MS. Although the peak uranium concentration measured was up to a factor of ten times higher than typical background concentrations, it is unlikely that the majority of the uranium present in this zone resulted from Hanford processing activities and is instead natural uranium solubilized by the high levels of carbonate in these sediments.

The nitrate values in the water extracts for borehole C4297 were elevated beginning at a depth that corresponded to the bottom of tank C-105 (12.2 m bgs) to as deep as 36.6 m bgs. Additionally, there were several anomalously high nitrate samples collected throughout the soil profile that could be related to lithology. Nitrate migration in the subsurface is considered to be entirely conservative, i.e., being unreactive and moving freely with the infiltrating water. Thus, nitrate concentration can be used to estimate the total vertical extent of a contaminant plume. Based on data from borehole C4297, it appears that a multi-modal, at least bimodal, waste signature is present. Based on the nitrate profile, it appears that the maximum penetration of the first or primary plume is currently at a depth of approximately 48.8 m bgs. The maximum of the peak of the second plume occurred as deep as 34.7 m bgs and appears to be less concentrated than the primary plume.

The first observance of ^{99}Tc in sediment samples from borehole C4297 occurred at 12.4 m bgs, a depth that corresponded closely to the bottom of tank C-105. Technetium-99, like nitrate, is considered to be completely conservative with respect to mobility in aqueous systems. Therefore, it is not surprising that ^{99}Tc exhibited a similar concentration profile to nitrate. Some differences were observed between the ^{99}Tc and nitrate profiles. As with nitrate, a bimodal concentration profile of ^{99}Tc contamination was present in C4297 borehole samples, with the primary ^{99}Tc peak occurring between 32.0 and 48.8 m bgs, and a smaller secondary peak present between 12.2 and 20.1 m bgs. Similar to the nitrate, the peak ^{99}Tc concentration present in these sediment samples was measured in the sample collected from approximately 41.8 m bgs.

Molybdenum, which is a fission product generated during the operation of nuclear reactors, can sometimes be used to delineate the profile of waste plumes in the subsurface. In the case of samples from borehole C4297, fission-produced molybdenum was clearly present between 7.92 and 19.5 m bgs (data not shown). The primary zone of fission-produced molybdenum occurred between 16.8 and 19.5 m bgs. However, unlike the ^{99}Tc and nitrate contamination, it appears that all the fission-produced molybdenum in this borehole forms a contiguous plume that is the result of a single contamination event. Therefore, the bimodal ^{99}Tc contamination profiles versus a single contaminant plume for molybdenum supports a two source contamination model.

Based on evaluating all these measurements, Brown et al. (2006a) concluded that the C4297 borehole data established the maximum vertical extent of tank contamination at this location to be approximately

48.8 m bgs. Six of the eight parameters measured (pH, electrical conductivity, sodium, nitrate, ^{99}Tc, and molybdenum) exhibited distinct contaminant profiles as a function of depth. Additionally, two of the contaminants (nitrate and ^{99}Tc) could be further characterized as having bi- or potentially multimodal profiles, perhaps indicative of at least two distinct waste sources present in this borehole or alternatively the presence of an irregular plume flow path as a function of depth (horizontal spreading followed by more vertical movement).

Selected concentration ratios of mobile contaminants in a) the vadose zone sediments sampled from borehole C4297, b) the WMA C groundwater contaminant plumes, and c) specific SSTs at the time of suspected leaks were used to assess whether there were indications that the groundwater contamination present at WMA C is related to current vadose zone contamination. Comparisons of contaminant ratios from all available data sets, as well as those measured in samples from borehole C4297, were performed. Initial attempts to relate the groundwater and pore water compositions used the ratios of the concentrations of various contaminants (^{99}Tc, fluoride, sulfate, sodium, and nitrate) to one another. The agreement between the vadose zone pore water and contaminated groundwater data sets was not good (Brown et al. 2006a). The ^{99}Tc/nitrate ratios for samples from the contaminated zones in borehole C4297 were generally greater than about 0.2 pCi/μg. Such values are greater than the ^{99}Tc/nitrate ratios in all of the groundwater wells except well 299-E27-4 suggesting that contaminated vadose zone pore water from C4297 is not the source of the entire groundwater ^{99}Tc plume. The agreement between other ratios such as fluoride/nitrate, sulfate/nitrate, sodium/nitrate, between groundwater from well 299-E27-4 and pore water from borehole C4297 was also not good, although some fractionation between nitrate and the other constituents, especially sodium, likely occurred. Therefore, analysis of the ratios of these constituents for pore waters and nearby groundwaters did not clarify whether contaminated fluids in borehole C4297 sediments were a significant contributor to the groundwater contaminant plumes.

In summary, there is no current similarity between the present or past groundwater contamination and current pore-water compositions from the contaminated borehole sediments at WMA C. Therefore, the contaminants currently in the vadose zone pore water, believed to be derived from liquids released from tank C-105, cannot be linked to current groundwater concentrations or those in the past.

3.3.2 Geochemical Characterization: Sediments Contaminated from the C-152 Transfer Line Leak

Brown et al. (2007a) presents the results of a geochemical investigation of sediment samples taken near the C-152 transfer-line leak. Specifically, their report contains all the geologic, geochemical, and selected physicochemical characterization data compiled on vadose zone sediment recovered from direct-push samples collected around the site of an unplanned release (UPR), UPR-200-E-82, adjacent to the 241-C-152 Diversion Box located in WMA C. Characterization probe holes locations are shown in Figure 3.12.

UPR 200-E-82 was a waste-loss event near the 241-C-152 Diversion Box that occurred in December 1969 and involved the loss of approximately 9,840 L (2,600 gal) of ^{137}Cs recovery process feed solution (Wood et al. 2003). The leak event created a temporary ground-surface puddle measuring 380 L (100 gal) in volume, which was quickly covered over with clean gravel. It is estimated that 11,300 Ci of ^{137}Cs, 18.3 kg of uranium, and 5.01 Ci of ^{99}Tc were released to the subsurface.
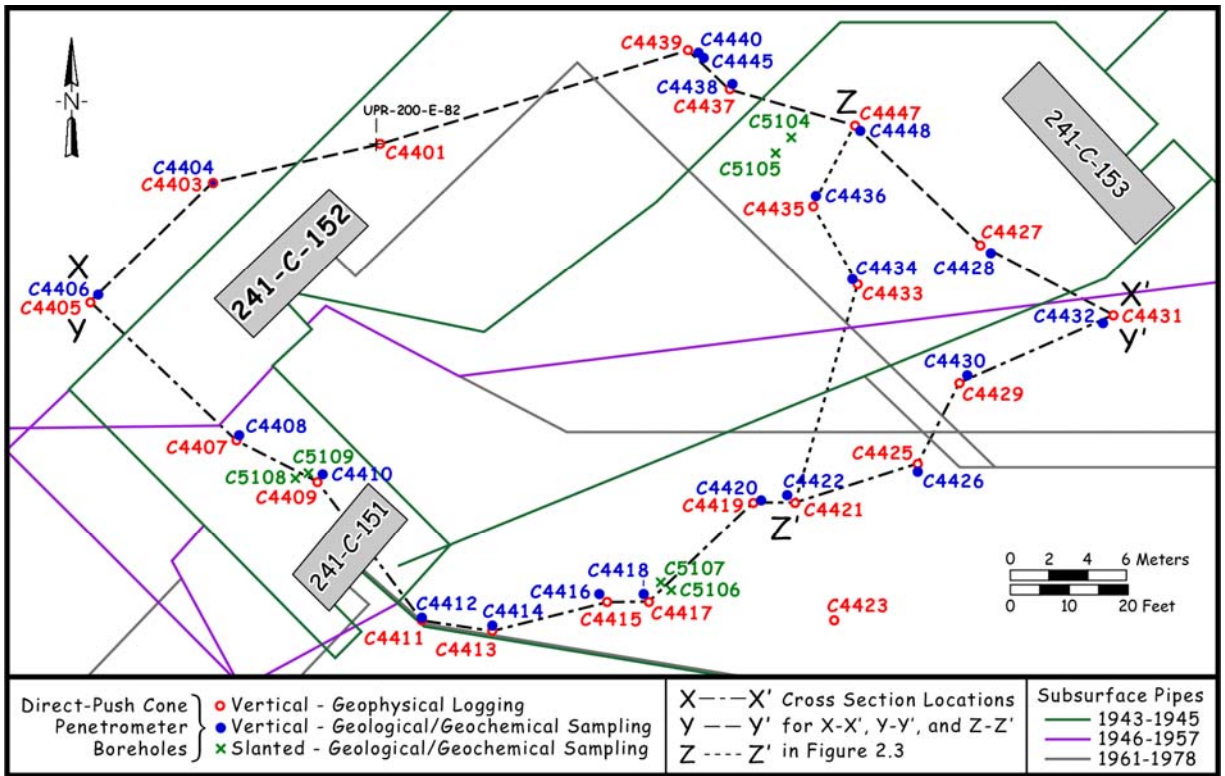
Figure 3.12. Selected Probe Hole Location Map for Waste Management Area C

An initial geologic/geochemical investigation in the vicinity of UPR-200-E-82 was performed using pairs of direct-push probe holes. A total of 41 vertical direct pushes extending to approximately 18.3 m bgs were completed between July and September 2005 to characterize vadose zone moisture and contaminant distribution. Twenty vadose zone sediment sample sets, containing one or two core samples in stainless-steel liners and one grab sample, were delivered to the laboratory for characterization and analysis. The sediments were collected around the documented location of the C-152 pipeline leak (UPR-200-E-82) and created an approximately 36.6-m diameter circular pattern around the waste site.

A second series of six probe holes were emplaced around the site of the pipeline leak between March and June 2006. Unlike their 2005 vertical counterparts, these probe holes were driven at angles of 30, 45, or 60 degrees from horizontal, and extended to approximately 24.4 m bgs. Up to three sets of samples (0.46 m of core, plus material recovered from the drive shoe) were retrieved from each slant probe hole. The goal of this operation was to collect a sample at depth from directly beneath the projected site of the pipeline leak.

A core log was generated for both sets of samples and a visual geologic evaluation of all liner samples was performed at the time of sample processing. Aliquots of sediment from the liners were analyzed and characterized in the laboratory for the following parameters: moisture content, gamma-emitting radionuclides, 1:1 sediment/water extracts (which provided soil pH, electrical conductivity, cation, trace metal, and anion data), total carbon and inorganic carbon content, and 8 M nitric acid leaches (which provided a measure of the total leachable contaminant content in the sediment). Two key radioactive contaminants, ^{99}Tc and ^{238}U, along with other trace metals, were determined in acid and water extracts using ICP-MS.

Some of the most significant parameters measured in the direct-push samples from the C-152 transfer-line investigation are presented in Figure 3.13 as a function of depth. These include parameters that can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and moisture content. All of the parameters were elevated in at least some of the samples analyzed as part of this study. Specifically, soil pH was elevated (up to 9.99) in samples collected northeast and southwest of the C-152 pipeline leak, as well as in samples collected directly beneath the projected leak location (at a depth of 12.8 m bgs). Similarly, samples collected from these same direct-push holes contained elevated water-extractable sodium (more than 90 μg/g of dry sediment), uranium (as much as 0.766 μg/g of dry sediment), nitrate (up to 30 μg/g of dry sediment), and [99]Tc (up to 28.6 pCi/g of dry sediment). Most of the samples containing elevated concentrations of water-extractable sodium also had decreased levels of water-extractable calcium and/or magnesium, indicating that tank-related fluids that were high in sodium were present in these sediments.

After evaluating all the characterization and analytical data, Brown et al. (2007a) concluded that the vadose zone surrounding the C-152 pipeline leak site had been contaminated by tank-related waste. The two regions that contained the largest amount of contaminants, either in concentration or by occurrence of several key constituents/contaminants of concern, were located: 1) between the 241-C-151 and 241-C-152 Diversion Boxes, and 2) west of the C-153 Diversion Box. Additionally, the slant push data showed that mobile constituents associated with the pipeline leak event have migrated to a depth of at least 24.4 m bgs at this locale.

Although a distinct waste signature was observed in the sediment surrounding the C-152 pipeline leak site, immobile contaminants were not detected in significant concentrations. The samples collected for study by Brown et al. (2007a) were retrieved as close as possible to the cap overlying the pipeline leak site, as well as directly beneath the projected leak point. Collectively, the data indicate that the bulk of the activity associated with the leak event (i.e., ^{137}Cs) is constrained to the shallow vadose zone in close proximity to the discharge point. However, data from the vertical and slant push samples indicate that more mobile key contaminants of concern (i.e., ^{99}Tc) have migrated much farther laterally (beyond the edge of the cap) and vertically (at least 24.4 m bgs) than was initially predicted.

3.3.3   Estimated K_d Values for Key Contaminants at Waste Management Area C

As described in Section 3.3.2, one borehole has been placed near a suspected release from tank C-105 in WMA C. However, Field and Jones (2005) list eight tanks as having released fluids to the vadose zone. The waste compositions of the fluids that were released from the eight tanks in WMA C are listed in Table 3.8. All the waste streams are dominated by molar concentrations of sodium and nitrate/nitrite with some caustic nature as evidenced by some excess free hydroxide, and in one case high-dissolved aluminate. The hot semiworks (HS) waste stream also contains 0.6 M organics consisting of mostly acetate and ethylenediaminetetraacetate acid (EDTA). The latter organic ligand might mobilize metal-like contaminants. All these fluids would cause sediments to have zones of high to intermediate impact near the point of release.

The K_d values for WMA C sediments in the highly and intermediate impacted zones are listed in Table 3.9. Sediments beyond these locations are assumed to adsorb contaminants with K_d values (Table 3.4) similar to uncontaminated sediments contacted with uncontaminated vadose zone pore water.

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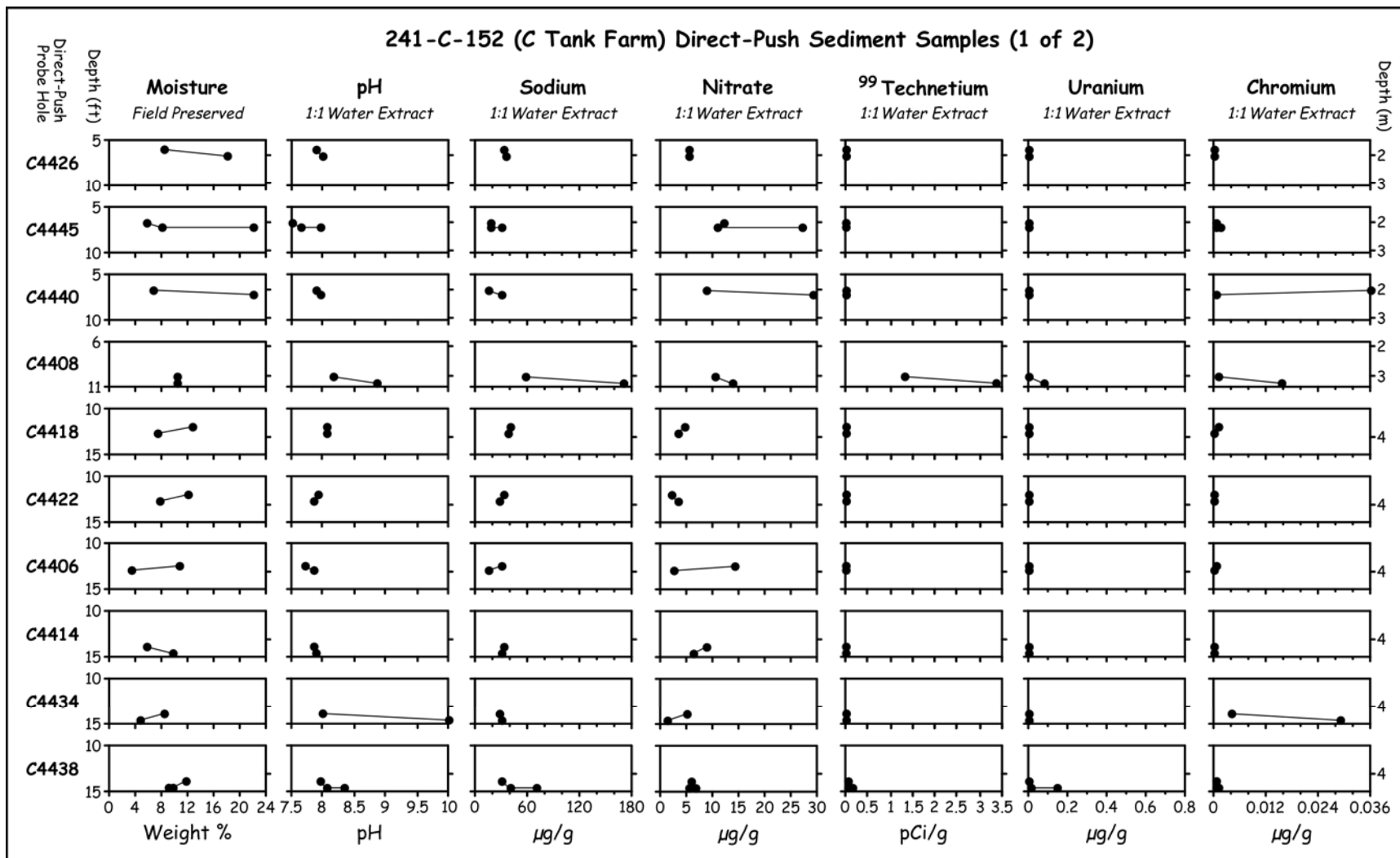
Figure 3.13.   Moisture Content and Significant Geochemical Parameters Measured in Direct-Push Sediment Samples Collected in the Investigation of the C-152 Transfer-Line Leak in C Tank Farm (Brown et al. 2007a) (Page 1 of 2)
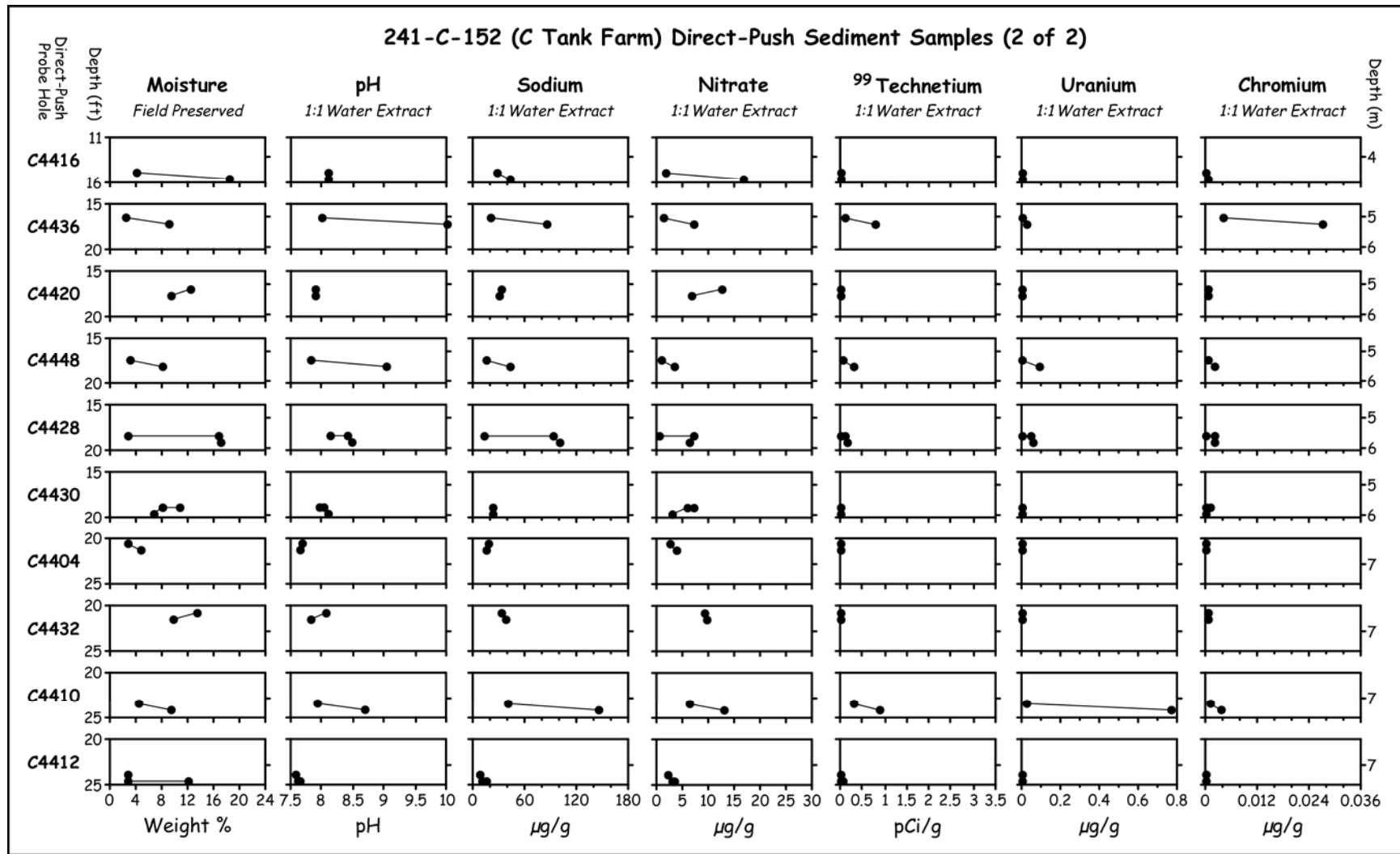
Figure 3.13. Moisture Content and Significant Geochemical Parameters Measured in Direct-Push Sediment Samples Collected in the Investigation of the C-152 Transfer-Line Leak in C Tank Farm (Brown et al. 2007a) (Page 2 of 2)

Table 3.8. Waste Composition of Fluids Leaked at Waste Management Area C (from Corbin et al. 2005)

Waste Type	Concentration (mol/L)						
	1C1	TBP/UR	P1	P2	PL1	CWP1	HS
Na^+	2.49	4.04	0.72	1.17	3.31	2.38	2.22
Ca^{2+}	0.0038	0.0038	0.0037	0.0037	0.0038	0.0037	0.0049
K^+	1.00E-02	0.016	0.003	0.006	0.015	0.0015	0.089
Sr^{2+}	7.00E-08	6.33E-07	5.00E-07	5.00E-07	2.20E-07	1.33E-07	2.05E-05
NH_4^+	1.17E-01	4.08E-04	0.008	0.031	3.05E-06	9.10E-05	3.60E-03
Cr	0.0069	0.0032	0.008	0.008	0.008	0.003	0.0076
Mn	0	0	0	0	0	0	0
Fe	0.0019	0.0019	0.0018	0.0018	0.0019	0.0018	0.048
Ni	1.70E-03	0.0016	0.0018	0.0018	0.0018	0.0015	0.004
Bi	4.60E-04	1.80E-04	0	0	0	0	0
NO_3^-	1.74	2.99	0.175	0.12	2.89	0.69	0.798
NO_2^-	0.067	0.162	0.277	0.615	0.021	0.8	0.29
CO_3^{2-}	0.0038	0.188	0.004	0.004	0.0038	0.004	0.0049
PO_4^{3-}	0.071	0.071	0	0	0.071	0	0
SO_4^{2-}	0.074	0.124	0.044	0.124	0.057	0.009	0.067
Cl^-	0.046	0.097	0.014	0.026	0.068	0.007	0.049
F^-	0.198	0	0	0	0	0	0
OH^-	0.1	0.0023	0.184	0.185	0.054	0.019	0.261
$Al(OH)_4^-$	0	0	0	0	0	0.852	0
Organics	0	6.20E-05	0	0	0	0	0.63

3.4   Integrated Disposal Facility

CH2M HILL Hanford Group, Inc. is assessing the future performance of a near-surface IDF to receive solid low-level waste, mixed low-level waste, immobilized low-activity waste (ILAW), and failed or decommissioned melters. The goal of the Hanford Site IDF Performance Assessment is to provide a reasonable expectation that waste disposal is protective of the general public, groundwater resources, air resources, surface-water resources, and inadvertent intruders. Achieving this goal will require predicting contaminant migration from the facilities. This migration is expected to occur primarily through the movement of water through the disposal areas, and the consequent transport of dissolved contaminants through the vadose zone to groundwater, where contaminants may be reintroduced to receptors via drinking water wells or mixing in the Columbia River.

Two boreholes have been drilled in support of the IDF Performance Assessment (Reidel et al. 1998, Horton et al. 2003). Some hydrologic and geochemical characterization work was conducted on the first borehole (299-E17-21). In particular, batch K_d measurements were performed for key contaminants of concern (Kaplan et al. 1998). The K_d values, as well as other hydrologic data from measurements on sediments from this borehole, are found in the IDF data packages for the 2001 IDF performance assess- ment (see Khaleel [1999], Meyer and Serne [1999], and Krupka et al. [2004] for details). Samples from the second borehole (C3177/299-E24-21) were characterized for physical and geochemical properties. A summary of these results is discussed below. These results are included in this report because of their close proximity to the tank farms and the extensive characterization work that was done on the samples.

Because of the location of the IDF boreholes relative to the 200 East Area, knowledge gained from the detailed characterization of the sediment geology at the IDF boreholes is important in understanding the geology at the 200 East Area tank farms.

Table 3.9. K$_d$ Values for Impacted Sediments at Waste Management Area C (K$_d$ units are mL/g)

Chemicals	Sand-Sized Sediments					
	High Impact			Intermediate Impact		
	Best	Min	Max	Best	Min	Max
F$^-$	0	0	0	0	0	1
Cr(VI)	1	0	3	0	0	3
Hg(II)	0	0	0	0	0	0
NO$_3^-$, NO$_2^-$	0	0	0	0	0	0.1
Pb	3	0	10	10	3	100
U(VI) – all isotopes	1	0.5	5	2	2	20
Radionuclides						
^{241}Am(III)	3	1	50	600	200	2000
^{14}C	5	0	50	1	0	100
^{60}Co(II,III)	0	0	10	0	0	10
^{137}Cs	10	10	50	100	10	1000
Eu(III) – all isotopes	3	1	50	10	3	100
^{3}H	0	0	0	0	0	0
^{129}I	0	0	0.2	0.2	0	2
^{63}Ni	0	0	10	3	1	20
^{237}Np(V)	0	0	5	10	2	30
Pu – all isotopes	3	1	50	600	200	2000
^{226}Ra(II)	1	0.2	20	10	5	20
^{79}Se(VI,IV)	0	0	3	0.1	0	3
^{126}Sn(IV)	0	0	10	0.5	0	20
^{90}Sr	1	0.2	20	10	5	100
^{99}Tc(VII)	0.1	0	1	0.1	0	3
For gravel-size sediments, modify sand-size K$_d$ values using Equations (2.3) and (2.4) in Section 2.4. See Appendix A for references and selection rationale.						

   As part of the IDF Performance Assessment, a geochemical data package (Krupka et al. 2004) was compiled to document the basis for selecting geochemical parameters and input values that were used in the 2005 version of the IDF Performance Assessment. Included in this data package is a discussion of the philosophy and justification for selection and use of the empirical distribution coefficient (K$_d$) and empirical solubility concentration limits as inputs for contaminant migration analyses. Brief descriptions of the spatial zone approach and the resulting tables of information were provided in Krupka et al. 2004 and are also included in Appendix C of the Geochemical Processes Data Package (Cantrell et al. 2007).

3.4.1 Brief Description of Geology of the Integrated Disposal Facility

The geology of the IDF trench, which was constructed in 2004–2005, is summarized in Reidel (2005). The geology of the IDF is described in Reidel and Chamness (2007) and is based on the material from Reidel (2005). The statigraphy of the IDF is shown in Figure 3.14, which was taken from Reidel and Chamness (2007).
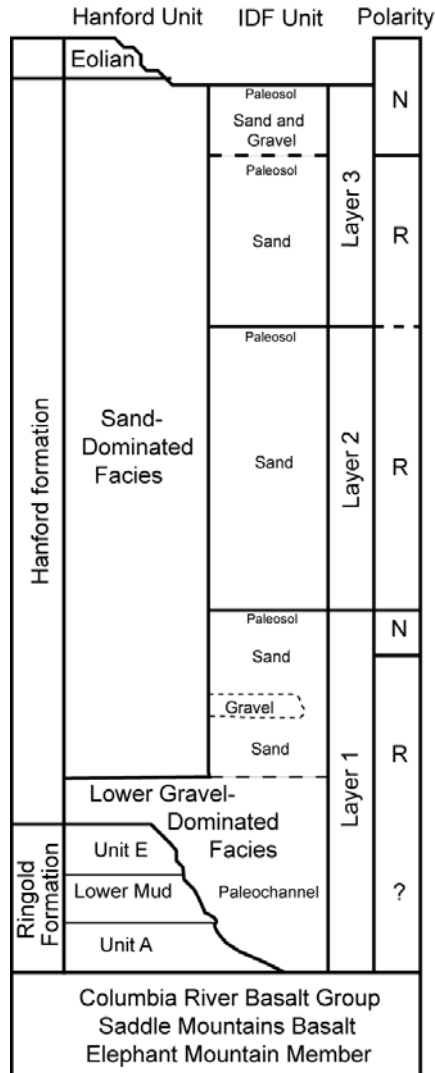
Figure 3.14.   Stratigraphy Below the Integrated Disposal Facility (from Reidel and Chamness 2007)

3.4.2 Geochemical Characterization: Borehole 299-E17-21

As indicated in Section 6.0 of the Geology Data Package (Reidel and Chamness 2007), Reidel et al. (1998) completed some hydrologic and geochemical characterization studies on the first ILAW borehole (299-E17-21). The results of geochemical characterization analyses of vadose zone sediments collected from borehole 299-E17-21 indicated that no radioactive or chemical contaminants were present. Geophysical logging of borehole 299-E17-21 corroborated the absence of radionuclide contamination. In addition, analysis of groundwater samples collected from the Ringold Formation did not indicate the presence of contamination.

3.4.3 Geochemical Characterization: Borehole 299-E24-21

Physical and geochemical properties were determined for six large composite sediment samples and six discrete-depth sediment samples from the second ILAW borehole C3177 (299-E24-21) (Horton et al. 2003). The composite samples were made to provide sufficiently large volumes of well-characterized material that would be available for future geochemical studies. The results of these characterization studies were used to determine the geochemical interactions between Hanford formation sediment and contaminants that may leach from the glass waste forms scheduled to be disposed in the IDF.

All the 299-E24-21 samples were analyzed for particle-size distribution, moisture content, whole sediment chemical composition, carbon content, surface area, and mineralogy. In addition, 1:1 sediment/ water extracts were analyzed for pH, electrical conductivity, alkalinity, and concentrations of major and trace metals and anions. This investigation determined that all composite samples are sand or gravelly sand. The moisture content ranges from 1.7 to 5.3 wt.%. The bulk chemistry and mineralogy of the samples are typical of the Hanford formation sand-dominated sequence. Likewise, the chemical characteristics of the 1:1 sediment/water extracts are similar to extracts from other samples of the Hanford formation sand-dominated sequence from other boreholes. The water extracts (and by inference the natural vadose zone pore water) from borehole C3177 are dominated by calcium, bicarbonate (as determined from the alkalinity values), magnesium, sodium, and sulfate.

3.4.4 Synopsis of Integrated Disposal Facility Geochemical Data Package

Estimates of the geochemical properties of the materials comprising the IDF, the disturbed region around the facility, and the physically undisturbed sediments below the facility (including the vadose zone sediments and the aquifer sediments in the upper unconfined aquifer) have been compiled in Krupka et al. (2004). The geochemical properties were expressed as parameters that quantify the adsorption of contaminants and the solubility constraints that might apply for those contaminants that may exceed solubility limits. The parameters used to quantify adsorption and solubility were the distribution coefficient (K_d) and the thermodynamic solubility product (K_{sp}), respectively.

In addition to the best-estimate K_d values, a reasonable conservative value and a range are provided in Krupka et al. (2004). The IDF data package provides both the K_d values and empirical solubility concentration limits for different spatial zones in and surrounding the IDF system and provides time-varying K_d values for cement solidified waste. The IDF data package does not list estimates for the range in empirical solubility concentration limits or their uncertainties. The values for each impact zone and the rationale for their choice are found in tables in Krupka et al. (2004). However, the specific dimensions for each impact zone within the vadose zone are hypothetical because no wastes have been disposed and no field data are available to estimate the distance that waste leachates might travel and the distances over which waste leachate-sediment reactions would occur.

K_d values and empirical solubility concentration limits for each contaminant were presented in an earlier version of the IDF data package (Kaplan and Serne 2000) prepared for the 2001 ILAW Performance Assessment and were updated to include applicable data from investigations completed since 2000 when the first report was issued. These updated data are also presented in Appendix C of the Geochemical Processes Data Package (Cantrell et al. 2007). A discussion was also included in Krupka et al. (2004) on the evolution of the K_d values recommended from the original 1999 ILAW performance assessment (Mann et al. 1998) through the 2001 ILAW (Mann et al. 2001) and 2003 supplemental performance

assessments (Mann et al. 2003) to the current values used for the 2005 IDF performance assessments for the key contaminants of concern: Cr(VI), nitrate, ^{129}I, ^{79}Se, ^{99}Tc, and U(VI). Krupka et al. (2004) provides rationale for why some K_d values have changed over time. Typically, these changes were based on more recent adsorption measurements for certain contaminants on IDF-specific sediment samples, or improved understanding of the adsorption properties and migration behavior of a contaminant.

3.5 Waste Management Area S-SX

Characterization studies have been completed on vadose zone sediment samples from five boreholes and outcrop grab samples collected within or near WMA S-SX (Serne et al. 2002b, 2002d, 2002e, 2002f). In the first study (Serne et al. 2002d), intact core from two clean boreholes (299-W22-48 and 299-W22-50) near the SX Tank Farm and four large-quantity grab samples from sediment outcrops on or near the Hanford Site were sampled for characterization studies. Serne et al. (2002d) contains results and interpretation of the geological, physical, chemical, and mineralogical characterization work conducted on these sediments. Three additional studies were conducted on intact core samples from contaminated boreholes. Borehole 299-W23-19 was drilled at the southwestern edge of tank SX-115 (Serne et al. 2002e). Borehole 41-09-39 (299-W23-234) was an extension (to deeper depths) of an existing monitoring dry well adjacent to tank SX-109 (Serne et al. 2002f). Slant borehole SX-108 (C3082) was installed at an angle to reach beneath tank SX-108 (Serne et al. 2002b). The geology, stratigraphy, and lithology of these drill core samples were described in the field and in the laboratory. Laboratory characterization work that was conducted on the drill core samples from the contaminated boreholes included measurement of physical, chemical, and hydraulic properties. A map of WMA S-SX with the facilities, groundwater wells, and borehole locations is provided in Figure 3.15.

3.5.1 Brief Description of Geology of Waste Management Area S-SX

Geologic characteristics of sediments from WMA S-SX have been extensively studied. Price and Fecht (1976g, 1976h) presented an initial detailed interpretation of the geology. DOE-GJO (1996) presented an interpretation of the geology that was based primarily on geophysical logging of ground-water monitoring wells constructed around the perimeter of the tank farm in the early 1990s. In Johnson and Chou (1998), the geologic interpretation was refined and updated. Johnson et al. (1999) further described the geology and other subsurface contaminants. Lindsey et al. (2000) provided additional interpretations on the geology. Most recently, Sobczyk (2001) presented a reinterpretation of the geology based on gross gamma-ray logs of 98 boreholes within the SX Tank Farm and the most recently published geology reports of the area by Johnson et al. (1999) and Lindsey et al. (2000). The main source of geologic information for the S and SX Tank Farms is borehole information.

Reidel and Chamness (2007) give a detailed description of the geology of WMA S-SX in the SST geology data package for the SST WMAs. A summary table from Reidel and Chamness (2007) of the statigraphic terminology and thicknesses of units beneath the S, SX, and SY Tank Farms is provided in Table 3.10. Conceptual geologic models have also been developed at each of the five characterization boreholes (Serne et al. 2002b, 2002d, 2002e, 2002f).
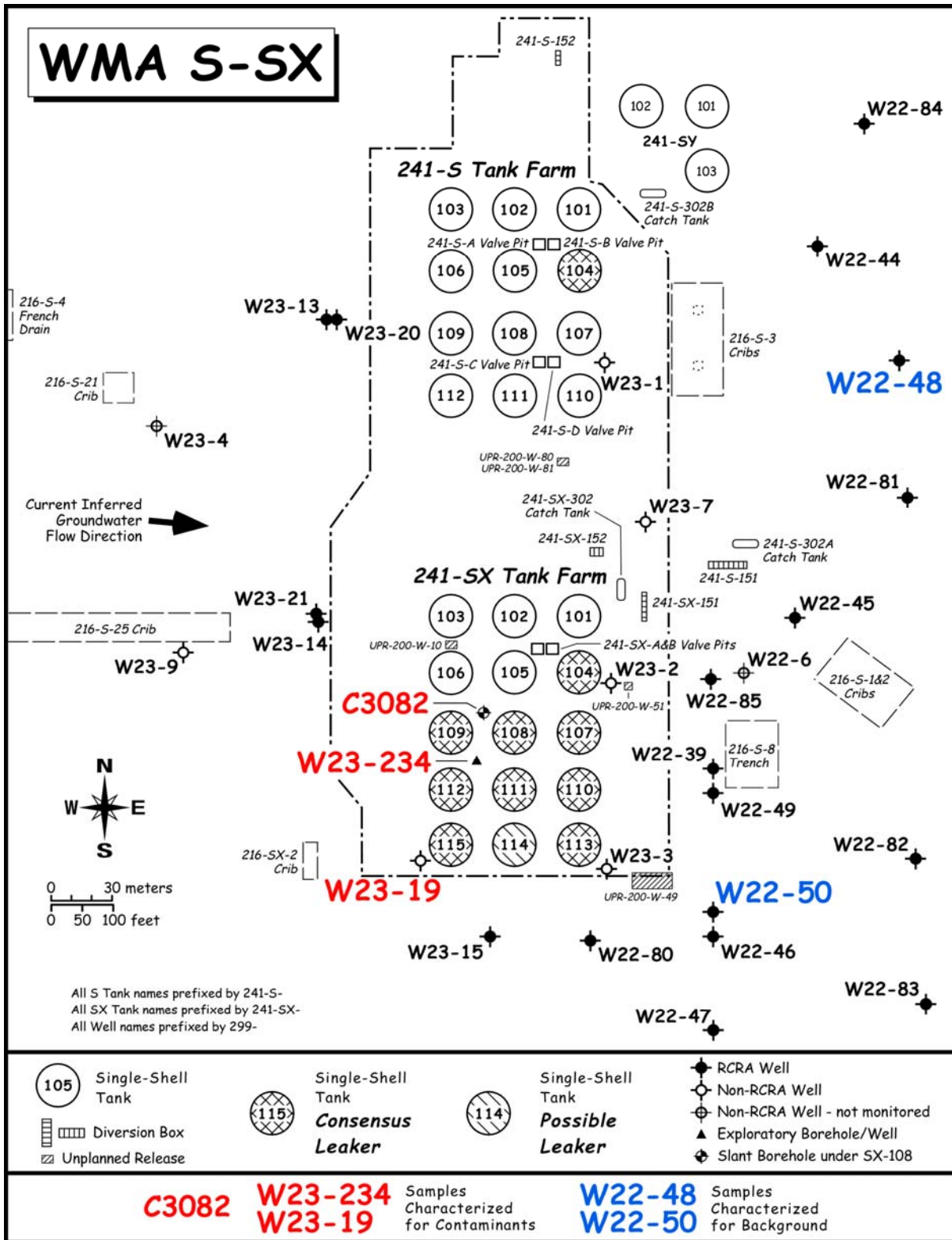
Figure 3.15. Map of the Waste Management Area S-SX with Single-Shell Tank Locations, RCRA Borehole Wells, and Boreholes Where Vadose Zone Sediments Were Obtained

Table 3.10. Stratigraphy at Waste Management Area S-SX (from Reidel and Chamness 2007)

Stratigraphic Symbol	Formation	Facies/Subunit	Description	Thickness
Holocene/Fill	NA	Backfill	Poorly-sorted gravel to medium sands and silt derived from the Hanford formation (Price and Fecht 1976g, 1976h).	18.6 m
H1a	Hanford formation	Sand	Sand to silty sand sequence occurs sporadically on either side of both tank farms and in a channel beneath SX farm	0 – 8 m
		Unit H1b – gravelly sand, upper gravel-dominated unit	Top coarse sand and gravel sequence equivalent to the Johnson et al. (1999) "Gravel Unit B."	12 m
		Unit H1a – slightly silty sand; upper sand-dominated unit	Fine sand and silt sequence	9 – 12 m
H1		Unit H1 – lower gravel-dominated unit	Middle coarse sand and gravel sequence equivalent to "Gravel Unit A" described by Johnson et al. (1999) and "Hanford Unit A" described by Sobczyk (2001).	1 – 10 m
H2		Unit H2 – slightly silty sand; lower-sand dominated unit	Lower fine sand and silt sequence	24.3 m
CCU_u and/or Hf/CCU	Cold Creek unit	Upper	Very fine sand to clayey silt sequence is interstratified silt to silty very fine sand and clay deposits at least partially correlative with the "early Palouse soils" described by Tallman et al. (1979) and DOE (1988) and the "unnamed Hanford formation [?] or Plio-Pleistocene Deposits [?]" described by Lindsey et al. (2000), and the Hf/PP deposits in Wood et al. (2001).	10.7 m
CCU_l		Lower	Carbonate-rich sequence. Weathered and naturally altered sandy silt to sandy gravel, moderately to strongly cemented with secondary pedogenic calcium carbonate.	1 – 4 m
R_{wie}	Ringold Formation	Member of Wooded Island	Moderate to strongly cemented, well rounded gravel and sand deposits, and interstratified finer-grained deposits.	Unit E: 75 – 85 m;
R_{lm}				Lower Mud: 12 – 30 m;
R_{wia}				Unit A: 30 m

CCU_l =   Lower Cold Creek unit.
CCU_u =   Upper Cold Creek unit (Cold Creek fine-grained unit).
Hf/CCU =   Hanford formation/Cold Creek unit.
NA   =   Not applicable.
R_{wie} =   Ringold Formation, member of Wooded Island, unit E.

3.5.2 Geochemical Characterization: Borehole 299-W22-48, Borehole 299-W22-50, and Grab Samples

Intact core from two clean boreholes (299-W22-48 and 299-W22-50) near the SX Tank Farm and four large-quantity grab samples from sediment outcrops on or near the Hanford Site were sampled for characterization studies (Serne et al. 2002d). For boreholes 299-W22-48 and 299-W22-50, detailed lithologic sections were made using geologic descriptions of the sediments and the results of geophysical logs. Later, analytical results (grain-size distribution, calcium carbonate content, and moisture content) were used to refine the resulting stratigraphic and lithologic interpretations. The combined use of the

geologists' observations with geophysical logs and incorporation of the laboratory data resulted in an improved geologic interpretation of the extent and migration potential of contaminants at the S and SX Tank Farms.

Sediment samples were analyzed for 1) mass water content; 2) particle-size distribution; 3) particle density; 4) calcium carbonate and organic carbon contents; 5) chemical composition of bulk sediment; 6) mineralogy; 7) cation exchange capacity; 8) exchangeable base cation distribution; 9) 1:1 sediment/ water extract pH, electrical conductivity, major cation and anion composition and trace metal composition; 10) 8 M nitric acid extract composition; and 11) pore water composition. Not all analyses were performed on all sediment samples.

A number of sediment analyses (i.e., particle-size distribution, particle density, moisture content, calcium carbonate content and cation exchange capacity) are in agreement with the geologic interpretations and mineralogy. The chemical composition of the sediments generally reflects the mineralogy and particle-size distribution. Samples high in calcium correspond to samples from the calcareous CCU_l unit. Such samples also tend to be low in sodium and relatively high in magnesium, the latter reflecting coprecipitation of magnesium with calcium in calcite. Samples high in potassium reflect the relatively high illite content of the Cold Creek unit and finer-grained portions of the Hanford formation. Although some relationships can be made comparing cation exchange capacities to the lithology, mineralogy and grain-size distribution of some samples, enough discrepancies exist to make most comparisons tentative.

The results from the 1:1 sediment/water extracts are similar for samples from both SX Tank Farm boreholes. Also, most results for the water extracts yield a reasonable charge balance among cations and anions. The vadose zone pore waters from the two RCRA borehole sediments are dominated by calcium, sodium, magnesium, bicarbonate (based on the pH and alkalinity data), sulfate, and nitrate. There are minor amounts of chloride, potassium and dissolved silicon but no elevated levels of trace metals, except in the caliche. The caliche 1:1 water extract shows elevated levels of natural uranium and selenium compared to the other geologic strata. The caliche also shows elevated electrical conductivity, alkalinity, calcium, magnesium, strontium, silicon, sulfate, and nitrate compared to the other geologic strata. The Ringold Formation (R_{wie})water extracts show lower alkalinity, sodium, barium, chromium, and uranium concentrations than the Hanford formation and Cold Creek unit water extracts.

3.5.3   Geochemical Characterization: Borehole 299-W23-19

Borehole 299-W23-19 was drilled at the southwestern edge of tank SX-115 (Serne et al. 2002e). Geologic, chemical, physical, and mineralogical characterization was conducted on intact core samples. Results for some of the most significant parameters measured in the sediments collected from borehole 299-W23-19 are presented in Figure 3.16 as a function of depth. These include parameters that can have a significant influence on contaminant mobility and can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and indicators of hydrologic control (lithology, statigraphy, and moisture content). Several parameters were used as primary indicators of the leading edge of the tank-leak plume, including moisture content, pH, electrical conductivity, nitrate, sodium, chromium, and ^{99}Tc concentrations in water extracts.

Figure 3.16. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole 299-W23-19 Located in Waste Management Area S-SX (Serne et al. 2002e)

Based on these measurements, Serne et al. (2002e) established the vertical extent of tank-leak contamination at tank SX-115. The pH for sediments between 22.9 to 26.2 m bgs (in the Hanford H1 unit) and 30.2 to 32.0 m (in the Hanford H2 unit) is elevated, indicating the presence of caustic-waste interaction. It was concluded that the SX-115 leak was at a location distal to the borehole such that sediments at shallower depths were not impacted by the leaked fluids. The elevated pH values range from 9.2 to 9.7 and are not nearly as high as would be expected for tank liquor completely saturating sediments. One plausible explanation for the lower than expected pH values is that the pH is neutralized slowly with time due to the slow dissolution of aluminosilicate minerals present in these sediments. Likewise, it is possible for the tank liquor to react with carbon dioxide in the vadose zone air-filled porosity such that the initial pH excursion to high values is diminished over time.

There is obvious elevated electrical conductivity and nitrate contamination in sediment water extracts starting at about 19.8 m bgs and extending down to near the bottom of the fine-grained CCU_u at 47.5 m bgs. Below the CCU_u, the electrical conductivity and nitrate are not elevated compared to the profiles in the two uncontaminated RCRA boreholes. It therefore appears that the anion data, which are generally good indicators of all mobile contaminants, show that tank fluids have contacted the sediments at 299-W23-19 from a depth of 19.8 to ~47.5 m bgs. Serne et al. (2002e) concluded the main portion of the plume resides in the fine-grained CCU_u. There is no evidence from water-extraction data that the plume has penetrated into and through the caliche unit and entered the underlying coarse Ringold sediments at this borehole.

The sodium pore-water profile shows elevated concentrations start abruptly at 22.2 m bgs and can be readily traced to a depth of 38.4 m bgs, which is very close to the contact between the Hanford H2 unit and the CCU_u. The bottom of the elevated sodium profile is not sharp, and higher than natural leachable sodium can be followed to a depth of 43.6 m bgs within the CCU_u. The vertical distribution of other cations (i.e., barium, calcium, potassium, magnesium, and strontium) shows remarkable consistency. Each of these cations shows a large increase in the amount that is water extractable at 35.5 m bgs. These profiles for the various cations appear to be a traditional ion-exchange process wherein the high concentration of sodium in the leaked fluid is displacing the other cations that were originally on the surface exchange sites of the natural sediment. The displaced cations are effectively pushed ahead of the sodium in the profile. The displaced cations almost reach the contact between the CCU_u and the CCU_l caliche facies at 47.5 m bgs

At borehole 299-W23-19, elevated concentrations of chromium and ^{99}Tc were found in the vadose zone pore water. The elevated chromium starts at 20.6 m bgs and is significantly elevated versus values in the clean RCRA boreholes in the Hanford H1 and H2 units. The largest chromium concentration is found at 32.6 m bgs. The elevated chromium stops ~ 1.2 m below the contact of the H2 with the fine-grained CCU_u at 38.4 m bgs. Technetium-99 is found in the pore water/water extracts from 22.25 m bgs all the way down to the contact between the CCU_U and caliche units (CCU_u and CCU_l contact) at 47.5 m bgs. The higher concentrations of ^{99}Tc are found in the upper CCU_u where the peak value is at 39.3 m bgs. The majority of the ^{99}Tc is found in the CCU_u and no ^{99}Tc appears to migrate into or below the CCU_l caliche facies.

In summary, it is believed based on the water-extract data that the tank fluids impacted the sediments at borehole 299-W23-19 from about 22.25 m bgs to near the base of the CCU_u at 47.5 m bgs. The bulk of the leaked fluid currently resides in the CCU_u between 38.1 and 47.5 m bgs. This is slightly deeper than the plume under tank SX-108 and at borehole SX41-09-39, which both also have some of the tank liquor

residing in the shallower Hanford H2 unit. Therefore, the authors conclude that the contaminant pathway through the CCU$_l$ and Ringold unit to the groundwater must be somewhere downgradient of well 299-W23-19 but close by.

Serne et al. (2002e) also found that there are very low concentrations of ^{137}Cs between 20.6 and 22.6 m bgs in the vadose zone sediments at 299-W23-19. The ^{137}Cs concentrations in the vadose zone sediments vary between 0.1 to 0.2 pCi/g. Despite the fact that borehole 299-W23-19 is only 3.05 m away from the south-south-west edge of tank SX-115 and that ~17,000 curies of ^{137}Cs has been estimated to still exist from the 1965 leak, little ^{137}Cs was found in the borehole sediments. The position of the borehole is considered to be downgradient from the tank, and thus if the leaked fluid was following a lithologic contact, the samples analyzed by Serne et al. (2002e) should have intercepted any mobile ^{137}Cs. The data obtained thus indicate that ^{137}Cs is not very mobile at the SX-115 leak. There is no indication that the vadose zone sediment in this borehole contains ^{90}Sr but there is a small amount of tritium present between 21.3 m and at least 38.1 m bgs. The tritium profile was not investigated in detail so that it is difficult to determine how deep in the profile that elevated levels could be measured. The sample with the largest tritium activity is found at the contact between the Hanford H2 laminated fine sand and the finer-grained CCU$_u$.

To assess whether the vadose zone sediments at this borehole is a wetting or draining profile, soil suction was measured on about ten sleeves from the sediment profile at 299-W23-19, although only one sample was from below the Cold Creek unit where the plume was believed to have reached. The soil suction values for the ten sleeves from borehole 299-W23-19 are low (sediments are relatively wet) throughout the profile and drainage is predicted to be occurring.

Serne et al. (2002e) could not determine unequivocally from the available data if water line leakage or meteoric water sources, or a combination of both, are responsible for the low soil suction values in the sediments at 299-W23-19. Based on a simple model for SX-115, the depth of meteoric water penetration would be nearly 59 m, which is deeper than the water table was during the 1970s to mid-1980s. Outside WMA S-SX, meteoric water has apparently not penetrated much past the 30.5 m depth at the two new RCRA borehole vadose zone profiles. However, within the tank farm near tank SX-115, meteoric sources (winter rain and snowmelt) appear to have penetrated to the water table. These observations do not exclude the possibility that water line leakage also caused accelerated drainage but known leak volumes and the meteoric sources could easily account for the observed soil suction and elevated water content values at this location.

More detailed characterization activities by Serne et al. (2002e) on selected sediment samples from 299-W23-19 added some insight on the processes that control the observed vertical distribution of contaminants and on their migration potential into the future. Their first key finding was that the 1:1 sediment/water extracts were shown to give a good estimate of the pore-water chemistry in the vadose zone sediments. The chemical composition of the actual pore water (obtained by ultra-centrifugation) was found to be fairly well estimated by dilution correcting the 1:1 sediment/water extracts. This is an important finding because it is much easier to obtain a water extract of the vadose zone sediments than a water sample by other means such as with the UFA^{TM} (i.e., unsaturated flow apparatus).

The actual pore waters in the sediments from 299-W23-19 in the Hanford (H1a, H1, and H2) and Cold Creek units (CCU$_u$ and CCU$_l$) were dominated by sodium, magnesium, calcium, and nitrate. The most concentrated pore water removed from the sediments was essentially 0.3 M sodium nitrate but the

highest calculated pore water would have been at the leading edge of the salt plume with 0.1 M calcium, 0.05 M magnesium, and 0.1 M sodium and 0.4 M nitrate. This is much more dilute than the 5 to 6 M NaNO$_3$ pore water found at 299-W23-234.

The nitrite distribution suggests that once tank waste leaked into the sediments, the nitrite oxidized to nitrate because the ratio of nitrite to nitrate is much lower than the values within the tanks. As mentioned previously, chromium does not migrate in sediments as fast as ^{99}Tc and its leading edge is found nearer to 38.4 m bgs than 47.5 m bgs for [99]Tc. The bulk of the water-leachable chromium has been confirmed as Cr(VI) [chromate] by its distinct yellow color and by ion chromatography. There are at least two plausible mechanisms for the slight retardation of chromium (and selenium) compared to ^{99}Tc and molybdenum. The first is that there could be chemical reduction of the chromium from the +6 to +3 oxidation state. The second possible mechanism is the formation of coprecipitates. Serne et al. (2002e) speculated that the concentrations of chromate and selenate might have been affected by precipitation of alkaline earth coprecipitates such as calcium chromate or calcium/barium mixed chromates/ selenate/sulfates. In summary, Serne et al. (2002e) suggested that ion exchange, heterogeneous (solid phase-liquid solute) redox reactions, and coprecipitation may have influenced the distribution of contaminants in the vadose zone sediments at boreholes 299-W23-19, C3082, and 299-W23-234.

By combining the solution analyses for the dilution corrected 1:1 sediment/water extracts, which is assumed to represent pore water compositions, with the measured concentrations of contaminants on the sediments, Serne et al. (2002e) were able to get a semi-quantitative determination of the desorption K$_d$ for these contaminants. Using these measured distributions, the in situ desorption K$_d$ for uranium varies from 8 to 230 mL/g in the SX Tank Farm sediments. For ^{99}Tc, chromium, arsenic, selenium, and molybdenum in the zone of elevated concentrations, the K$_d$ varies between 0 and 0.09, 0.4 and 8, 2 to 6, 0.3 to 2, and 0.05 to 0.10 mL/g, respectively. Another technique to estimate mobility is to compare the ratio of a suspected contaminant to ^{99}Tc or nitrate in the borehole sediment water extracts. The ratios of ^{99}Tc/nitrate, chloride/nitrate, and chloride/^{99}Tc are fairly constant suggesting that these three constituents migrate in a similar fashion and do not significantly react with the sediments. For the other ratios, the constituent in the numerator (i.e., chromium, arsenic, selenium, and molybdenum) shows retardation in comparison to the nitrate or [99]Tc. The ratios for chromium, arsenic, selenium, or molybdenum to ^{99}Tc or nitrate decrease with increasing depth in the sediment column as these constituents react more strongly than ^{99}Tc or nitrate with the vadose zone sediments and are preferentially removed from the pore fluids as they percolate through the sediment. In general, the reactive constituents chromium, molybdenum, selenium, arsenic, and sodium interact with the vadose zone sediment in the bottom of the Hanford laminated sand [H2] unit or the top of the CCU$_u$. The estimated K$_d$ measurements for ^{99}Tc from borehole 299-W23-19 are consistent with the literature (see summary in Cantrell et al. 2003) that finds essentially no ^{99}Tc adsorption onto Hanford Site sediments from low salinity waters.

Mineral assemblages and concentrations were similar to data reported earlier on uncontaminated sediment from the Hanford site (Serne et al. 2002d). No evidence of caustic tank liquor reacting with the sediment to alter the mineral phases or properties was observed in sediments from 299-W23-19.

3.5.4   Geochemical Characterization: Borehole 41-09-39 (299-W23-234)

Results and analyses of geologic, geochemical, and selected physical characterization data collected on vadose zone sediments recovered from borehole 299-W23-234 installed adjacent to tank SX-109 were reported in Serne et al. (2002f). The geology under SX Tank Farm provides the basis with which to

interpret and extrapolate the physical and geochemical properties that control the migration and distribution of contaminants. Of particular interest are the interrelationships between the coarser and finer-grained facies, and the degree of contrast in their physical and geochemical properties. Results for some of the most significant parameters measured in the sediments collected from borehole 299-W23-234 are presented in Figure 3.17 as a function of depth. These include parameters that can have a significant influence on contaminant mobility and can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and indicators of hydrologic control (lithology, statigraphy, and moisture content).

The vertical distribution of ^{137}Cs based on borehole gamma logging and the laboratory analysis of the sediments at borehole 299-W23-234 suggest that much of the tank fluid that leaked from tanks SX-108, SX-109, SX-111, and SX-112 traveled within the coarse-grained Hanford H1 unit that is found between 20.4 and 26.8 m bgs at borehole SX41-09-39.

Serne et al. (2002f) found it difficult to determine whether zones with higher moisture reflect solely the known moisture content relationship with particle size (finer-grained material retains higher moisture contents) or whether some of the elevated moisture represents residual (undrained) water from tank fluid releases. Serne et al. (2002f) found no clear indication of the vertical extent of the plume based on the measured moisture content distribution. However, the measured moisture content did help identify intervals that have been impacted by drilling operations such as hard-tooling resistant sediments.

The sediment-water extract pH values (7.9 to 9.8) at borehole 299-W23-234 are not nearly as high as would be expected for SX tank liquor completely saturating sediments; pH values were predicted to be >14 inside the tank. Therefore it would appear that significant tank liquor-sediment-vadose zone pore water and air-filled pore space reactions occur that significantly lower pH from the extreme values inside the tank. The pH lowering (neutralizing back towards ambient values) reactions occur from the tank bottoms at ~16.8 m to a maximum of 27.4 m bgs for sediment surrounding the SX tanks. Below 27.4 m bgs at the locations samples, the water-extract pH values are at natural (ambient) values.

The sediment-water electrical conductivity results suggested that tank-leak fluid dominates the pore water down to a depth of 38.8 m bgs and the deepest (leading edge of plume) reaches a depth of 41.4 m. For other borehole sediments below 41.4 m bgs, the electrical conductivity measurements did not show any significant deviations from values found for vadose zone sediments at nearby uncontaminated RCRA boreholes. The groundwater obtained at wells near the SX Tank Farm, including one water sample obtained at the bottom of the 299-W23-234 borehole extension, has an electrical conductivity of ~250 μS/cm. This suggests that the groundwater beneath the SX Tank Farm still shows the influence of the large volumes of dilute-salt waste liquids disposed of to facilities upgradient (north and west). Sediment-water extract sodium, nitrate, and ^{99}Tc also indicate the leading edge of the plume is at 41.4 m bgs. The concentration profiles of these mobile constituents all suggest that the leading edge of the plume resides about 3.4 m into the fine-grained CCU_u unit at ~41.4 m bgs. A key finding for Serne et al. (2002f) was the lack of any observed continuous vertical distribution of elevated nitrate concentrations or those of any other tank constituent from the elevation of the tank bottoms to the water table at this borehole.
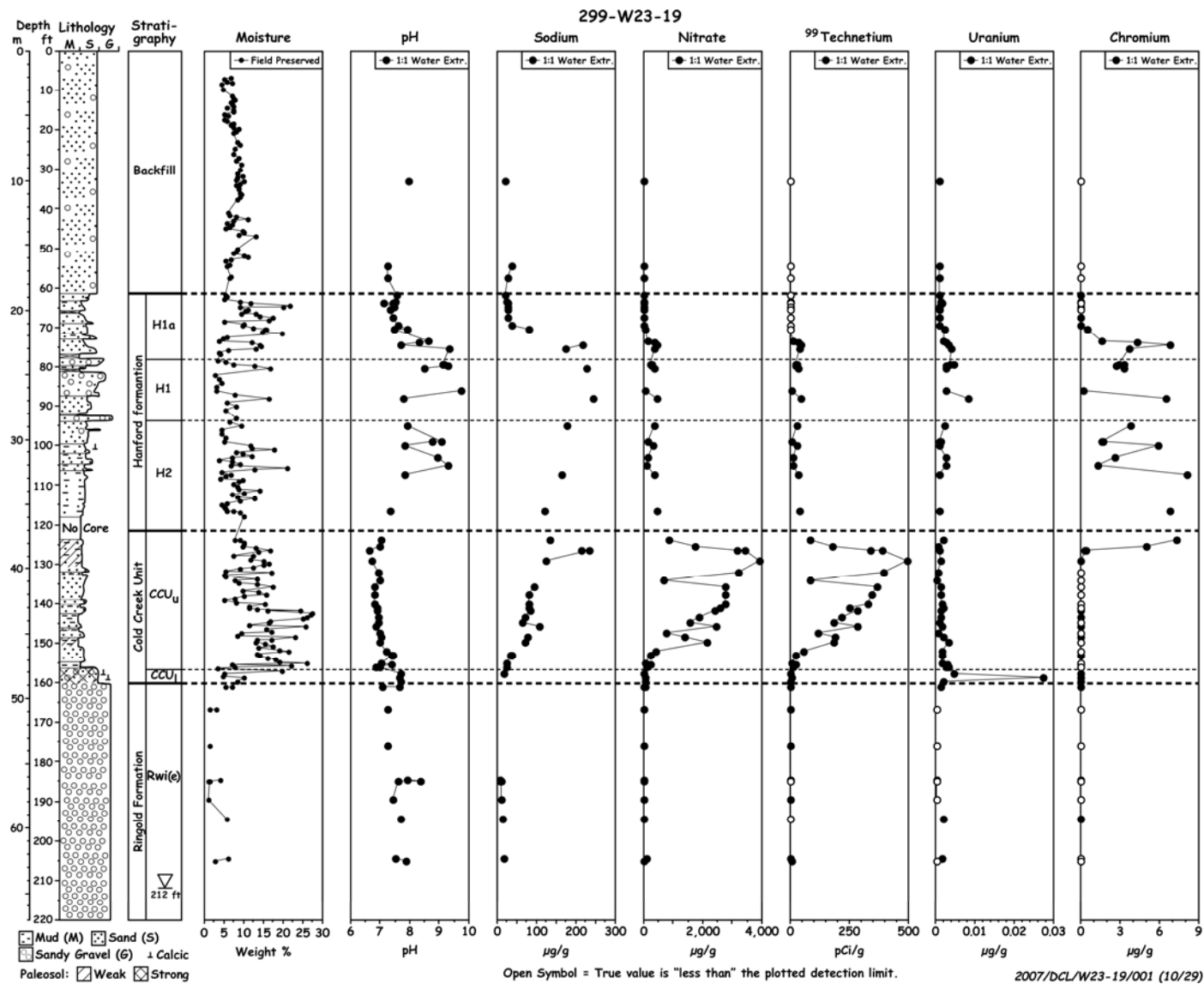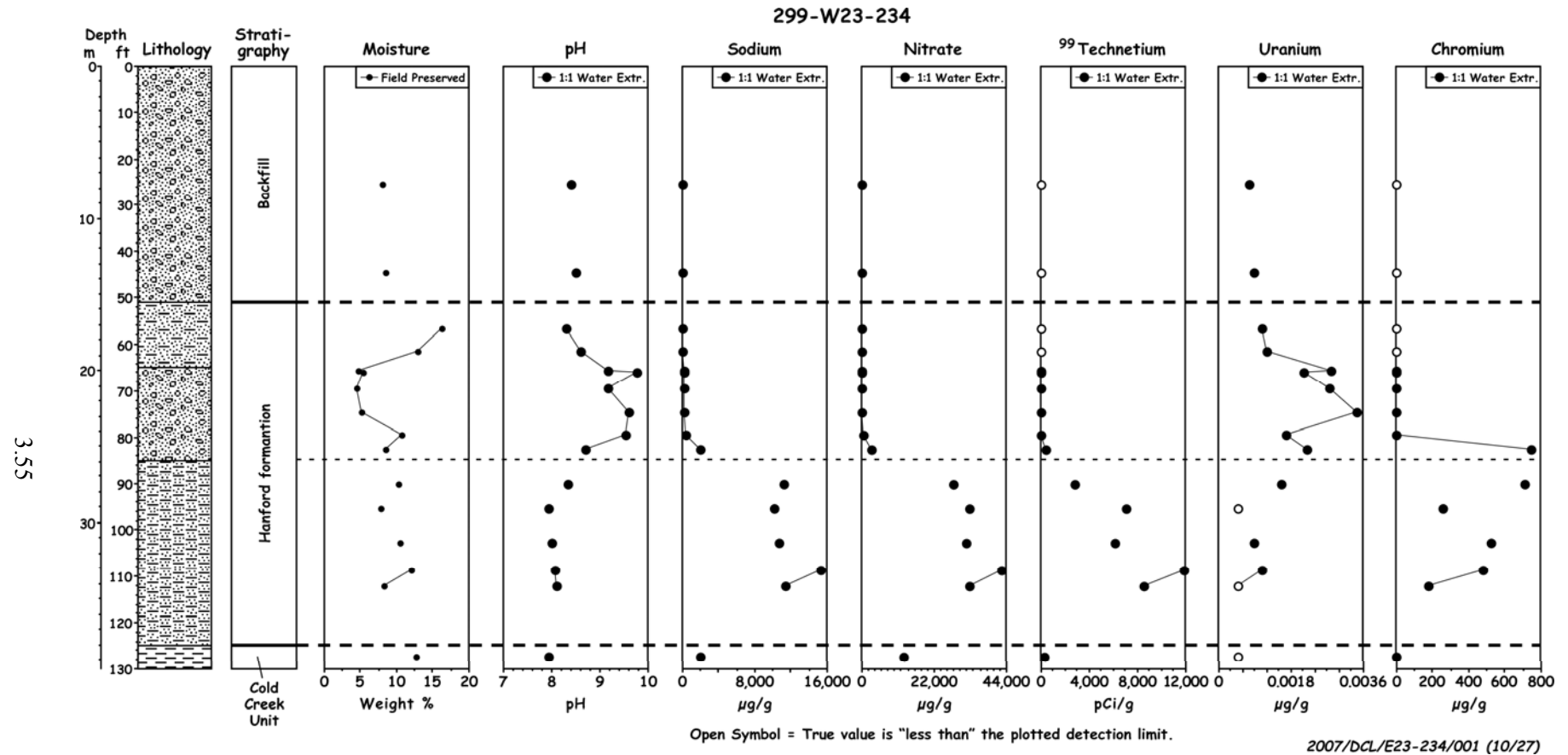
Figure 3.17. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole 299-W23-234 Located in Waste Management Area S-SX (Serne et al. 2002f)

Another key finding from Serne et al. (2002f) was that the 1:1 sediment/water extracts provided a good estimate of the pore-water chemistry in the vadose zone sediments. The chemical composition of the actual pore water, obtained by ultracentrifugation, was found to be fairly well estimated by dilution correcting the 1:1 sediment/water extracts. The most concentrated pore water was essentially 5 to 6 M sodium nitrate with several tenths molar concentrations of calcium and chromate. Because it is much easier to complete a water extract from vadose zone sediments than extracting in situ fluid, the finding is important for determining the pore-water chemistry throughout the vadose zone (Serne et al. 2002f).

The first significant sign of elevated ^{99}Tc is at 24.2 m bgs and a high concentration plume is found from 27.4 to 38.8 m bgs. Molybdenum distribution in the sediment is quite similar. The ^{99}Tc in situ K_d varies from 0.01 to about 5 mL/g over the whole zone of contamination. The most significant chemical contaminant in the sediments is chromium. The leading edge of the chromium appears to stop at 34.1 m bgs, thus indicating that it does not migrate as quickly as molybdenum and ^{99}Tc. The bulk of the water-leachable chromium has been confirmed as Cr(VI) (chromate) by its distinct yellow color and by ion chromatography. The apparent slight chromium retardation was more thoroughly investigated and discussed next.

Based on comparison of the depth of penetration of various contaminants and the percentages that are water leachable, it was determined that chromium migrates faster than ^{137}Cs but slower than ^{99}Tc and nitrate. The slight retardation for the Cr(VI) was likely caused by a reduction process where the ferrous [Fe(II)] minerals in the sediment react with the tank fluids and cause a portion of the soluble Cr(VI) to $Cr(OH)_3$ or Fe(III)/Cr(III) hydroxide solid solution precipitates (Zachara et al. 2004 and Qafoku et al. 2003).

The vast majority of ^{137}Cs activity in the borehole 299-W23-234 sediment is concentrated between the depths 20.1 to 25.6 m bgs, with moderate amounts of ^{137}Cs reaching 31.1 m bgs and the leading edge perhaps reaches 39.9 m to 41.5 m bgs. However, Serne et al. (2002f) believed that the high ^{137}Cs at 40.3 m bgs was from compressed sediment that was dragged down during the original pile driving of the closed-end casing. In traditional batch sorption tests, the cesium K_d value for several sediments from the borehole was measured at a moderate range of 4 to 40 ml/g for a very high ionic strength (7.4 M sodium nitrate), neutral pH solution. The cesium K_d increases slightly for the 4 M sodium nitrate solution as would be expected for a cation exchange dominated process. The K_d range of 4 to 40 mL/g for batch laboratory test is similar to the "in situ" desorption K_d values (4 to 25 mL/g) calculated from the water-extract concentrations and direct counting of the borehole sediment.

The water-extractable cations suggest that an ion-exchange process dominates the pore water/ sediment interactions in the zone where tank fluid passed by or currently exists. The leading edge of the tank-leak plume is enriched in alkaline earth cations that were displaced from the native sediment exchange sites. Combining the atypical high nitrate with the sodium/calcium ratio data for water extracts suggests that the leading edge of a tank-leak plume is at 41.1 m bgs at borehole SX41-09-39. One plausible explanation for this depth is that the tank-leak plume traveled horizontally and vertically over a relatively short time period through the more permeable Hanford formation sediments and perched on the less-permeable Cold Creek unit sediment. Over the next four decades, the soluble elements slowly diffused and percolated into the top of the CCU_u down another 3.4 m into the Hanford formation.

The matric suction data for borehole 299-W23-234 sediments suggest that the sediment profile at borehole SX41-09-39 is draining. A recharge rate of somewhat greater than 5 mm/yr was estimated from

the matric suction data and other simple assumptions (Serne et al. 2002f). This is lower than expected based on a number of studies at the Hanford Site (Gee 1987; Gee et al. 1992, 1994) that show coarse gravel surface covers, as found at the tank farms, cause as much as 50% of the annual precipitation to recharge to the water table. Another source of localized recharge near tank farms has been hypothesized to be leaking water lines. With the gravel cover, one might expect up to 50% of annual precipitation to recharge groundwater (several centimeters as opposed to 5 mm).

Cation exchange measurements show that the fine-grained Cold Creek unit silts have a relatively high exchange capacity (13 to 16 meq/100 g). The coarse-grained Ringold sediments have a very low cation exchange capacity (~1 to 3 meq/100 g). Although not measured, the Hanford formation sediments should fall in between these two values (Serne et al. 2002f).

In summary, ion exchange and in the case of chromium, heterogeneous (solid phase-liquid solute) redox reactions were identified as two possible mechanisms that are influencing the distribution of contaminants in the vadose zone sediments at borehole 299-W23-234 within the zone impacted by tank liquor. Serne et al. (2002f) did not observe significant indications of pH alteration of the sediment mineralogy or porosity, but they did observe slightly elevated pH values (8.3 to 9.6) between 16.8 to 27.4 m bgs.

3.5.5   Geochemical Characterization: Slant Borehole SX-108 (C3082)

Serne et al. (2002b) conducted characterization studies of sediment samples from slant borehole SX-108 (C3082). The slant borehole intersected three primary stratigraphic units: 1) backfill, 2) the Hanford formation, and 3) the top of the Cold Creek unit. The backfill appears to extend to a depth of about 16.2 m bgs where it contacts the Hanford formation. The location of the H1a/H1 contact is 18.7 m bgs. Below H1a lies the coarse sand and gravel sequence (Hanford H1 unit) extending to a vertical depth of approximately 23 m bgs. The lower fine sand and mud sequence (Hanford formation H2 unit) extends to a vertical depth of 38.5 m bgs. About 5.6 vertical meters of the CCU_u was penetrated by the slant borehole but the lower contact of this unit was not encountered before borehole drilling refusal was met. Based on the overall tank farm regional geology, Serne et al. (2002b) concluded the Hanford formation units dip towards the southwest.

Results for some of the most significant parameters measured in the sediments collected from slant borehole SX-108 (C3082) are presented in Figure 3.18 as a function of depth. These include parameters that can have a significant influence on contaminant mobility and can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and indicators of hydrologic control (lithology, statigraphy, and moisture content).

In general, the near horizontal but dipping sediment layers likely caused preferred pathways for water flow. The vertical distribution of ^{137}Cs at both the slant borehole under tank SX-108 (C3082) and at borehole 299-W23-234 suggest that much of the tank fluid that leaked from surrounding tanks traveled within the coarse-grained Hanford H1 unit. At the slant borehole under SX-108 (C3082), there is also a large mass of ^{137}Cs in the fine-sand Hanford H2 unit that lies below H1. At the slant borehole there is a fine-grained lens in the Hanford H2 unit at 32.2 m bgs that was not impacted much by the tank fluids. This unit was mostly bypassed by the migrating plume under the tank. Because this region had limited interaction with tank fluid, Serne et al. (2002b) found it difficult to fully interpret the vertical distribution of contaminants under SX-108.
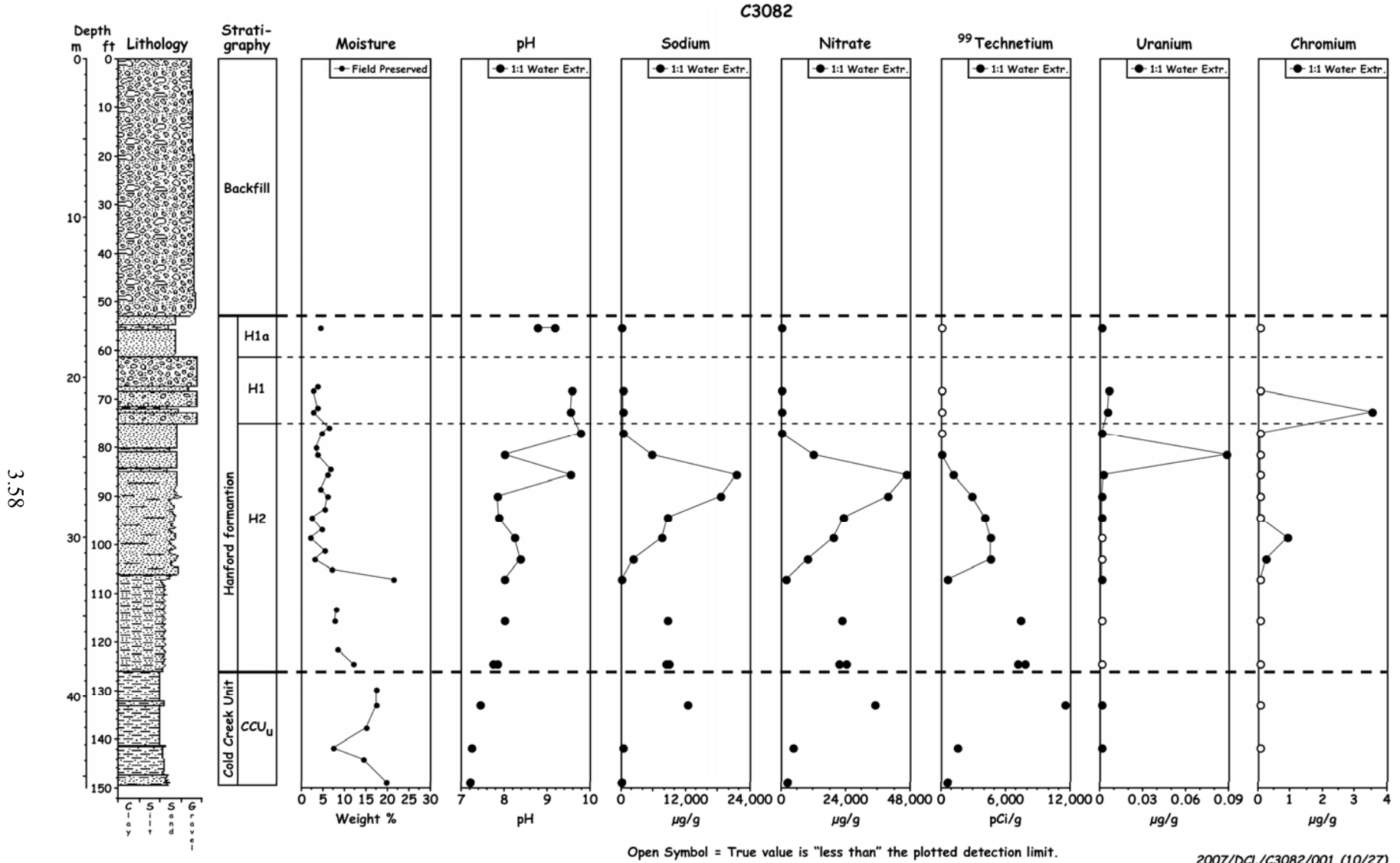
Figure 3.18. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole C3082 Located in Waste Management Area S-SX (Serne et al. 2002b)

Moisture readings obtained from the vadose zone samples collected below the tank bottom from 16.8 to 21.8 m and 26.8 to 30.8 m bgs are drier than the comparable sediments from borehole 299-W23-234. Temperature measurements at the wall of the slant borehole casing, previous in-tank temperature measurements, and thermal modeling suggest that complicated convection cells of water vapor and liquid water were active under tank SX-108 (Serne et al. (2002b). Thus, Serne et al. (2002b) did not consider that the measured moisture contents were indicative of the vertical migration of tank liquor beneath tank SX-108.

At the SX-108 slant borehole, the H1a sediment-water extracts show high pH (9.2) and elevated electrical conductivity (9.3 mS/cm as pore water). In contrast, there was no indication that the H1a sediment at borehole 299-W23-234 was impacted by tank fluids. However, the pH values in the sediments below tank SX-108 are not nearly as high as would be expected for tank waste completely saturating sediments. The closest sample obtained below tank SX-108 was ~ 3.66 m (12 ft) below the tank bottom. Therefore, it would appear that any zone of highly altered pH occurs in a zone that is less than 3.66-m thick. At the SX-108 slant borehole (C3082), the pH is slightly elevated down to at least 25.6 vertical meters bgs. At 26.8 m bgs to the final depth of the borehole, the slant borehole sediment pH is normal. Sediment pH was not believed be sensitive to the distance tank liquor traveled and might be more sensitive to time of reaction.

The electrical conductivity results suggest that tank fluid dominates the pore water at the slant bore-hole down to a depth of 39.3 m bgs, about 1.5 m into the CCU_u sediments. The electrical conductivity of the two deeper sediment-water extracts does not drop to natural background levels, but the electrical conductivity in the two deepest water extracts is significantly lower than all the samples shallower in the profile. Thus, the leading edge of the plume is below the total depth sampled but the bulk of the salt is still above 39.3 m bgs. Based on the nitrate profile at borehole 41-09-39 (299-W23-234), which does show the whole extent of the plume, Serne et al. (2002b) estimated that the leading edge of the plume beneath SX-108 may have stopped at the contact of the CCU_u and CCU_l near 45.7 m bgs. This estimate does not consider any complications due to convection cells that may have transported water vapor and recondensed water under tank SX-108. The SX-108 plume center of mass traveled deeper than the plume at borehole 299-W23-234 but shallower than the plume at SX-115 that predominately resides in the CCU_u unit.

The ^{99}Tc data show that there are extremely high (10^{+3} to 10^{+4} pCi/g sediment) concentrations of ^{99}Tc between the depths of 25.9 to 42.1 m bgs in the sediments from the slant borehole. The leading edge of the ^{99}Tc plume appears to reach 42.1 m bgs, although even the deepest sample at 44.0 m bgs is slightly elevated (5 x 10^{+2} pCi/g) in technetium. Compared to the ^{137}Cs distributions, there is very little ^{90}Sr in the sediments suggesting that ^{90}Sr is not mobile in the REDOX fluid that leaked from the tanks at the SX Tank Farm.

The pore waters in the sediments from the cores in the three Hanford formation units [H1a, H1, and H2] were dominated by sodium and nitrate. At the slant borehole, the most concentrated pore water was in the Hanford H2 unit and was essentially 16 to 17 M sodium nitrate with 1.0 M calcium, 0.5 M chromate and several tenths molar sulfate, chloride, potassium, and magnesium. This extremely hypersaline composition is about three times higher in all constituents as found in the Hanford H2 unit pore water at borehole 299-W23-234, but the increase is more likely caused by sediment desiccation (i.e., drying of the sediments resulting in a more concentrated or saline pore water) than different leak chemical compositions. The waste components present in the contaminated pore waters at both boreholes are remarkably similar.

The water-leachable chromium profiles suggest that chromium is not as mobile as [99]Tc. This is also true at the other boreholes within the SX Tank Farm. As previously cited in the last section, researchers (Zachara et al. 2004, Qafoku et al. 2003) have identified a caustic catalyzed reaction where ferrous [Fe(II)] bearing minerals are dissolved and the Fe(II) released to the pore fluids reduces Cr(VI) to Cr(III) that then coprecipitates as a ferric-chromic hydroxide.

The analyses of water-extractable cations suggest that an ion-exchange process dominates the pore water/sediment interactions in the slant borehole sediments through which tank fluids have migrated or have stopped . The leading edge of the tank-leak plume is enriched in alkaline earth cations that were displaced from the native sediment exchange sites. Serne et al. (2002b) suggested that the results indicated the presence of two ion-exchange fronts present in the slant borehole sediment, which would imply two separate leak events. However, Serne et al. (2002b) noted that this hypothesis is likely affected by the fact that the hole is slanted and the apparent presence of unaltered sediment at about 32 m bgs at the slant borehole location. The water extracts of the sediment sample and the direct measurement of gamma emitters in the sediment at 32 m bgs did not show any significant indication that tank fluids had interacted with the sediment at this depth. It therefore appears there is a region below the tank where released fluids have not percolated through in any significant amount. Irregular and strongly anisotropic flow paths are common in the heterogeneous vadose zone of the Hanford Site subsurface.

The in situ desorption K_d for cesium is highly variable from a low of 2.3 to a high of 307 mL/g. In the sediments where the estimated pore-water composition was >10 M sodium nitrate (between 24.4 and 29.6 m), the in situ desorption K_d varied between 2 and 10 mL/g. Much of the variability is correlatable to the major cation composition of the pore water, especially the sodium concentration. Above 24.4 and below 27.4 m bgs, the cesium in situ desorption K_d is larger because the pore fluids do not contain high sodium concentrations that compete for adsorption sites. Serne et al. (2002b) concluded that in the future if natural recharge remains the driving force, cesium will be adequately retarded once it is completely separated from the high sodium pore-water plume.

The ^{99}Tc desorption measurements were consistently near zero, which means ^{99}Tc is not interacting with the sediments. Despite findings such as those of Zachara et al. (2004) that about one-third of the chromium appears to get reduced via caustic dissolution of Fe(II) containing minerals, the chromium desorption K_d values are still <1 mL/g in the entire zone where the bulk of the tank fluid currently resides. Based on comparing the depth of penetration of various contaminants and comparing the percentages that are water leachable, Serne et al. (2002b) suggested that chromium and molybdenum migrate faster than ^{137}Cs but slower than ^{99}Tc, selenium, and nitrate.

Unlike similar ratio discussions for the other two contaminated boreholes (299-W23-234 and 299-W23-19), the ratios of COI concentrations in the pore waters in the slant borehole are not constant. The possibility of two distinct leak events that caused additional irregular mixing between the two plumes or dynamic convection currents driven by the time varying heat load under the tank confounds the use of this ratio approach. The ratio of ^{99}Tc to nitrate in slant borehole water extracts, although not as constant as it was at 299-W23-19, is much lower than the ratio in the groundwater below the SX Tank Farm. Thus, it is much more plausible that the source of the contamination in the groundwater under the SX Tank Farm is the vadose zone pore fluids originally lost from tank SX-115, which show a ^{99}Tc/nitrate ratio closer to that present in the groundwater than the leaked fluid from tank SX-108.

No evidence of mineral alteration or precipitation resulting from interaction of tank liquor with sediment was observed based on XRD measurements. However, SEM analysis of some of the samples

suggest that there is evidence of caustic attack on the sample obtained just under tank SX-108 and ~3.7 m deeper than the tank bottom (see McKinley et al. 2001).

In summary, ion exchange and in the case of chromium, heterogeneous (solid phase-liquid solute) redox reactions were identified as two mechanisms that are influencing the distribution of contaminants in the vadose zone SX Tank Farm sediments within the zone impacted by tank liquor. Significant indications of pH alteration of the sediment mineralogy or porosity were not observed but slightly elevated pH values (8.4 to 9.8) and minor indications of caustic reactions with the sediments within 9.1 m of the tank bottom were found.

3.5.6   Estimated K_d Values for Key Contaminants at Waste Management Area S-SX

Ten tanks within WMA S-SX have released fluids into the vadose zone sediments as shown in Table 3.11. The chemical composition of the fluids released from tank S-104 and the nine SX tanks are shown in Table 3.12. The waste released at tank S-104 is relatively low salt and moderately caustic compared to most of the wastes released in the SX Tank Farm. The K_d values for the high and intermediate impact zones are shown in Table 3.13 for sand, silt and carbonate-rich sediments found below the tanks in WMA S-SX. The K_d values for unimpacted sediments are listed in Table 3.4.

3.6   Waste Management Areas T and TX-TY

Three characterization studies have been completed covering WMAs T and TX-TY. The first study includes four boreholes drilled in or near WMA TX-TY (Serne et al. 2004a). The boreholes were C3830, C3831, C3832 and 299-W10-27. The second study includes sediment samples from four boreholes placed in or near the T Tank Farm (Serne et al. 2004b). The second study included three boreholes drilled near WMA T (C4104, C4105, and 299-W11-39). In addition to these three boreholes, the second study included characterization data of samples from a fourth older borehole (299-W10-196). The most recent study conducted detailed analyses of vadose zone sediment collected by direct-push methods within the T and TY Tank Farms Brown et al. (2007b).

These data were used to determine changes over the ~10 yr time between the drilling of 299-W10-196 and C4104, which are located within 4.57 m (15 ft) of each other. Both reports provide results and interpretation of geological, geochemical, and selected physical analyses conducted on vadose zone sediments. Included in the interpretation of the data from these reports are geologic models, the vertical extent of contamination, migration potential of the contaminants, and the likely source of the contamination in the vadose zone and groundwater below the TX and T Tank Farms. Figures 3.19 and 3.20 show the location of the tanks, RCRA wells, the boreholes from which vadose zone sediments were obtained, and other facilities around WMAs TX-TY and T, respectively.

3.6.1   Brief Description of Geology of Waste Management Areas T and TX-TY

The geology of the T, TX, and TY Tank Farms and vicinity is well understood as a result of several decades of site characterization activities and has been described in numerous reports (Price and Fecht 1976i, 1976j, 1976k; Tallman et al. 1979; Last et al. 1989; Connelly et al. 1992b; DOE-GJO 1997; Wood et al. 2001). A detailed description of the geology of WMAs T and TX-TY is provided in the SST WMA geology data package by Reidel and Chamness (2007). A summary table of the statigraphic terminology and thicknesses of units beneath WMAs T and TX-TY from Reidel and Chamness (2007) is provided below in Table 3.14. Conceptual geologic models were also developed for the TX and T Tank Farms in the borehole characterization reports (Serne et al. 2004a, 2004b).

Table 3.11. Waste Management Area S-SX Leak Event Locations, Times, and Volumes (from Field and Jones 2005)

Site	Operating Years	Site Description--Principal Wastes	Total Volume (L)
241-S-104	1965	Zero solids. Adjusted SMM definition to this tank. SMM ideal mixing rules do not apply to this CWR2 overfill event because of the manner in which wastes were added. [CWR2]	9.08E+04
241-SX-104	1988	Zero solids. Unadjusted SMM definition for tank-leak date of 1988. Mixture of S1-SltCk and S2-SltSlr.	2.27E+04
241-SX-107	1963	Zero solids. Adjusted 1963 SMM definition because of tank self-concentration effect. Used [R2] in SX tanks where the supernatant volume (Sup Vol) is less then half of the SMM volume (e.g., unconcentrated, original waste volume). [R2]	5.68E+04
241-SX-108	1966	Zero solids. Adjusted 1966 SMM definition because of tank self-concentration effect. Used [R2] in SX tanks where the supernatant volume (Sup Vol) is less then half of the SMM volume (e.g., unconcentrated, original waste volume). [R2]	1.32E+05
241-SX-109	1966	Zero solids. Adjusted 1966 SMM definition because of tank self-concentration effect. Used [R2] in SX tanks where the supernatant volume (Sup Vol) is less then half of the SMM volume (e.g., unconcentrated, original waste volume). [R2]	7.57E+03
241-SX-110	1976	Zero solids. Unadjusted SMM definition for tank-leak date of 1976. mixture of Sr-Cs Rec Org Waste [CSR, T2-SltCk, and Sr-Cs Rec Org Waste aqueous BL]	3.79E+03
241-SX-111	1958	After review of WSTRS level/transfer records for 241-SX-111 (Agnew et al. 1997), the drywells had been improved/deepened just prior to the leak detection date (1974) cited in Field and Jones (2005) and RPP-7884 (Knepp 2002). This date assignment seems suspicious, or at least convenient, in that the tank would leak right after those newer drywells were drilled. In this case, it appears that the 1974 date is simply the leak declaration date (i.e., that is when tank farms became aware of the leak). On further investigation, around 1958, WSTRS shows unexplained level drops for this tank. From the SMM-assigned 1958 date until 1971, the waste type is the same in the tank. This process history gives a wide margin for error in selecting the leak date. On top of this, the tank contained different types of REDOX waste both in the 1950s and in the 1970s. The 1958 date is assigned contrary to tank farms convention because it is unclear how valid the 1974 date is (or if it is simply a detection date as it appears) and 1958 gives a longer period of the same waste type and wider margin for error in waste selection. Mixture of Sr-Cs Rec Org Wst [CSR and R2]	1.89E+03
241-SX-112	1969	Zero solids. Adjusted 1969 SMM definition because of tank self-concentration effect. Used [R2] in SX tanks where the supernatant volume (Sup Vol) is less then half of the SMM volume (e.g., unconcentrated, original waste volume). [R2]	3.79E+03
241-SX-113	1958	Zero solids. Unadjusted SMM definition for tank-leak date of 1958. [R1]	5.68E+04
241-SX-115	1965	Zero solids. Unadjusted SMM definition for tank-leak date of 1965. mixture of [CWR2, R1, and R2]	1.89E+05

SMM   = Supernatant mixing model.
WSTRS = Waste Status and Transaction Record Summary.

Table 3.12. Compositions of Waste Streams Released from Tanks in Waste Management Area S-SX (from Corbin et al. 2005)

Waste Type	Concentration (mol/L)							
	CWR2	S1-SltCk	S2-SltSlr	R1	R2	T2-SltCk	BL	CSR
Na^+	1.83	12.9	13.1	5.57	5.54	10.6	3.67	4.15
Ca^{2+}	0.0035	0.0038	0.0038	0.0038	0.0038	0.0038	0.01	0.0038
K^+	0	0.0764	0.0827	0.0267	0.0202	0.0661	0.015	0.021
Sr^{2+}	2.49E-07	5.29E-07	5.31E-07	5.50E-07	5.50E-07	5.34E-07	1.50E-05	5.30E-07
NH_4^+	4.45E-05	0.0859	0.107	0.0096	0.0367	0.119	6.55E-04	0.025
Cr	0.0031	0.0554	0.0554	0.055	0.055	0.0554	2.00E-07	0.032
Mn	0	5.56E-04	5.55E-04	5.54E-04	0	5.36E-04	0	3.24E-04
Fe	0.0019	0.0019	0.0019	0.00187	0.00187	0.0019	0.017	0.0019
Ni	0.0015	0.0018	0.0018	0.0018	0.0018	0.0018	0.01	0.0018
Bi	0	1.54E-04	2.22E-04	0	0	2.97E-04	0	5.10E-06
NO_3^-	0.886	3.5	3.5	2.25	1.3	3.5	0.772	1.25
NO_2^-	0.288	2.43	2.52	0.769	1.41	1.79	0.117	0.86
CO_3^{2-}	0.0037	0.388	0.435	0.0038	0.0038	0.385	0.271	0.184
PO_4^{3-}	0	0.0478	0.0587	0	0	0.063	0.01	0.0065
SO_4^{2-}	0.0061	0.124	0.124	0.0193	0.0303	0.124	0.044	0.094
Cl^-	0.016	0.268	0.291	0.0957	0.093	0.236	0.069	0.07
F^-	0	0.0662	0.0947	0	0	0.126	0	0.0016
OH^-	0.02	3.23	3.21	1.76	1.77	2.13	0.043	0.994
$Al(OH)_4^-$	0.629	1.75	1.75	0.848	0.994	1.4	0.261	0.385
Organics	0	0.32	0.32	0	0	0.448	0.7	0.07

Table 3.13. K_d Values for Impacted Sediments at Waste Management Area S-SX (K_d units are mL/g)

	Sand-Sized Sediments						Silt-Sized Sediments						Carbonate Dominated Sediments					
	High Impact			Intermediate Impact			High Impact			Intermediate Impact			High Impact			Intermediate Impact		
	Best	Min	Max	Best	Min	Max	Best	Min	Max	Best	Min	Max	Best	Min	Max	Best	Min	Max
Chemicals																		
F⁻	0	0	0	0	0	1	0	0	0	0.05	0	1	0	0	1	0.05	0	1
Cr(VI)	0.2	0	3	0	0	8	0.4	0	8	0	0	10	0.2	0	3	0	0	8
Hg(II)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NO₃⁻, NO₂⁻	0	0	0	0	0	0.1	0	0	0	0	0	0.1	0	0	0.1	0	0	0.1
Pb	3	0	10	10	3	100	0	0	30	30	10	300	3	0	10	10	3	100
U(VI) – all isotopes	0.1	0	10	0.8	0.2	17	0.3	0	3	2.5	0.6	15	0.3	0	30	2.5	0.6	30
Radionuclides																		
²⁴¹Am(III)	3	0	50	600	200	2000	10	0	150	600	200	2000	10	0	150	600	200	2000
¹⁴C	5	0	50	1	0	100	5	0	50	1	0	100	5	0	50	1	0	100
⁶⁰Co(II,III)	0	0	10	0	0	10	0	0	30	0	0	30	0	0	30	0	0	30
¹³⁷Cs	1	0	10	100	10	1000	1	0	30	100	30	3000	1	0	10	100	10	1000
Eu(III) – all isotopes	1	0	10	10	3	100	3	0	30	30	10	300	3	0	30	30	10	300
³H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
¹²⁹I	0	0	0.2	0.2	0	2	0	0	0	0.2	0	2	0	0	0	0.2	0	2
⁶³Ni	0	0	10	3	1	20	0	0	30	10	3	60	0	0	30	10	3	60
²³⁷Np(V)	0	0	5	10	2	30	0	0	15	10	2	50	0	0	15	10	2	50
Pu – all isotopes	3	0	50	600	200	2000	5	0	150	600	200	2000	3	0	50	600	200	2000
²²⁶Ra	1	0.2	20	10	5	20	3	0.6	60	10	5	60	3	0.6	60	10	5	60
⁷⁹Se(VI,IV)	0	0	3	0.1	0	3	0	0	3	0.3	0	10	0	0	3	0.1	0	3
¹²⁶Sn(IV)	0	0	10	0.5	0	20	0	0	30	1.5	0	60	0	0	30	1.5	0	60
⁹⁰Sr	1	0.2	20	10	5	20	3	0.6	60	10	5	100	3	0.6	60	10	5	100
⁹⁹Tc(VII)	0	0	1	0	0	5	0	0	1	0	0	5	0	0	1	0	0	5

For gravel-size sediments, modify sand-size K_d values using Equations (2.3) and (2.4) in Section 2.4.
See Appendix A for references and selection rationale.

Figure 3.19. Location Map of Waste Management Area TX-TY with Details for Recent Boreholes Around TX Tanks From Which Vadose Sediments Were Characterized

3.65
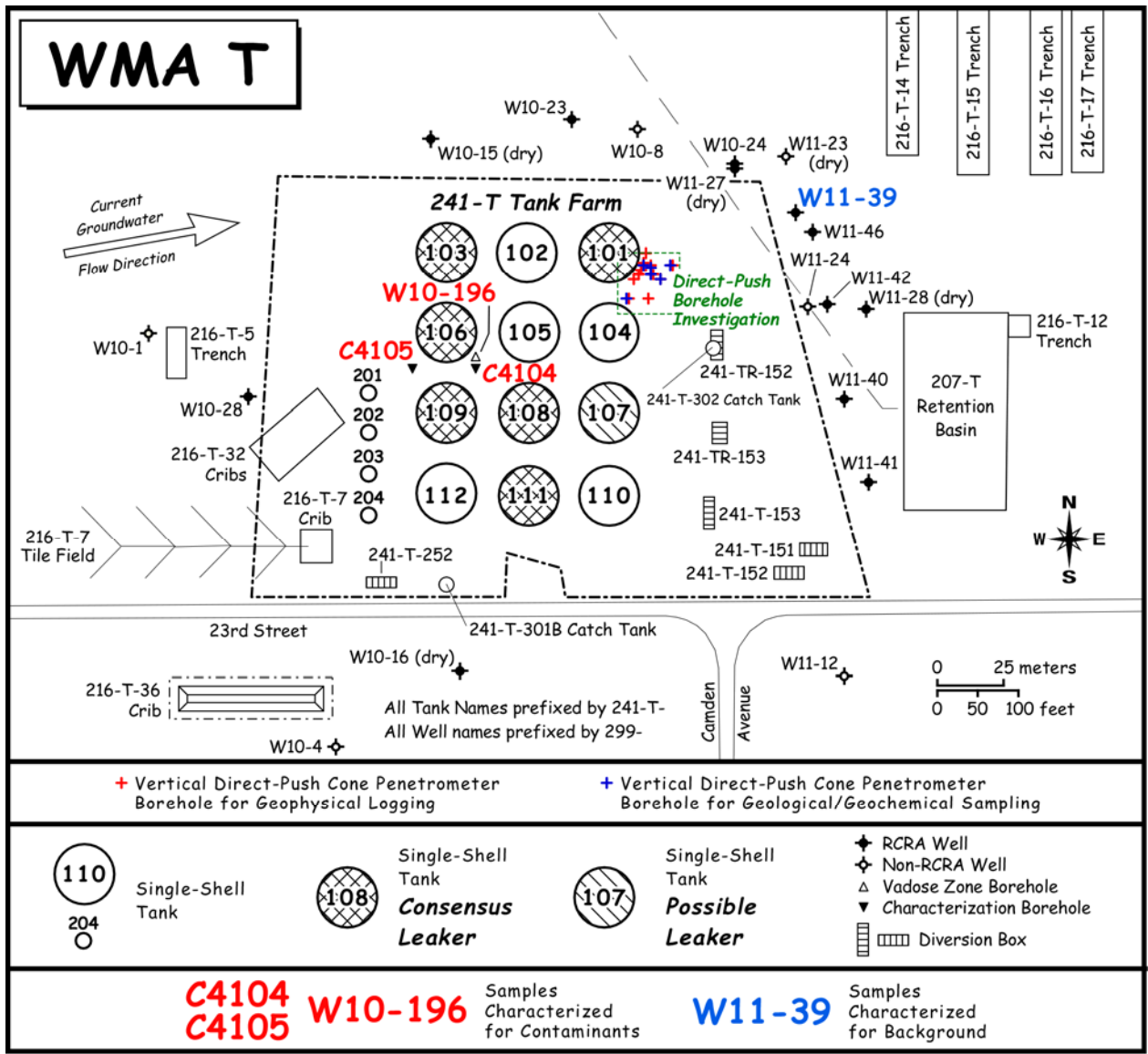
Figure 3.20. Location Map of Waste Management Area T with Recent Boreholes Identified From Which Vadose Zone Sediments Were Obtained

Table 3.14. Stratigraphy Below the Waste Management Areas T and TX-TY (from Reidel and Chamness 2007)

Stratigraphic Symbol	Formation	Facies/Subunit	Description	Thickness
Backfill	NA	Backfill – Anthropogenic	Gravel-dominated consisting of poorly to moderately sorted cobbles, pebbles, and coarse to medium sand with some silt derived from coarse-grained Hanford formation (H1 unit) excavated around tanks (Price and Fecht 1976i, 1976j, 1976k; Wood et al. 2001); occasional layers of sand to silty sand occur near the base of the backfill sequence.	18 m
H1	Hanford formation	Unit H1 (Gravel-dominated facies association). Cataclysmic flood deposits (high-energy)	Gravel-dominated flood sequence; composed of mostly poorly-sorted, basaltic, sandy gravel to silty sandy gravel. Equivalent to the upper gravel sequence discussed by Last et al. (1989), the Q_{fg} documented by Reidel and Fecht (1994), Hanford Gravel Unit A of Johnson et al. (1999), coarse-grained sequence (H1 unit) of Wood et al. (2001) and gravel facies of unit H1 of Lindsey et al. (2001b), and gravel-dominated facies association of DOE-RL (2002).	10 – 12 m
H2		Unit H2 (Sand-dominated facies association). Cataclysmic flood deposits (moderate energy)	Sand-dominated flood sequence; composed of mostly horizontal to tabular cross-bedded sand to gravelly sand. Some sand beds capped with thin layers of silty sand to sandy silt. Equivalent to Hanford Sands of Johnson et al. (1999), Fine-Grained Sequence (H2 unit) of Wood et al. (2001) and unit H2 of Lindsey et al. (2001b), the sandy sequence of Last et al. (1989) and Lindsey et al. (1992), and to Q_{fs} documented by Reidel and Fecht (1994), and sand-dominated facies association of DOE-RL (2002).	9 – 18 m
Hf/CCU	Undifferentiated Hanford formation and Cold Creek unit	NA	Silty sequence. Similar to Cold Creek unit but distinguished by having a lower natural gamma response.	2 – 5 m
CCU_u	Cold Creek unit	Upper subunit Post-Ringold Formation eolian and/or overbank alluvial deposits	Silty sequence; consisting of interstratified well-sorted silt and fine sand. Uncemented but may be moderately to strongly calcareous from detrital $CaCO_3$. Equivalent to the "early Palouse soil" (Tallman et al. 1979, DOE 1988, DOE-GJO 1997) and the Hf/PP deposits of Wood et al. (2001). Also equivalent to the upper Plio-Pleistocene unit in Lindsey et al. (2001b) and the fine-grained, laminated to massive lithofacies of the Cold Creek unit (DOE-RL 2002).	2 – 7 m
CCU_l		Lower subunit calcic paleosols developed on eroded Ringold or post-Ringold Formation eolian and/or fluvial deposits	Calcic paleosol sequence; consisting of interbedded layers of pedogenically altered to unaltered gravel, sand, silt, and/or clay, cemented together with one or more layers of secondary $CaCO_3$, originally referred to as "caliche" (Brown 1959). Since then the name has evolved from the Plio-Pleistocene unit (DOE 1988, DOE-GJO 1997, Slate 2000), the Plio-Pleistocene calcrete facies (DOE 1988; Wood et al. 2001), the lower Plio-Pleistocene unit (Lindsey et al. 2001b), and the coarse- to fine-grained, $CaCO_3$-cemented lithofacies of the Cold Creek unit (DOE-RL 2002).	0 – 8 m
R_{tf}	Ringold Formation	Member of Taylor Flat Ancestral Columbia River System fluvial channel, crevasse splay, and overbank deposits	Fine-grained Ringold Formation sequence consisting of interstratified, well-bedded fine to coarse sand to silt. Equivalent to the upper Ringold Formation unit (DOE 1988).	10 m

Table 3.14. (contd.)

Stratigraphic Symbol	Formation	Facies/Subunit	Description	Thickness
R$_{wi}$ unit		Member of Wooded Island Ancestral Columbia River System braided-stream deposits	Coarse-grained Ringold Formation sequence, consisting of mostly moderately sorted, quartzitic sandy gravel to silty sandy gravel. Equivalent to middle Ringold unit (DOE 1988) and the Ringold Formation unit E and unit A gravels (Wood et al. 2001, Lindsey et al. 2001b). Contains mud (LM).	Unit E: 85 m; LM: 6 – 11 m; Unit A: 20 m

CaCO$_3$	=	Calcium carbonate.
CCU$_l$	=	Lower Cold Creek unit.
CCU$_u$	=	Upper Cold Creek unit (Cold Creek fine-grained unit).
Hf/CCU	=	Hanford formation/Cold Creek unit.
LM	=	Lower mud unit.
NA	=	Not applicable.

3.6.2   Geochemical Characterization of the TX Tank Farm: Boreholes C3830, C3831, C3832, and RCRA Borehole 299-W10-27

Sediment samples from the four boreholes were analyzed and characterized in the laboratory for the following parameters: moisture content, gamma-emitting radionuclides, 1:1 sediment/water extracts (which provide soil pH, electrical conductivity, cation, trace metal, and anion data), total carbon and inorganic carbon content, and 8 M nitric acid extracts (which provide a measure of the total leachable sediment content of contaminants) (Serne et al. 2004a). Two key radionuclide contaminants, ^{99}Tc and ^{238}U, along with other trace metals were determined in acid and water extracts by ICP-MS.

Results for some of the most significant parameters measured in the sediments collected from WMA TX-TY boreholes C3830, C3831, and C3832 are presented in Figures 3.21, 3.22, and 3.23, respectively, as a function of depth. These include parameters that can have a significant influence on contaminant mobility and can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and indicators of hydrologic control (lithology, statigraphy, and moisture content).

Overall, the analyses showed that ion exchange is a key mechanism that influences the distribution of contaminants within that portion of the vadose zone affected by tank liquor. Unlike the vadose zone sediments at the SX and BX Tank Farms, zones of elevated pH values in samples from the three boreholes (C3830, C3831, and C3832) were not observed at WMA TX-TY.

Sediments from the three TX Tank Farm boreholes show that sodium-, nitrate-, and sulfate-dominated fluids are present below tanks TX-104, TX-105, and TX-107 and have formed three salt plumes (note that tanks TX-104 and TX-105 are not considered to have released fluids based on the current assessment documented in Field and Jones [2005]). More discussion is provided below. The fluids are more dilute than tank fluids observed below tanks at the SX and BX Tank Farms. Most of the chemical data for contaminants intercepted by boreholes C3831 and C3832 suggest that fluid leaked from tank TX-107 and may have percolated deeper into the sediments and traveled southwest to C3832. However, more uranium is present in the sediments and water extracts at C3832. This confounds the hypothesis that tank TX-107 is the sole source of fluids that were intercepted by both boreholes. Therefore, it is hypothesized that a small-volume leak with elevated uranium also occurred from tank TX-104. Borehole C3830 suggests another small-volume leak occurred from tank TX-105.

Figure 3.21. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole C3830 Located in the TX Tank Farm (Serne et al. 2004a)

Figure 3.22. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole C3831 Located in the TX Tank Farm (Serne et al. 2004a)

Figure 3.23.   Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole C3832 Located in the TX Tank Farm (Serne et al. 2004a)

The conceptual model of the geology between core samples is based on our interpretation of the geophysical log and blow-count data.[5] Three primary stratigraphic units were encountered in each of the three TX boreholes: 1) backfill material, 2) the Hanford formation, and 3) the Cold Creek unit. At C3830, we infer that there are four, thin, fine-grained layers in the Hanford formation H2 stratigraphic unit. At C3831, Serne et al. (2004a) found possibly at least eight fine-grained layers in the Hanford H2 unit. Also at C3831, a clastic dike was observed within the Hanford formation H2 unit at about 18.3 m bgs. Because contamination at this borehole starts at the depth where the clastic dike was intercepted, Serne et al. (2004a) suggested that the dike may represent a preferred pathway for fluids that leaked from tank TX-107. There are at least eight thin, fine-grained interbeds in the Hanford formation H2 unit at C3832. These thin fine-grained lenses within sands of the Hanford formation H2 unit may impact the flow of leaked fluids and produce irregular and horizontal flow.

The boreholes could not penetrate below the calcium-carbonate-rich strata of the CCU_l subunit (refusal was met at about 35 m bgs at all three holes). Therefore, Serne et al. (2004a) did not identify the maximum vertical penetration of the tank-related plumes. However, the more elevated portions of the electrical conductivity profile at C3830 currently reside at the bottom of a fine-grained thin lens in the Hanford formation H2 unit at 26.5 m bgs. At C3831, Serne et al. (2004a) lacked good sample coverage in the fine-grained CCU_u subunit and the caliche unit to ascertain whether the salt plume has significantly descended into the Cold Creek unit sediments. There is strong indication that at C3832, the saline plume has migrated into the Cold Creek unit to the bottom of the borehole. The electrical conductivity, nitrate, and ^{99}Tc profiles versus depth do not identify the leading edge of the plume with any certainty. The profiles do collectively suggest that the deepest penetration of tank-related fluids is found in C3832 and that the plume has reached the caliche material in the CCU_l subunit at least to a depth of 35.4 m bgs.

Despite the evidence that elevated electrical conductivity values may be present in all three boreholes to their depth of refusal, the values are not large. For example, the maximum dilution-corrected electrical conductivity at C3832 is 6.27 mS/cm. At C3830, the maximum is 12.5 mS/cm, and at C3831 the maximum is 43.3 mS/cm. The leaks near tanks SX108-109 and BX-102 had peak vadose zone pore-water concentrations that were much more concentrated waste fluids: 524 to 1774 and 77 mS/cm, respectively. The dilution corrected electrical conductivity values for uncontaminated vadose zone sediments in 200 East and 200 West Areas generally range from 2 to 8 mS/cm.

The water potential data from 299-W10-27's Hanford formation H2 unit, the unit where most of the contaminants reside in the TX Tank Farm boreholes, are consistent with a draining profile. The inventories of potential contaminants of concern (nitrate, ^{99}Tc, uranium, and chromium) as a function of depth are provided in Serne et al. (2004a). In addition, in situ desorption K_d values for these potential contaminants are provided based on the difference between acid and water extracts of the contaminated sediments. Analysis by Serne et al. (2004a) of their data did not indicate any current similarity between the present or past groundwater contamination and current vadose zone pore-water compositions from the contaminated borehole sediments within the TX Tank Farm. Therefore, contaminants in the groundwater, currently or during the era of contaminant introduction into the vadose zone, cannot be linked to the pore

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[5] Blow count refers to how many times the hydraulic hammer is contacted with the drill rod to advance the casing down through the sediment. High blow counts reflect the degree of difficulty in advancing the casing through the sediments and is semi-quantitatively related to the grain size and degree of cementation present in the sediments at the depth being contacted. An experienced driller or geologist can identify the geologic stratigraphy from knowledge of blow counts and location of the borehole.

waters currently in the borehole sediments, which are known to be derived from liquids that leaked from tank TX-107. Thus, Serne et al. (2004a) suggested that TX Tank Farm tank leaks are not the sole source of the contamination present in the groundwater below the TX Tank Farm in the past or present.

3.6.3 Geochemical Characterization of the Waste Management Area T: Boreholes C4104, C4105, 299-W10-196, and RCRA Borehole 299-W11-39

Serne et al. (2004b) characterized vadose zone sediment recovered from boreholes C4104 and C4105 in the T Tank Farm, and from borehole 299-W-11-39 installed northeast of the T Tank Farm. Results from borehole C4104 were compared with a nearby borehole (299-W10-196) drilled in 1993 through the tank T-106 leak plume.

Sediment samples from the boreholes were characterized in the laboratory for moisture content, gamma-emitting radionuclides, 1:1 sediment/water extracts (which provide soil pH, electrical conductivity, cation, trace metal, radionuclide and anion data), total carbon and inorganic carbon content, and 8 M nitric acid extracts (which provide a measure of the total leachable sediment content of contaminants). The concentrations of key radionuclides, ^{99}Tc, actinides, fission products (including ^{90}Sr, europium radioisotopes, ruthenium and molybdenum), ^{60}Co, uranium, and other trace metals were determined in acid and water extracts using several techniques, including ICP-MS, gamma energy analysis, liquid scintillation, and alpha spectrometry.

Results for some of the most significant parameters measured in the sediments collected from WMA T boreholes C4104, C4105, and 299-W11-39 are presented in Figures 3.24 through 3.26, respectively, as a function of depth. These include parameters that can have a significant influence on contaminant mobility and can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and indicators of hydrologic control (lithology, statigraphy, and moisture content).

Overall, the analyses of contaminated sediments showed that ion exchange is a key mechanism that influences the distribution of contaminants within that portion of the vadose zone affected by tank liquor. As was the case for vadose zone sediments at the SX and BX Tank Farms, elevated pH values (from 8.6 to almost 10) were observed in samples between the depths of 14.3 to 28.2 m bgs from borehole C4104 at WMA T. No signs of elevated pH were found in the sediments from borehole C4105, which is downgradient from the leak at tank T-106.

The sediments from the three T Tank Farm boreholes (C4104, C4105, and 299-W10-196) do show that sodium-, nitrate-, and sulfate-dominated fluids are present below tank T-106 and have formed a salt plume. The fluids are more dilute than tank fluids observed below tanks at the SX and BX Tank Farms. Most of the chemical data for contaminants intercepted by boreholes C4104, 299-W10-196, and C4105 suggest that fluid leaked from tank T-106 and percolated deeper into the sediments below C4104. More interesting is that the fluids traveled horizontally, within the lower Hanford formation H2 unit and the two Cold Creek Formation units, to the west at least as far as borehole C4105. Other spectral gamma logging data suggest that the tank T-106 leak also migrated east of tank T-106. To the east, the tank T-106 plume is overlain by a small leak from tank T-103. Thus, near tank T-106 there are signs of significant horizontal spreading of the original leak.
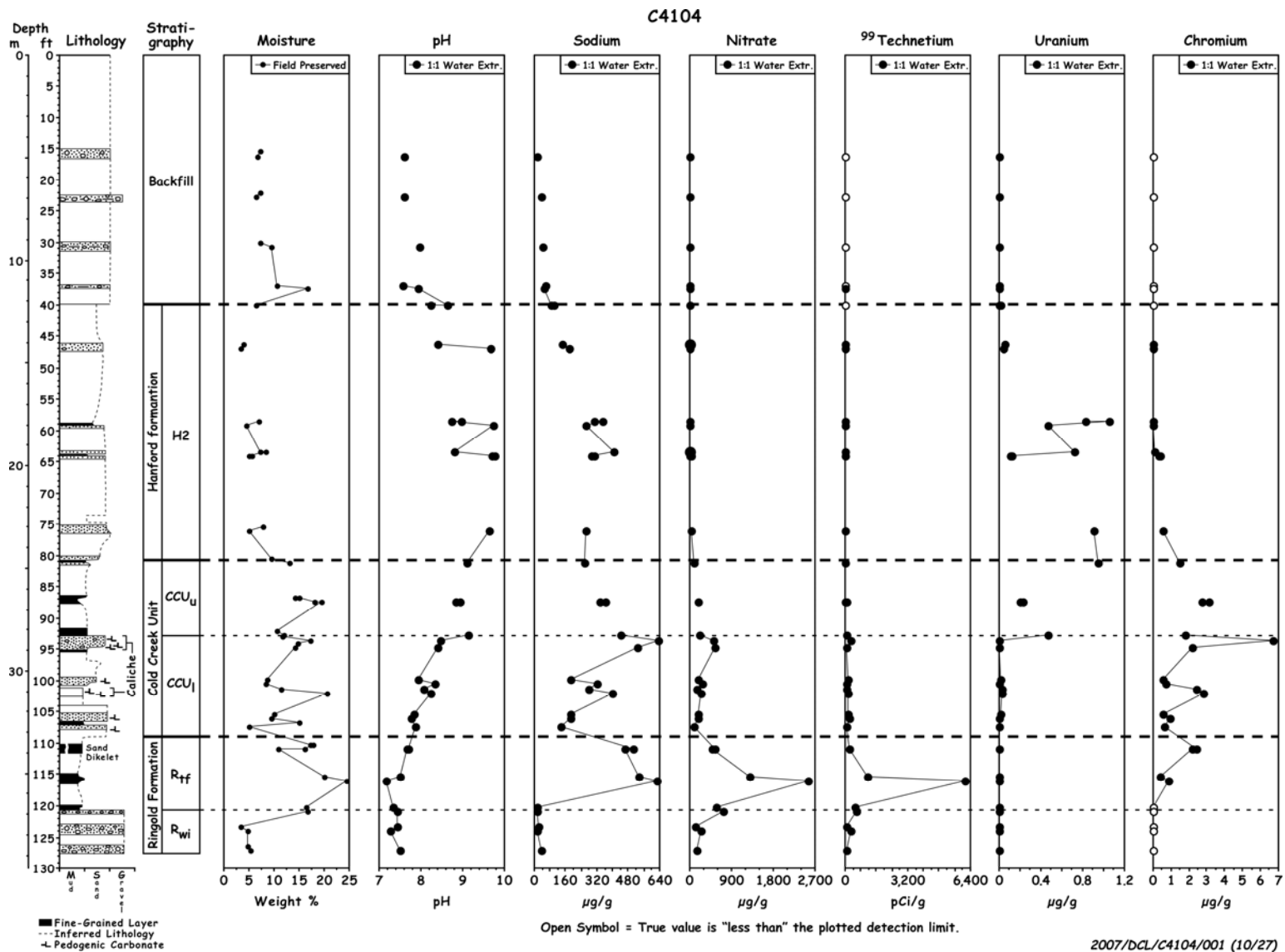
Figure 3.24. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole C4104 Located in Waste Management Area T (Serne et al. 2004b)
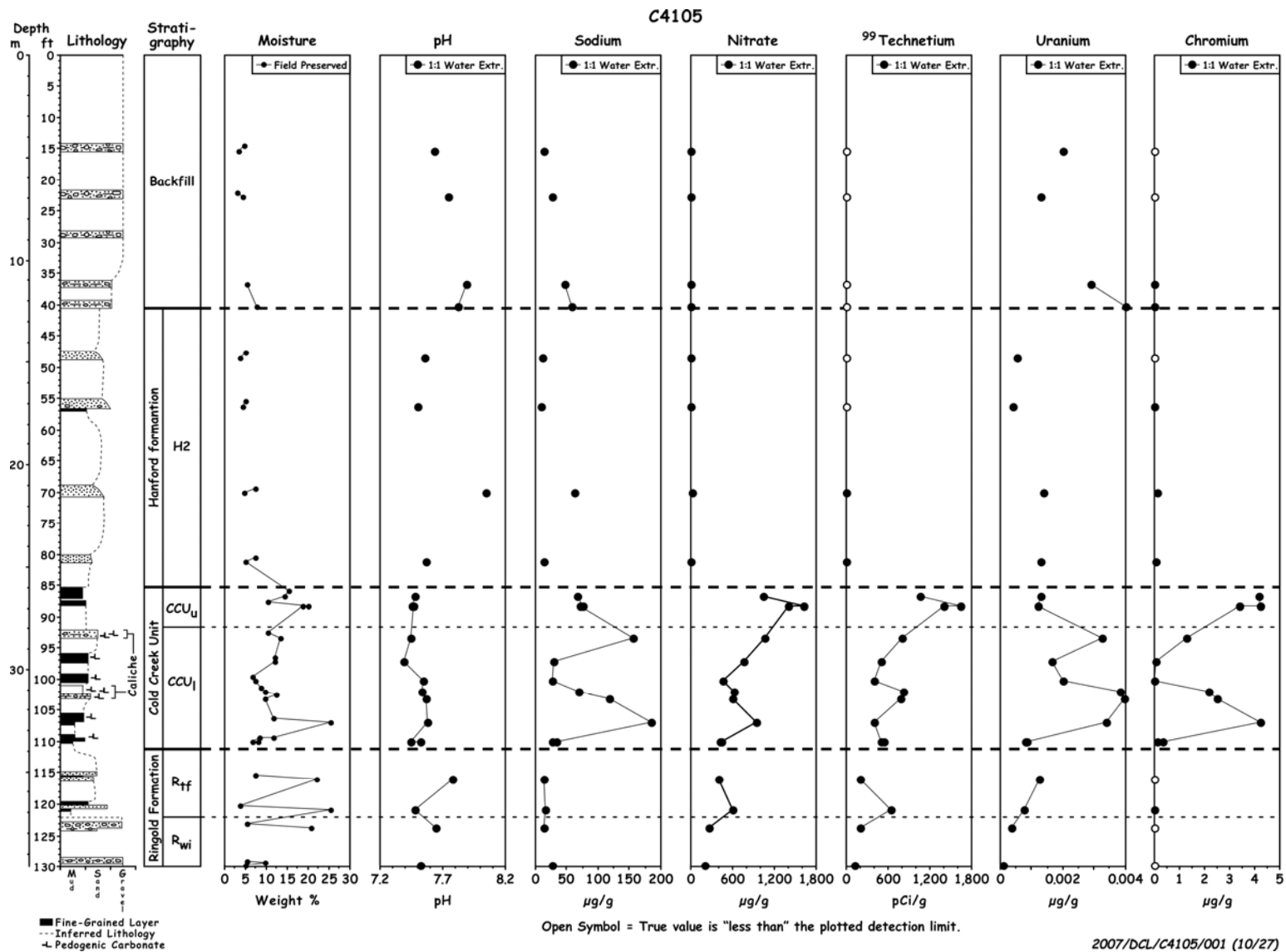
Figure 3.25. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole C4105 Located in the Waste Management Area T (Serne et al. 2004b)

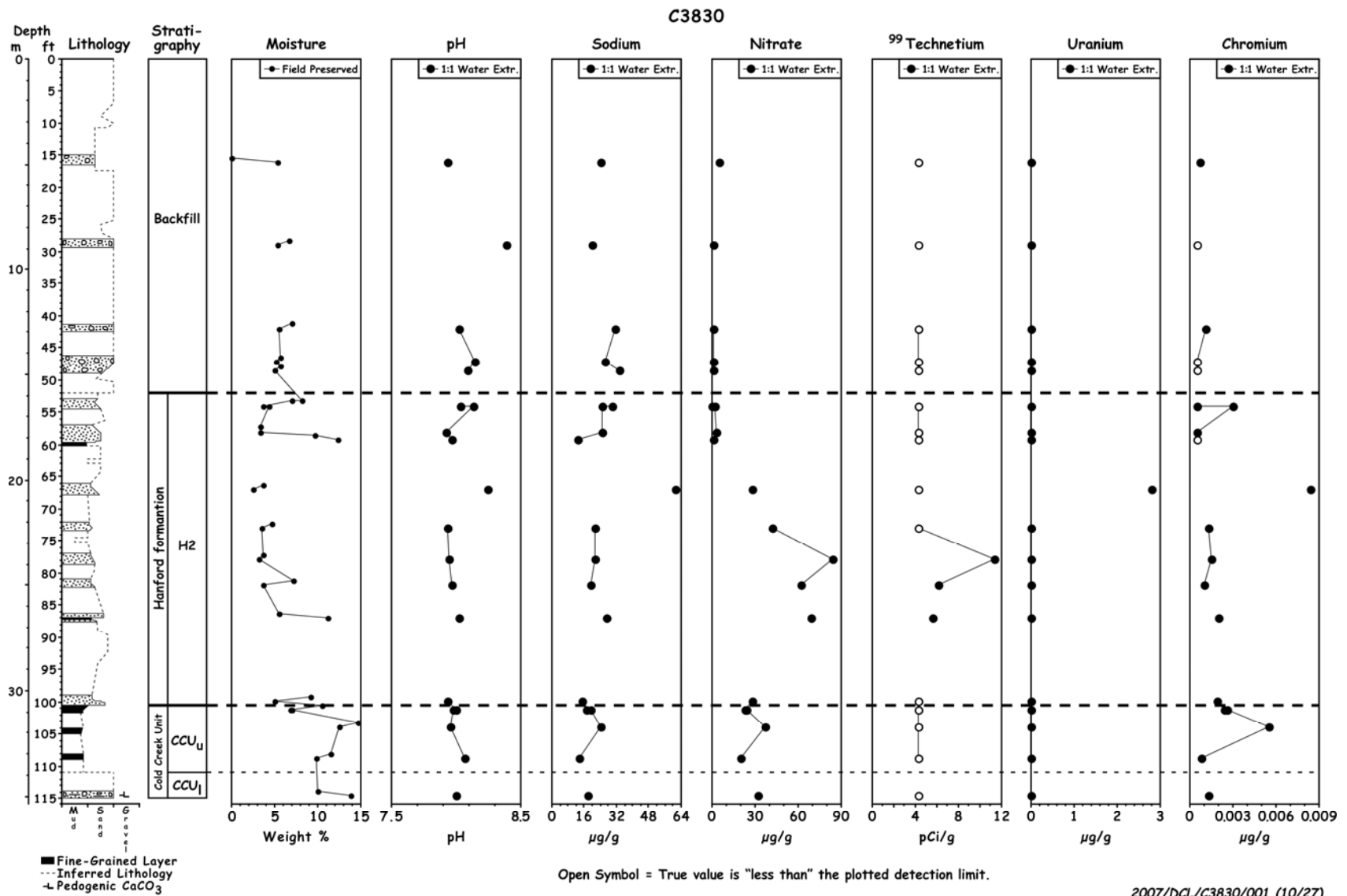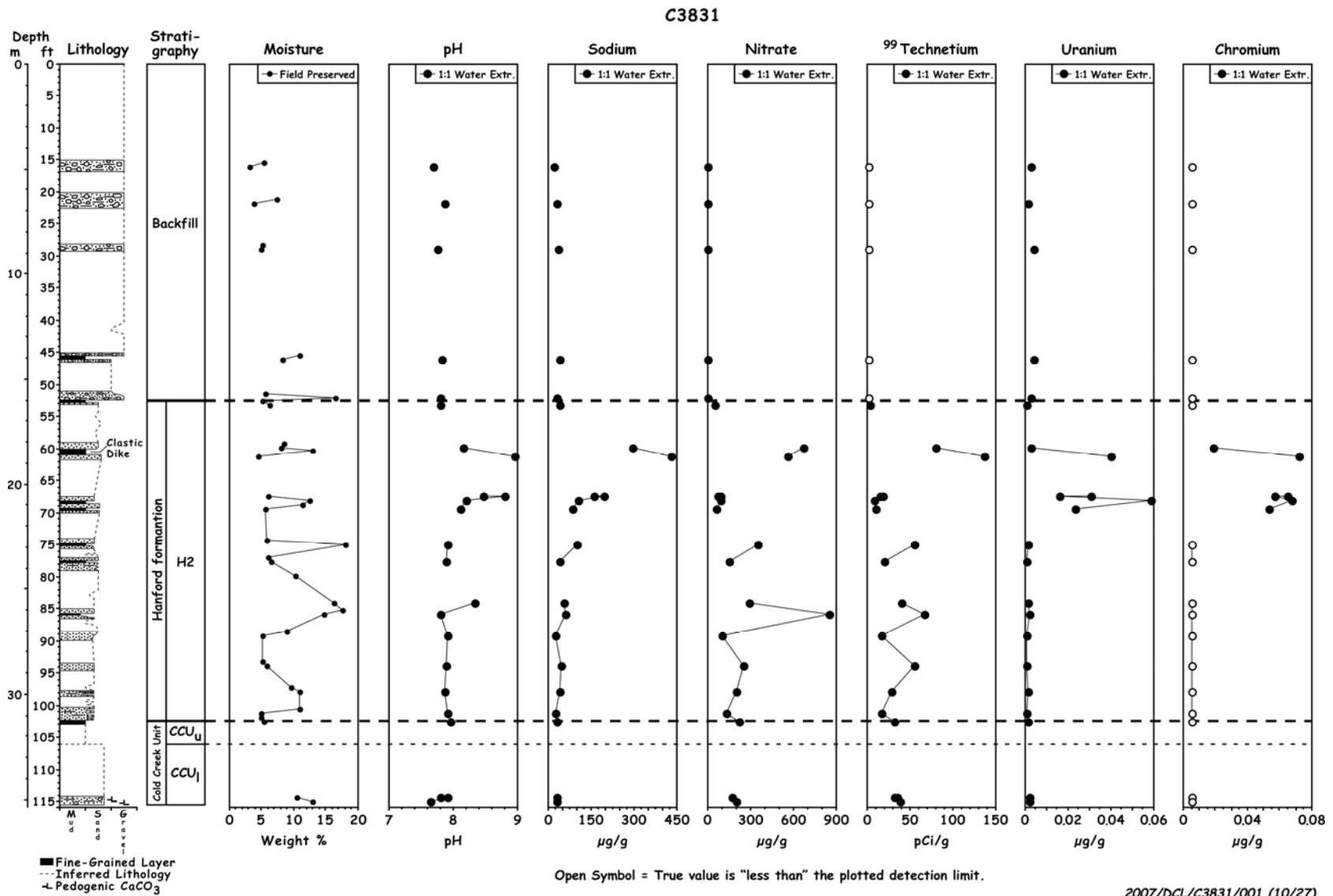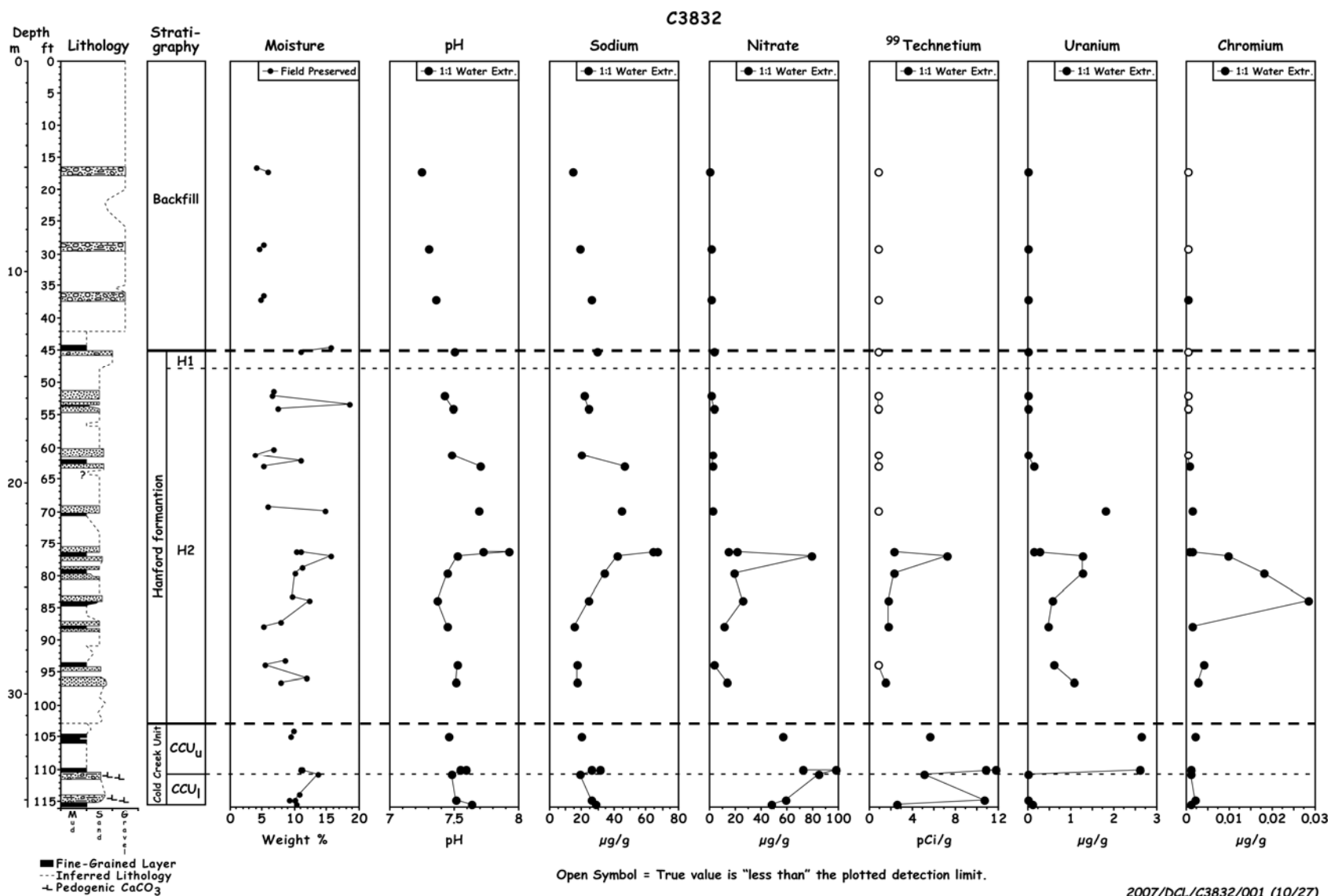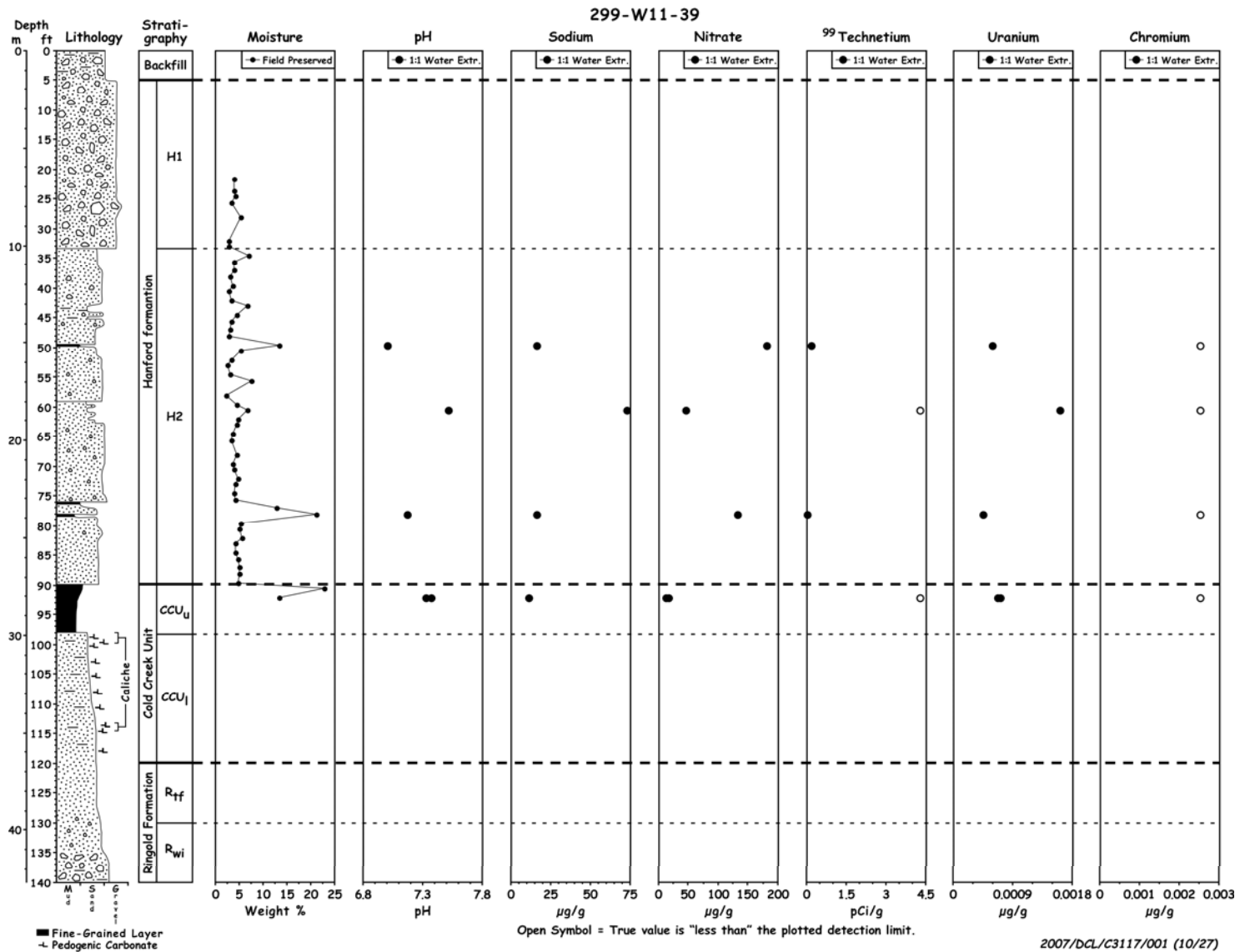**Figure 3.26**. Litho-Stratigraphic Log, Moisture Content and Significant Geochemical Parameters Measured in Sediment Samples from Borehole 299-W11-39 Located in Waste Management Area T (Serne et al. 2004b)

The conceptual model of the borehole geology between core samples (note that sampling was intermittent and collected only ~25% of the sediment profile) is based on interpretation of the geophysical log and blow-count data. Three primary stratigraphic units were encountered in each of the three contaminated boreholes: 1) backfill material, 2) the Hanford formation, and 3) the Cold Creek unit. At C4104, it is inferred that there are at least two separate, relatively thin (≤0.15 m), moderately to well-sorted, silty fine sand beds in the Hanford formation H2 stratigraphic unit. These occur at depths starting at 17.9 and 20 m bgs. Up to four additional fine-grained beds may also be present between cored intervals in the profile at C4104. At C4105, it is inferred that there are at least two fine-grained layers within the Hanford formation H2 unit. These fine-grained layers were encountered at depths of ~17.2 and ~22.9 m bgs. These thin, fine-grained lenses within sands of the Hanford formation H2 unit may impact the flow of leaked fluids and produce irregular and horizontal flow.

Boreholes C4104 and C4105 did not penetrate below the gravel-rich strata of the Ringold Formation Wooded Island member (R_{wi}); refusal was met at about 39.6 m bgs at both holes. Therefore, Serne et al. (2004b) could not identify the maximum vertical penetration of the tank-related plume. However, there is elevated electrical conductivity values in the C4104 borehole sediments from 14.3 m bgs to the bottom of the borehole near 38.7 m. At 14 m bgs, electrical conductivity of the C4104 water extracts and actual pore waters are six times higher than background values and differences reach values of ~40 times larger than background at 35.4 m bgs. The electrical conductivity values for the dilution-corrected (calculated) pore waters between 18.0 and 23.2 m bgs are also quite elevated. The highest values of dilution-corrected pore-water electrical conductivity found at C4104 (33.4 mS/cm at 35.4 m bgs) are equivalent to a pore solution of 0.21 M KCl, the salt solution used to calibrate the conductivity probe. There is also evidence of elevated electrical conductivity starting at 26.4 m bgs to the bottom of the C4105 borehole. The electrical conductivity values for 1:1 sediment/water extracts from the Cold Creek units' sediments at C4105 range from 1.2 to 3.1 mS/cm, which is about 10 to 30 times higher than found in dilution-corrected pore waters from nearby background sediments. The highest values of dilution-corrected pore water electrical conductivity in borehole C4105 occur in two zones, between 26.5 to 33.5 m bgs and at 37.5 m bgs. The dilution-corrected electrical conductivity and actual pore-water values for these two zones are equivalent to a pore solution of 0.10 to 0.175 M KCl. The peak electrical conductivity values for these two T boreholes are lower than the dilution-corrected electrical conductivity maximum at borehole C3831 near tank TX-107, which peaked at 18.4 m bgs with a value equivalent to a pore solution of 0.4 M KCl.

Despite the evidence that elevated electrical conductivity values may be present in both T boreholes to their depth of refusal, the concentrations are not large. For example, the maximum dilution corrected electrical conductivity values at C4104 and C4105 are 33.4 and ~ 19 mS/cm, respectively. The leaks near tanks SX-108, SX-109 and BX-102 had peak vadose zone pore-water concentrations that were much more concentrated waste fluids, 524 to 1774 and 77 mS/cm, respectively.

The inventories of potential COIs (nitrate, ^{99}Tc, uranium, and chromium) as a function of depth are provided in Section 6.6 in Serne et al. (2004b). In addition, in situ desorption K_d values for these contaminants are provided based on the difference between acid (for ^{60}Co direct sediment gamma activities were used) and water extracts of the contaminated sediments.

A ^{99}Tc groundwater plume exists northeast and east of WMA T. The highest ^{99}Tc concentration in fiscal year 2003 was 9,200 pCi/L in well 299-W11-39. The most probable source for the ^{99}Tc is WMA T. Groundwater from wells in the west (up gradient) and north of WMA T appear to be highly influenced by wastes disposed to the cribs and trenches on the west side of the WMA. Groundwater from wells at the

northeast corner and the east side of the WMA appears to be evolving toward tank waste that has leaked from T-101 or T-106. In the vadose zone sediments at boreholes C4104 and C4105, the actual and derived pore waters between the depths of 26.5 to ~39.6 m bgs contain greater than 5×10^5 to 2×10^7 pCi/L ^{99}Tc.

3.6.4 Characterization Results of Direct-Push Vadose Zone Sediments from Waste Management Areas T and TY

Brown et al. (2007b) recently conducted detailed analyses of vadose zone sediment collected by direct-push methods within the T and TY Tank Farms. Specifically, geologic, geochemical, and selected physicochemical characterization data were compiled on vadose zone sediment recovered from direct-push samples collected near tanks TY-105 and TY-106 in the single-shell TY Tank Farm, and near tanks T-101 and T-104 in the single-shell T Tank Farm. Additionally, data collected on interim measures direct-push samples emplaced north of the T Tank Farm were compiled. A total of 13 vadose-zone, cone-penetrometer probe (direct push) holes were drilled in the vicinity of the T and TY Tank Farms for geologic and geochemical characterization. Seven of the holes were drilled in the T Tank Farm (Figure 3.27); the other six were drilled in the TY Tank Farm (Figure 3.28).

The geochemical investigation in the vicinity of tanks TY-105 and TY-106 was performed using direct-push probe holes. A total of 31 direct-pushes were driven within the TY Tank Farm. Twenty five of these holes were logged for moisture, gross gamma, and spectral gamma using calibrated probes; and six were driven for the purpose of retrieving vadose zone sediment for characterization and analysis. The samples were collected around tank TY-105, which was estimated to have leaked 132,000 L (35,000 gal) of tributyl phosphate (TBP) waste (UPR-200-W-152) from the uranium recovery process to the vadose zone in 1960 (Wood et al. 2001), and tank TY-106, which was estimated to have leaked 75,700 L (20,000 gal) of TBP-uranium recovery waste to the vadose zone in 1959 (UPR-W-153).

Additionally, Brown et al. (2007b) presents all the geochemical and selected physical characterization data collected on vadose zone sediment recovered from seven direct-push characterization holes emplaced to investigate vadose zone contamination associated with an overfill event and leak from tank T-101. Deaton (DOE-RL 1992) postulated that a leak from tank T-101 resulted in a loss of 28,390 L (7,500 gal) of tank waste to the subsurface. This event was the basis for placing tank T-101 on the list of assumed/ known leakers. It has been estimated that 1,230 Ci of ^{137}Cs, 0.0434 Ci of ^{60}Co, and 0.382 Ci of ^{99}Tc were lost to the vadose zone as a result of the 1992 leak event (Wood et al. 2001).

A total of 19 probe holes were emplaced around tanks T-101 and T-104. Fourteen of these holes were logged for moisture, gross gamma, and spectral gamma using calibrated probes. A zone or depth of interest was identified for sampling in each probe hole based on neutron moisture logging data. Once an appropriate sampling depth was identified, a second hole was pushed as close as possible to the logged hole for collection of 0.46 m (1.5 ft) of core material at the depth of interest. Due to lack of contaminants found during logging, field limitations, and poor sample recoveries, only five holes were driven for the purpose of collecting samples of vadose zone sediments.

A core log was generated for both sets of samples from the T and TY Tank Farms direct-push campaigns, and a visual geologic evaluation of all liner samples was performed at the time of sample processing. Aliquots of sediment from the liners were analyzed and characterized in the laboratory for the following parameters: moisture content, gamma-emitting radionuclides, 1:1 sediment/water extracts
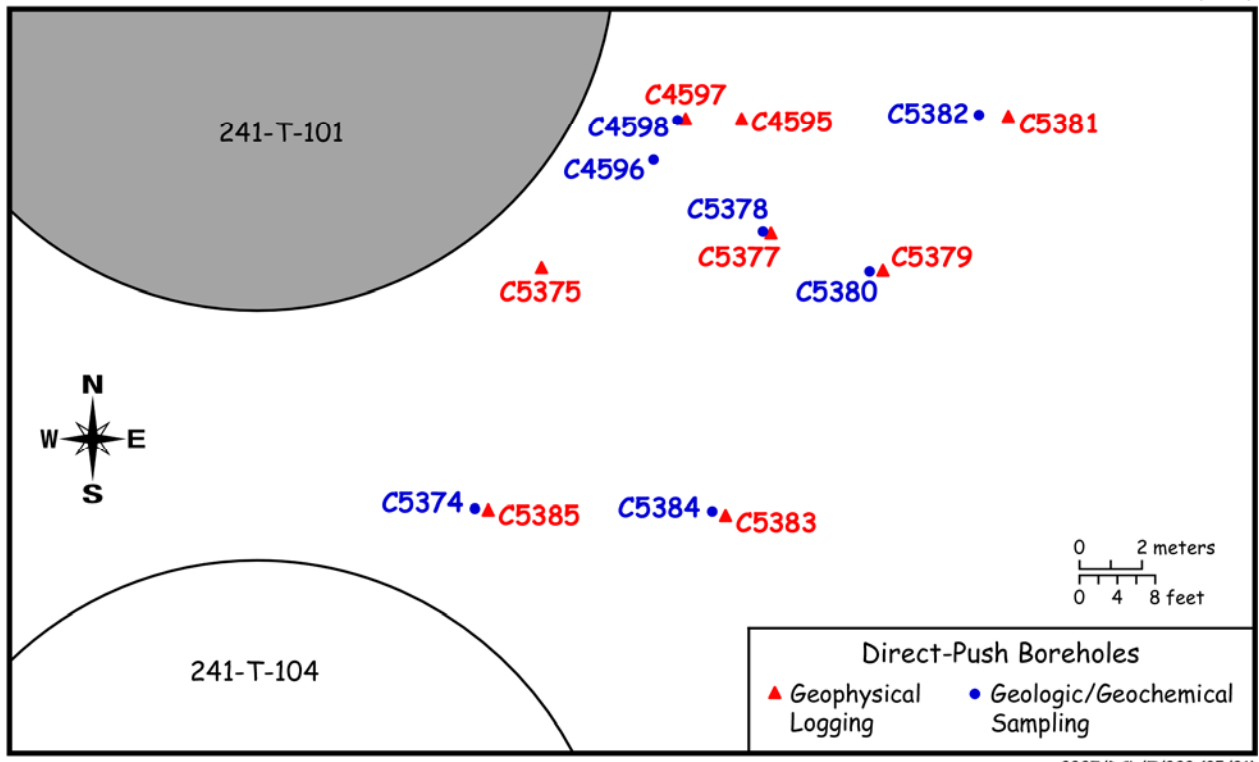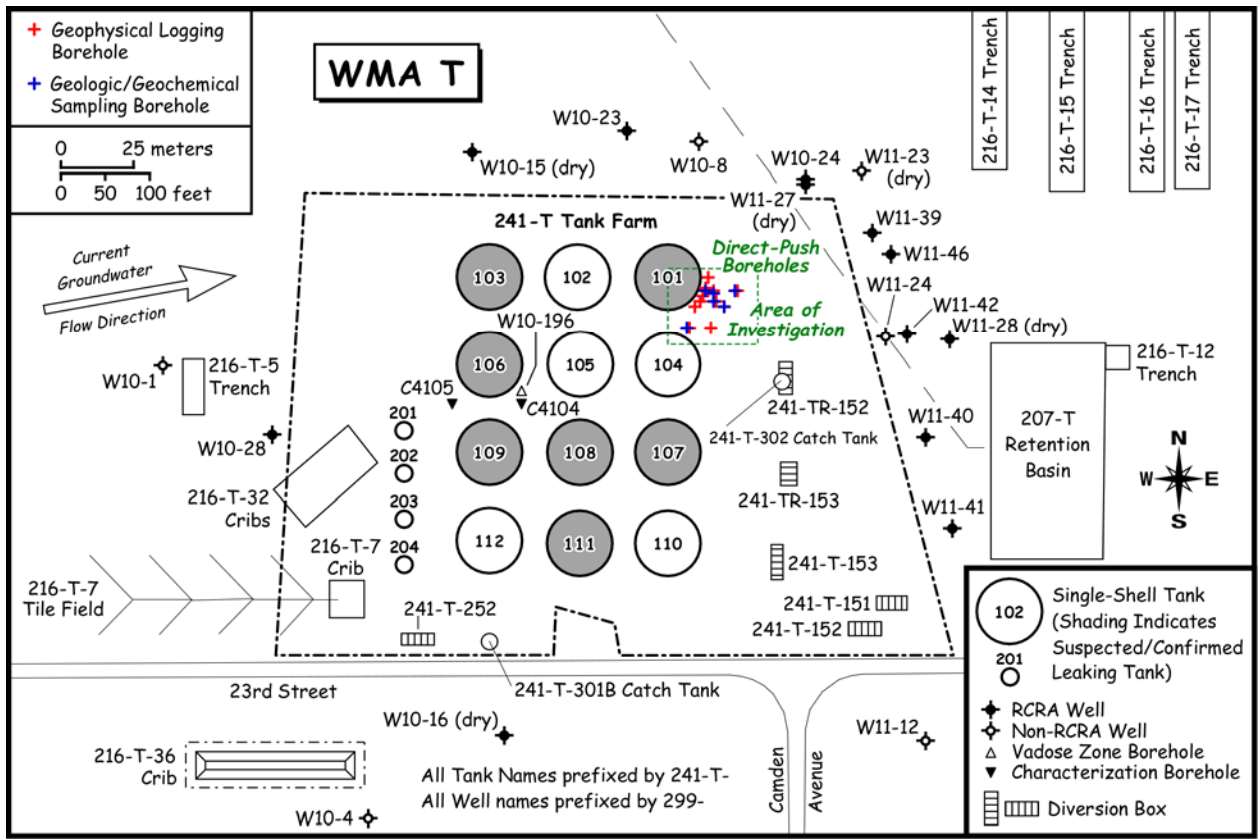
Figure 3.27. Locations of Direct-Push holes in Vicinity of the T Tank Farm

3.79
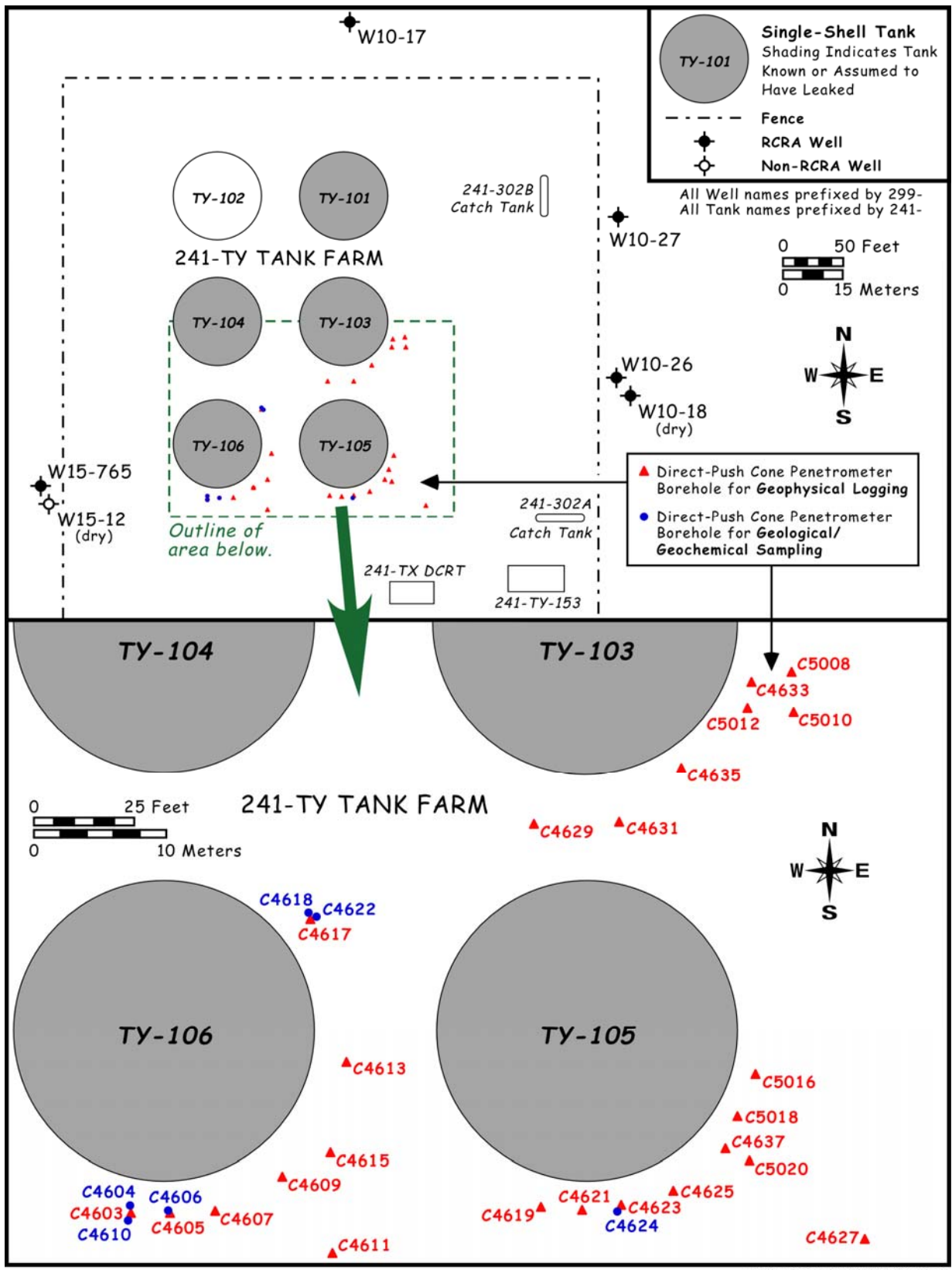
Figure 3.28. Locations of Direct-Push holes in Vicinity of the TY Tank Farm

(which provided soil pH, electrical conductivity, cation, trace metal, and anion data), total carbon and inorganic carbon content, and 8 M nitric acid leaches (which provided a measure of the total leachable contaminant content in the sediment). Two key radioactive contaminants, ^{99}Tc and ^{238}U, along with other trace metals were determined in acid and water extracts using ICP-MS. Some of the most significant parameters measured in the direct-push samples are presented as a function of depth for WMA T in Figure 3.29 and the TY Tank Farm in Figure 3.30. These include parameters that can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and moisture content. All of the parameters were elevated in at least some of the samples analyzed as part of this study.

The distribution of water-extractable major cations in the direct-push sediment samples indicates that an ion-exchange process dominates the pore water/sediment interactions where tank fluid has passed by or currently exists. Depth profiles for the divalent alkaline earth cations (calcium, magnesium, and strontium) versus sodium show significantly elevated sodium and depleted alkaline earth cation concentrations in the shallow Hanford formation sediments at both locations to depths up to 24.4 m (80 ft) bgs (the terminal depth of the deepest samples collected). Conversely, the water-extractable sodium concentrations in these zones were elevated. These trends suggest that tank fluids that are high in sodium are present at these locations. The lack of a significant amount of nitrate in the TY Tank Farm direct-push holes indicates that contamination has been present for a sufficiently long period of time to facilitate the migration of more mobile contaminants (i.e., nitrate and ^{99}Tc) deeper into the vadose zone. The observance of significantly elevated nitrate in the deepest direct-push samples collected as part of the T Tank Farm campaign further support the premise that mobile contaminants reside much deeper in the vadose zone at both of these locations.

After evaluating all the characterization and analytical data, Brown et al. (2007b) concluded that the vadose zone surrounding tank TY-106 was contaminated by tank-related waste. The elevated soil pH values and ^{137}Cs concentrations measured in close proximity to tank TY-106 indicate that the tank or infrastructure associated with the tank is responsible for the contamination. The poor recovery associated with the direct-push technique made it difficult to estimate the lateral spread of contamination. Moreover, the nature of the direct-push technique made it impossible to assess the vertical extent of the contamination. However, based on characterization of the three probe holes that were emplaced south of tank TY-106, it does not appear that a significant amount of lateral contaminant migration has occurred at the depth sampled. Interpretation of the water extract data associated with these samples indicates that the mobile constituents associated with this leak event reside deeper in the vadose zone at this location. However, the lack of depth discrete samples does not enable confirmation of this hypothesis.

The vadose zone south of tank TY-105 has also been affected by a tank-related waste solution. The presence of sodium as the dominant water-extractable cation indicates that a high sodium-bearing waste stream has created a cation exchange front in this region that has pushed the prominent divalent cations (calcium and magnesium) off the surface exchange sites of minerals in these sediment samples. The lack of elevated soil pH values or direct measurement of gamma-emitting radionuclides indicates that the point source of contamination is not in the direct vicinity of the only sample probe hole emplaced near tank TY-105. The lack of direct evidence of a point source waste signature near tank TY-105 does not mean the tank did not leak. Rather, the vadose zone sample set collected as part of this investigation by Brown et al. (2007b) was not sufficient to either confirm or refute the supposition that a leak from tank TY-105 led to UPR 200-W-152.
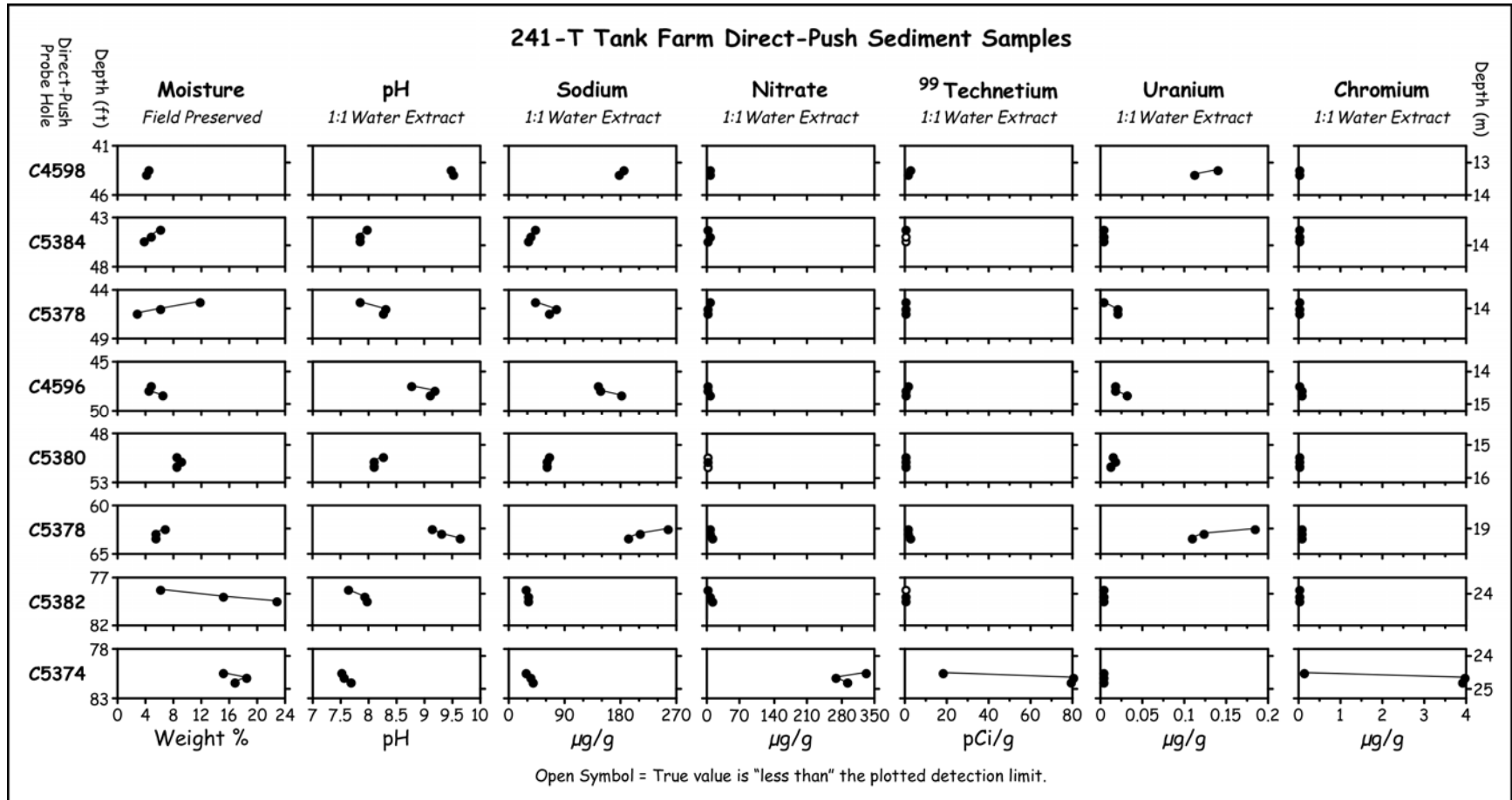
Figure 3.29. Moisture Content and Significant Geochemical Parameters Measured in Direct-Push Sediment Samples Collected from the T Tank Farm (Brown et al. 2007b)
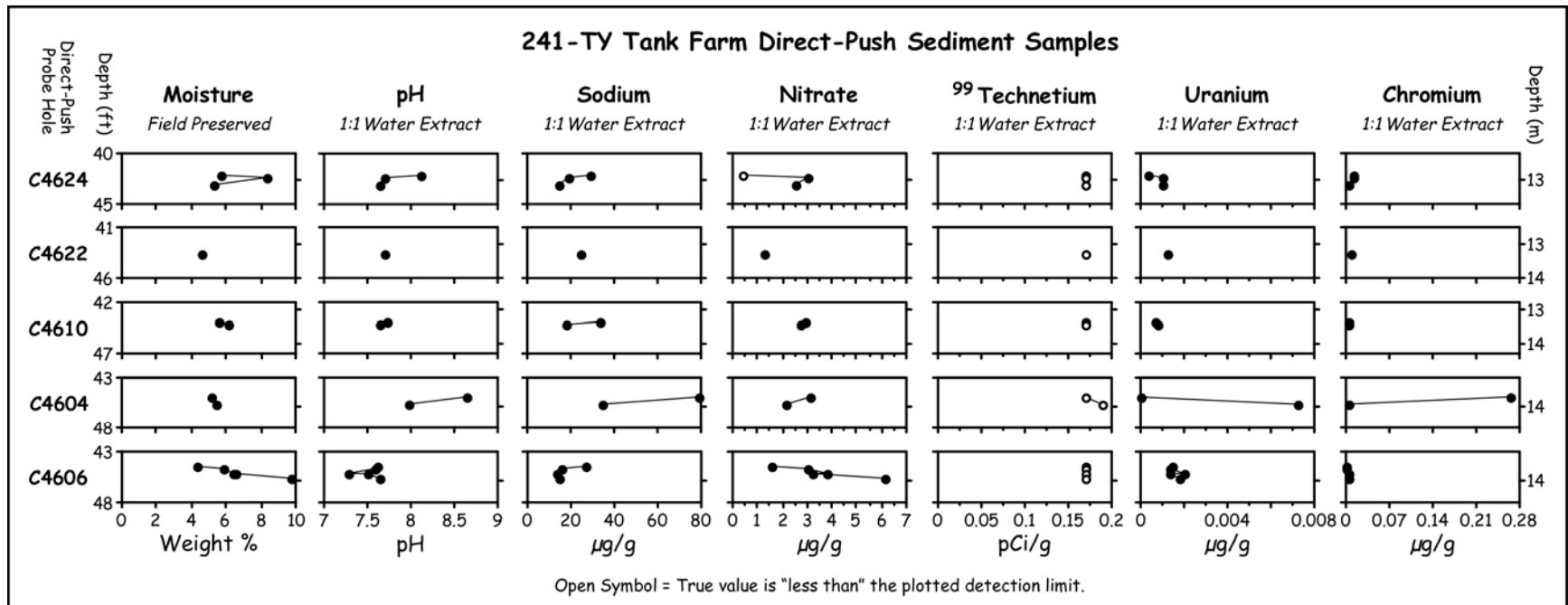
Figure 3.30. Moisture Content and Significant Geochemical Parameters Measured in Direct-Push Sediment Samples Collected from the TY Tank Farm (Brown et al. 2007b)

After evaluating all the characterization and analytical data associated with the T Tank Farm direct-push campaign, Brown et al. (2007b) concluded that the vadose zone in the vicinity of tank T-101 has been contaminated by tank-related waste. The measurements of elevated soil pH values; pore water corrected electrical conductivity values; elevated concentrations of nitrate, ^{99}Tc, elevated water-extractable sodium, and fission product isotopes of europium and ^{137}Cs in close proximity to tank T-101 indicates that the tank or its associated infrastructure is responsible for the contamination. The sparse sample coverage associated with the direct-push technique made it difficult for Brown et al. (2007b) to estimate the lateral spread of contamination, while the nature of the direct-push technique made it impossible for them to assess the vertical extent of contamination. However, based on characterization of the probe holes that were emplaced to the southeast of tank T-101, Brown et al. (2007b) determined that waste from tank T-101 migrated laterally several meters away from the tank. Interpretation of the water extract data associated with these samples indicates that the mobile constituents associated with this leak event reside deeper in the vadose zone at this location. However, Brown et al. (2007b) could not confirm this hypothesis due to the lack of samples from discrete depths.

The vadose zone directly northeast of tank T-104 also was found to be contaminated with tank waste constituents. It is not possible at this time to directly attribute the source of this contamination to a particular tank. Sufficient data do not exist to determine if the contamination observed in this region is a result of a loss from tank T-104 or if it is a result of lateral spreading of waste from tank T-101 (Brown et al. 2007b).

3.6.5 Estimated K_d Values for Key Contaminants at Waste Management Area T-TX-TY

Table 3.15 lists the current known or estimated dates of releases, volume of fluid released and type of fluid released for tanks in WMAs TX-TY and T. Besides the largest known volume release of 435,000 L from T-106, tanks T-101 (38,000 L) and TX-107 (30,000 L) represent significant releases of liquid to the vadose zone. The chemical compositions of the fluids that leaked from WMAs T and TX-TY are shown in Table 3.16. All the waste streams are multi-molar in sodium and dominated by the anions nitrate, nitrite, sulfate and free hydroxide. The waste streams leaked from T-106 are ~4 M in sodium balanced with the anions nitrate, nitrite, free hydroxide, aluminate, carbonate, and sulfate. The waste fluids also contain significant amounts of dissolved organics such as glycolate, hydroxyethylethylenediaminetriacetate acid (HEDTA), EDTA, and dibutylphosphate. The HEDTA and EDTA are known to be strong complexing agents of metal radionuclides that under certain circumstances can enhance their mobility (Serne et al. 2002g). The waste streams present in T-101 at the time it released fluids to the vadose zone mixed to form a similar ~4 M sodium solution with similar anions but less carbonate and sulfate and more aluminate. The T-101 waste stream mix also did not contain dissolved organics. The waste stream present in tank TX-107 at the time it released fluids was very highly concentrated in sodium (~10 M) with high nitrate, nitrite, aluminate, free hydroxide, and significant amounts of carbonate, sulfate, chloride, fluoride, dissolved organics, and some phosphate.

Table 3.17 lists K_d values based on field derived, in situ, desorption K_d values, when available for key mobile contaminants found in the contaminated sediments from the T and TX Tank Farms, and generic Hanford relevant K_d values for other potential contaminants. The very low desorption in situ K_d values for ^{60}Co shown in Table 3.17 likely reflect the impact of organic chelates present in the wastes released from both T-106 and TX-107. K_d values for un-impacted sediments are provided in Table 3.4.

Table 3.15. Waste Management Area T-TX-TY Leak Event Locations, Times, and Volumes (from Field and Jones 2005)

Site	Year of Release	Site Description--Principal Wastes	Total Volume (L)
241-T-101	1969	Zero solids. Unadjusted SMM definition for tank-leak date of 1969. Mixture of [CWR1], [CWR2], and [R2].	3.79E+04
`241-T-103	1973	Zero solids. Unadjusted SMM definition for tank-leak date of 1973. Mixture of Sr-Cs Rec Org Wst [CSR], [CWP2], and Sr-Cs Rec Org Wst aqu [BL].	1.14E+04
241-T-106	1973	Zero solids. Unadjusted SMM definition for tank-leak date of 1973. Sr-Cs Rec Org Wst [CSR] and Sr-Cs Rec Org Wst aqu [BL]	4.35E+05
241-T-108	1957	After review of WSTRS level/transfer records for 241-T-108 (Agnew et al. 1997b), there is a period around 1957 where the tank has no traffic activity but shows a level loss. Later in the tank process history the level rebounds. Assigning the waste composition from that date is more in keeping with the available observations than the 1970s era designation. That is to say, 3,800 L (1,000 gal) of the earlier wastes are going to be lower in contemporary Cs-137 activity than a loss of higher activity BL/IX wastes in the tank during the 1970s. Thus, the SMM date assignment in SIM for that leak does not align with tank farms convention. Mixture of [TBP and 1C1].	3.79E+03
241-T-109	1974	Zero solids. Unadjusted SMM definition for tank-leak date of 1974. Mixture of Sr-Cs Rec Org Wst [CSR, 1C Evap, and T2-SltCk]	3.79E+03
241-T-111	1971	Zero solids. Unadjusted SMM definition for tank-leak date of 1971. Mixture of [2C2 and PUREX P2']	3.79E+03
241-TX-107	1977	Zero solids. Unadjusted SMM definition for tank-leak date of 1977. [T2-SltCk]	3.03E+04
241-TY-101	1973	Zero solids. Unadjusted SMM definition for tank-leak date of 1973. Mixture of [T2-SltCk, TBP, and R2]	3.79E+03
241-TY-103	1971	Zero solids. Unadjusted SMM definition for tank-leak date of 1971. [T2-SltCk]	1.14E+04
241-TY-104	1953	In the case of 241-TY-104, the date initially presented is 1981, the date that the tank went on the leaker list. There are some slight level fluctuations observed for this tank, but it seems to remain at the same level as it was when the tank was closed. After review of WSTRS level/transfer records for 241-TY-104 (Agnew et al. 1997), there is evidence that the leak is a near surface leak. In 1953, there was a substantial potential overfilling of the tank indicated. The waste transfer records note that this tank was "Filled approx 1 1/3 ft above normal capacity during this time." Thus, for the SMM-designation date in SIM, 1953 was chosen over the tank farms indicated date of 1981. [TBP]	5.30E+03
241-TY-105	1957	Zero solids. Unadjusted SMM definition for tank-leak date of 1957. [TBP]	1.32E+05
241-TY-106	1959	Zero solids. Unadjusted SMM definition for tank-leak date of 1959. [TBP]	7.57E+04
SMM = Supernatant mixing model. WSTRS = Waste Status and Transaction Record Summary.			

Table 3.16. Chemical Composition of Waste Fluids Present in Tanks in Waste Management Areas T and TX-TY at Time of Releases (from Corbin et al. 2005)

Waste Type	Concentration (mol/L)										
	CWR1	CWR2	R2	CSR	CWP2	BL	TBP/UR	1C1	T2-SltCk	2C2	P2'
Na^+	3.73	1.83	5.54	4.15	1.62	3.67	4.04	2.49	10.6	1.3	1.17
Ca^{2+}	0.0038	0.0035	0.0038	0.0038	0.0037	0.01	0.0038	0.0038	0.0038	0.0038	0.0037
K^+	0.0023	0	0.0202	0.021	0.0025	0.015	0.016	1.00E-02	0.0661	0.0044	0.006
Sr^{2+}	1.46E-07	2.49E-07	5.50E-07	5.30E-07	1.33E-07	1.50E-05	6.33E-07	7.00E-08	5.34E-07	1.53E-09	5.00E-07
NH_4^+	1.87E-04	4.45E-05	0.0367	0.025	1.80E-05	6.55E-04	4.08E-04	1.17E-01	0.119	1.12E-10	0.031
Cr	0.0031	0.0031	0.055	0.032	0.003	2.00E-07	0.0032	0.0069	0.0554	5.88E-03	0.008
Mn	0	0	0	3.24E-04	0	0	0	0	5.36E-04	0.00E+00	0
Fe	0.0019	0.0019	0.00187	0.0019	0.0018	0.017	0.0019	0.0019	0.0019	0.0019	0.0018
Ni	1.56E-03	0.0015	0.0018	0.0018	0.0015	0.01	0.0016	1.70E-03	0.0018	0.0016	0.0018
Bi	0	0	0	5.10E-06	0	0	1.80E-04	4.60E-04	2.97E-04	4.60E-04	0
NO_3^-	0.902	0.886	1.3	1.25	0.69	0.772	2.99	1.74	3.5	0.81	0.12
NO_2^-	1.44	0.288	1.41	0.86	0.28	0.117	0.162	0.067	1.79	4.35E-05	0.615
CO_3^{2-}	0.0038	0.0037	0.0038	0.184	0.004	0.271	0.188	0.0038	0.385	0.0038	0.004
PO_4^{3-}	0	0	0	0.0065	0	0.01	0.071	0.071	0.063	0.071	0
SO_4^{2-}	9.43E-03	0.0061	0.0303	0.094	0.007	0.044	0.124	0.074	0.124	0.0317	0.124
Cl^-	0.011	0.016	0.093	0.07	0.012	0.069	0.097	0.046	0.236	0.02	0.026
F^-	0	0	0	0.0016	0	0	0	0.198	0.126	0.138	0
OH^-	0.018	0.02	1.77	0.994	0.019	0.043	0.0023	0.1	2.13	0.0702	0.185
$Al(OH)_4^-$	1.34	0.629	0.994	0.385	0.629	0.261	0	0	1.4	0	0
Organics	0	0	0	0.07	0	0.7	6.20E-05	0	0.448	0	0

Table 3.17. K_d Values for Impacted Sediments at Waste Management Areas T and TX-TY (K_d units are mL/g)

	Sand-Size Sediments						Silt-Size Sediments						Carbonate Dominated Sediments					
	High Impact			Intermediate Impact			High Impact			Intermediate Impact			High Impact			Intermediate Impact		
	Best	Min	Max	Best	Min	Max	Best	Min	Max	Best	Min	Max	Best	Min	Max	Best	Min	Max
Chemicals																		
F⁻	0	0	0	0	0	1	0	0	0	0.05	0	1	0	0	1	0.05	0	1
Cr(VI)	0.2	0	3	0	0	8	0.4	0	8	0	0	10	0.2	0	3	0	0	8
Hg(II)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_3^-, NO_2^-	0	0	0	0	0	0.1	0	0	0	0	0	0.1	0	0	0.1	0	0	0.1
Pb(II)	3	0	10	10	3	100	0	0	30	30	10	300	3	0	10	10	3	100
U(VI) – all isotopes	0.2	0.06	0.6	0.8	0.2	17	0.3	0	3	2.5	0.6	15	0.3	0	30	2.5	0.6	30
Radionuclides																		
²⁴¹Am(III)	3	0	50	600	200	2000	10	0	150	600	200	2000	10	0	150	600	200	2000
¹⁴C	5	0	50	1	0	100	5	0	50	1	0	100	5	0	50	1	0	100
⁶⁰Co(II,III)	0	0	10	0	0	10	0	0	30	0	0	30	0	0	30	0	0	30
¹³⁷Cs	1	0	10	100	10	1000	1	0	30	100	30	3000	1	0	10	100	10	1000
Eu(III) – all isotopes	1	0	10	10	3	100	3	0	30	30	10	300	3	0	30	30	10	300
³H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
¹²⁹I	0	0	0.2	0.2	0	2	0	0	0	0.2	0	2	0	0	0	0.2	0	2
⁶³Ni(II)	0	0	10	3	1	20	0	0	30	10	3	60	0	0	30	10	3	60
²³⁷Np(V)	0	0	5	10	2	30	0	0	15	10	2	50	0	0	15	10	2	50
Pu – all isotopes	3	0	50	600	200	2000	5	0	150	600	200	2000	3	0	50	600	200	2000
²²⁶Ra(II)	1	0.2	20	10	5	20	3	0.6	60	10	5	60	3	0.6	60	10	5	60
⁷⁹Se(VI,IV)	0	0	3	0.1	0	3	0	0	3	0.3	0	10	0	0	3	0.1	0	3
¹²⁶Sn(IV)	0	0	10	0.5	0	20	0	0	30	1.5	0	60	0	0	30	1.5	0	60
⁹⁰Sr	1	0.2	20	10	5	20	3	0.6	60	10	5	100	3	0.6	60	10	5	100
⁹⁹Tc(VII)	0	0	1	0	0	1	0	0	1	0	0	0.3	0	0	1	0	0	1

For gravel-size sediments, modify sand-size K_d values using Equations (2.3) and (2.4) in Section 2.4.
See Appendix A for references and selection rationale.

3.7 Waste Management Area U

WMA U is located on the Hanford Site in the south central portion of the 200 West Area between WMA S-SX to the south and WMAs T and TX-TY to the north. A map showing the location of the tanks and direct-push holes is shown in Figure 3.31. As of November 2007, the only detailed investigation of vadose zone sediment collected within the U Single-Shell Tank Farm is the study by Brown et al. (2007d) of sediment samples from 10 direct-push characterization holes. The purpose of their study was to investigate vadose zone contamination associated with potential leaks within the U Single-Shell Tank Farm.
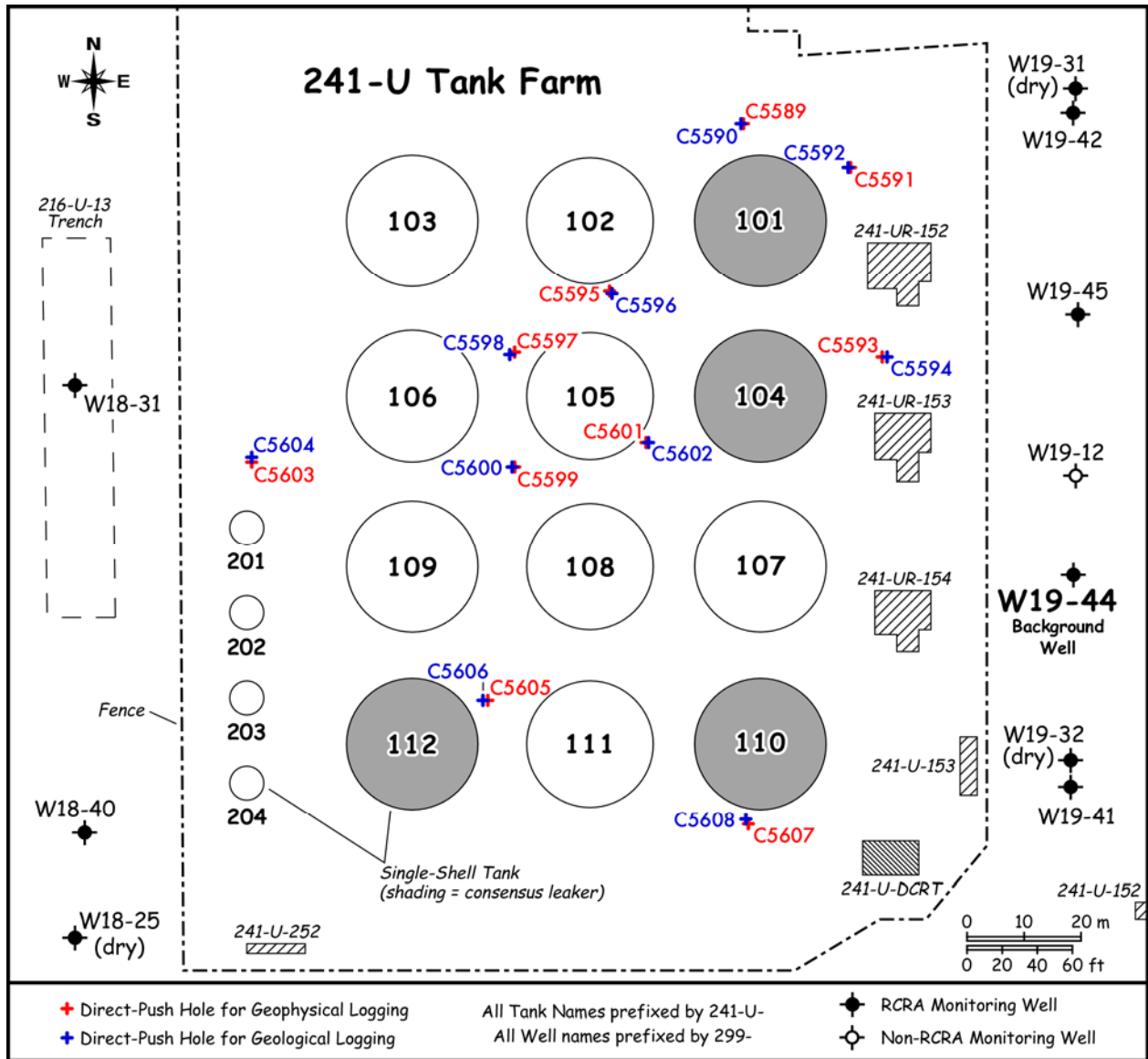
Figure 3.31. Location of Tanks and Direct-Push Holes in Vicinity of the U Tank Farm

3.7.1 Brief Description of Geology of the U Tank Farm

The geology of WMA U is well understood and has been described in several reports. These reports include Price and Fecht (1976l), Hodges and Chou (2000), Smith et al. (2001), and Lindsey (1991, 1995). The material presented in this section was excerpted from the SST WMA geology data package by Reidel and Chamness (2007). Geologic characterization of WMA U is based principally on borehole logs (i.e., geologic and drillers' logs) from 25 boreholes near the tank farm. The logs describe the physical and chemical characteristics of the subsurface system and include data such as grain-size distribution, calcium carbonate content, and moisture content. Interpretation is based also on existing reports that describe the regional, Hanford Site, 200 Areas, and local geology. The statigraphic terminology and unit thickness for the U Tank Farm is shown in Table 3.18 taken from Reidel and Chamness (2007).

3.7.2 Characterization Results of Direct-Push Vadose Zone Sediments from the U Waste Management Areas

Brown et al. (2007d) performed detailed analyses of vadose zone sediment collected within the U Single-Shell Tank Farm. Geochemical and selected physical characterization data were collected on vadose zone sediment recovered from ten direct-push characterization holes emplaced to investigate vadose zone contamination associated with potential leaks within the tank farm. Specific tanks targeted during this characterization campaign included tanks U-104/U-105, U-110, and U-112. Additionally, Brown et al. (2007d) produced data from direct-push samples collected north of tank U-201, as well as sediment collected from the background borehole (C3393).

The U Tank Farm geochemical investigation was performed using pairs of direct-push probe holes. A total of twenty direct-pushes were driven within the U Tank Farm. Ten of these holes were logged for moisture, gross gamma, and in some cases spectral gamma using calibrated probes and ten were driven for the purpose of retrieving vadose zone sediment for characterization and analysis. The locations of the direct pushes were chosen to investigate an estimated 189,000 L (50,000 gal) leak of bismuth phosphate metals waste from tank U-104, small leaks of REDOX supernatant from tanks U-110 and U-112, a 114,000-L (30,000-gal) leak of high-level waste from tank U-101, and a resistivity anomaly near the U Tank Farm 200 series tanks.

A core log was generated for all samples and a visual geologic evaluation of all liner samples was performed at the time of sample processing. Aliquots of sediment from the liners were analyzed and characterized in the laboratory for the following parameters: moisture content, gamma-emitting radionuclides, 1:1 sediment/water extracts (which provided soil pH, electrical conductivity, cation, trace metal, and anion data), total carbon and inorganic carbon content, and 8 M nitric acid leaches (which provided a measure of the total leachable contaminant content in the sediment). Two key radioactive contaminants, ^{99}Tc and ^{238}U, along with other trace metals, were determined in acid and water extracts using ICP-MS. Some of the most significant parameters measured in the U Tank Farm direct-push samples are presented in Figure 3.32 as a function of depth. These include parameters that can serve as tank waste indicators (pH, sodium and nitrate), important tank waste COIs (^{99}Tc, uranium, and chromium), and moisture content. All of the parameters were elevated in at least some of the samples analyzed as part of this study.

Table 3.18. Stratigraphy of Sediments at Waste Management Area U (from Reidel and Chamness 2007)

Stratigraphic Symbol	Formation	Facies/Subunit	Description	Thickness(a)
Backfill	NA	Backfill – Anthropogenic	Gravel-dominated consisting of poorly to moderately sorted cobbles, pebbles, and coarse to medium sand with some silt derived from coarse-grained Hanford formation (H1 unit) excavated around tanks (Price and Fecht 1976l, Wood et al. 2001); occasional layers of sand to silty sand occur near the base of the backfill sequence.	12 m
H1	Hanford formation	Unit H1 – (Gravel-dominated facies association). Cataclysmic flood deposits (high-energy)	Gravel-dominated flood sequence; composed of mostly poorly-sorted, basaltic, sandy gravel to silty sandy gravel. Equivalent to the upper gravel sequence discussed by Last et al. (1989), the Q_{fg} documented by Reidel and Fecht (1994), Hanford Gravel Unit A of Johnson et al. (1999), coarse-grained sequence (H1 unit) of Wood et al. (2001) and gravel facies of unit H1 of Lindsey et al. (2001b), and gravel-dominated facies association of DOE-RL (2002).	2 – 7 m
H2		Unit H2 – (Sand-dominated facies association). Cataclysmic flood deposits (moderate energy)	Sand-dominated flood sequence; composed of mostly horizontal to tabular cross-bedded sand to gravelly sand. Some sand beds capped with thin layers of silty sand to sandy silt. Equivalent to Hanford Sands of Johnson et al. (1999), Fine-Grained Sequence (H2 unit) of Wood et al. (2001) and unit H2 of Lindsey et al. (2001a), the sandy sequence of Last et al. (1989), and to Q_{fs} documented by Reidel and Fecht (1994) and sand-dominated facies association of DOE-RL (2002).	24 m
Hf/CCU	Undifferentiated Hanford formation and Cold Creek unit	NA	Silty sequence. Similar to Cold Creek unit but distinguished by having a lower natural gamma response.	4 – 8 m
CCU_u	Cold Creek unit	Upper subunit post-Ringold Formation eolian and/or overbank alluvial deposits	Silty sequence; consisting of interstratified well-sorted silt and fine sand. Uncemented but may be moderately to strongly calcareous from detrital $CaCO_3$. Equivalent to the "early Palouse soil" (Tallman et al. 1979, DOE 1988, DOE-GJO 1997) and the Hf/PP deposits of Wood et al. (2001). Also equivalent to the upper Plio-Pleistocene unit in Lindsey et al. (2001b) and the fine-grained, laminated to massive lithofacies of the Cold Creek unit DOE-RL (2002).	3 – 6 m

Table 3.18. (contd)

Stratigraphic Symbol	Formation	Facies/Subunit	Description	Thickness(a)
CCU$_l$		Lower subunit calcic paleosols developed on eroded Ringold Formation or post-Ringold Formation eolian and/or fluvial deposits	Calcic paleosol sequence; consisting of interbedded layers of pedogenically altered to unaltered gravel, sand, silt, and/or clay, cemented together with one or more layers of secondary CaCO$_3$, originally referred to as "caliche" (Brown 1959). Since then the name has evolved from the Plio-Pleistocene unit (DOE 1988, DOE-GJO 1997, Slate 2000), the Plio-Pleistocene calcrete facies (DOE 1988, Wood et al. 2001), the lower Plio-Pleistocene unit (Lindsey et al. 2001b), and the coarse- to fine-grained, CaCO$_3$-cemented lithofacies of the Cold Creek unit (DOE-RL 2002).	1 – 2 m
R$_{tf}$		Member of Taylor Flat Ancestral Columbia River System fluvial channel, crevasse splay, and overbank deposits	Fine-grained Ringold Formation sequence consisting of interstratified, well-bedded fine to coarse sand to silt. Equivalent to the upper Ringold Formation unit (DOE 1988).	Absent
R$_{wi}$	Ringold Formation	Member of Wooded Island Ancestral Columbia River System braided-stream deposits	Coarse-grained Ringold Formation sequence, consisting of mostly moderately sorted, quartzitic sandy gravel to silty sandy gravel. Equivalent to middle Ringold Formation unit (DOE 1988) and the Ringold Formation unit E gravels (Wood et al. 2001, Lindsey et al. 2001b). Well-stratified clay and interbedded silt and silty sand is equivalent to the lower mud Ringold Formation unit (DOE 1988). Fluvial gravels with intercalated sands are equivalent to the basal Ringold Formation unit (DOE 1988) and the Ringold Formation unit A gravels (Wood et al. 2001, Lindsey et al. 2001b).	Unit E: 90 m; LM: 15 m; Unit A: 30 m

(a) Multiply by 3.281 to convert meters to feet.
CaCO$_3$ = Calcium carbonate.
CCU   = Cold Creek unit.
CCU$_l$ = Lower Cold Creek unit.
CCU$_u$ = Upper Cold Creek unit (Cold Creek fine-grained unit).
Hf/CCU = Hanford formation/Cold Creek unit.
LM   = Lower mud unit.
NA   = Not applicable.
Q$_{fg}$ = Quaternary flood gravels.
Q$_{fs}$ = Quaternary flood silt and sand.
R$_{tf}$ = Ringold Formation, member of Taylor Flat.
R$_{wi}$ = Ringold Formation, member of Wooded Island.

Figure 3.32. Moisture Content and Significant Geochemical Parameters Measured in Direct-Push Sediment Samples Collected from the Waste Management Area U (Brown et al. 2007d) (Page 1 of 2)

Figure 3.32.   Moisture Content and Significant Geochemical Parameters Measured in Direct-Push Sediment Samples Collected from the Waste Management Area U (Brown et al. 2007d) (Page 2 of 2)

After evaluating all the characterization and analytical data, Brown et al. (2007d) concluded that the vadose zone in the vicinity of tanks U-104 and U-105 has been contaminated by tank-related waste. This observation is not new, as gamma logging of drywells in the area had previously identified uranium contamination at the same depths interrogated by push hole C5602. Given that the deepest sample string analyzed from push hole C5602 contained trace activities of ^{99}Tc, it is apparent that tank waste contamination has impacted the vadose zone to at least a depth of 28.0 m (92 ft) bgs at this location. However, the scope of the sampling campaign was to acquire additional samples to better understand the aerial extent of contamination in the U Tank Farm. Therefore, future characterization activities using sediment samples from a borehole will be required to understand the total vertical depth of contamination at this location.

The vadose zone south of tank U-110 has also been affected by a tank-related waste solution. The presence of sodium as the dominant water-extractable cation indicates that a high sodium-bearing waste stream has created a cation exchange front in this region that has pushed the prominent divalent cations (calcium and magnesium) off the surface exchange sites. The presence of significantly elevated concentrations of ^{99}Tc and nitrate in the deepest samples indicate that the vadose zone has been impacted to at least a depth of 29.9 m (98 ft) bgs. Given the high soil pH coupled with the presence of mobile contaminants deep in the vadose zone, Brown et al. (2007d) deduced that a release from tank U-110 is the source of contamination intercepted by push hole C5608. Again, the total vertical extent of contamination at this location could not be determined from the direct-push sampling results.

Of the remaining direct-push samples analyzed, only two contained quantifiable elevated concentrations of mobile tank waste contaminants. Samples from push hole C5600, which was emplaced southwest of tank U-105 contained a quantifiable activity of ^{99}Tc in the acid extract of the sample collected from 26.8 m (88 ft) bgs. Unfortunately, Brown et al. (2007d) could not corroborate this result using the water extract results, which failed to detect ^{99}Tc at a concentration above the sample estimated limit of quantification. While Brown et al. (2007d) could not dismiss this sole data point as an outlier, it was clear that additional data needed be collected prior to assessing and confirming the level of contamination southwest of tank U-105.

Two samples collected from push hole C5606 (emplaced northeast of tank U-112) contained slightly elevated concentrations of acid-extractable uranium. Tank U-112 was estimated to have released only 24 kg of uranium to the vadose zone; therefore, the lack of significant uranium contamination in a push hole emplaced near the tank is not an unreasonable finding. As with the data collected southwest tank U-105, Brown et al. (2007d) did not consider this data as conclusive evidence of the presence of tank waste in the vadose zone near tank U-112.

Aside from elevated concentrations of sodium in most water extracts or all acid extracts of the samples analyzed, no other tank waste constituents were observed at elevated concentrations in the push holes emplaced northeast of tank U-101 or north of the 200 series tanks. Additionally, the inferred pore water chemistry, based on water extracts of the samples collected from push hole C5604, do not support the resistivity anomaly observed by Rucker et al. (2006) north of the 200 series tanks.

3.7.3 Estimated K_d Values for Key Contaminants at Waste Management Area U

Table 3.19 lists the tanks within WMA U that have released fluids to the vadose zone and Table 3.20 shows the chemical composition of the various waste types that were present in the tanks at

Table 3.19. Waste Management Area U Leak Event Locations, Times, and Volumes (from Field and Jones 2005)

Site	Year of Release	Site Description--Principal Wastes	Total Volume (L)
241-U-101	1959	Zero solids. Unadjusted SMM definition for tank-leak date of 1959. R1	1.89E+04
241-U-104	1956	Zero solids. Unadjusted SMM definition for tank-leak date of 1956. MW1 and MW2	2.08E+05
241-U-110	1975	Zero solids. Unadjusted SMM definition for tank-leak date of 1975. PUREX (P2') Cool Wtr-Stm Cond, T2-SltCk, and CWR1	2.46E+04
241-U-112	1967	Zero solids. Unadjusted SMM definition for tank-leak date of 1967. R1, 1C1, and MW1	3.22E+04
SMM = Supernatant mixing model.			

Table 3.20. Chemical Composition of Waste Fluids Present in Tanks in Waste Management Area U at Time of Releases (from Corbin et al. 2005)

Waste Type	Concentration (mol/L)					
	MW1	MW2	R1	T2-SltCk	CWR1	1C1
Na^+	1.91	1.91	5.57	10.6	3.73	2.49
Ca^{2+}	0.0037	0.0037	0.0038	0.0038	0.0038	0.0038
K^+	7.74E-04	7.87E-04	0.0267	0.0661	0.0023	1.00E-02
Sr^{2+}	6.33E-07	6.33E-07	5.50E-07	5.34E-07	1.46E-07	7.00E-08
NH_4^+	7.18E-05	1.37E-04	0.0096	0.119	1.87E-04	1.17E-01
Cr	0.0035	0.0036	0.055	0.0554	0.0031	0.0069
Mn	0	0	5.54E-04	5.36E-04	0	0
Fe	0.0019	0.0019	0.00187	0.0019	0.0019	0.0019
Ni	0.0018	0.0018	0.0018	0.0018	1.56E-03	1.70E-03
Bi	3.13E-04	3.19E-04	0	2.97E-04	0	4.60E-04
NO_3^-	0.186	0.183	2.25	3.5	0.902	1.74
NO_2^-	0.017	0.023	0.769	1.79	1.44	0.067
CO_3^{2-}	0.624	0.627	0.0038	0.385	0.0038	0.0038
PO_4^{3-}	0.071	0.071	0	0.063	0	0.071
SO_4^{2-}	0.124	0.124	0.0193	0.124	9.43E-03	0.074
Cl^-	0.0036	0.0036	0.0957	0.236	0.011	0.046
F^-	0	0	0	0.126	0	0.198
OH^-	0.036	0.036	1.76	2.13	0.018	0.1
$Al(OH)_4^-$	0	0	0.848	1.4	1.34	0
Organics	0	0	0	0.448	0	0

the time of the leaks. The recommended K_d values for impacted zones for WMA U are shown in Table 3.21, and are quite similar to those recommended for WMAs S-SX and T, except for the use of WMA B-BX-BY values for uranium to accommodate the metal waste composition with very high dissolved uranium. Uranium K_d values drop at high dissolved uranium concentrations under conditions where solubility constraints are not reached (see Um et al. [2005] for details).

Table 3.21. K_d Values for Impacted Sediments at Waste Management Area U (K_d units are mL/g)

	Sand-Size Sediments						Silt-Size Sediments						Carbonate-Dominated Sediments					
	High Impact			Intermediate Impact			High Impact			Intermediate Impact			High Impact			Intermediate Impact		
	Best	Min	Max	Best	Min	Max	Best	Min	Max	Best	Min	Max	Best	Min	Max	Best	Min	Max
Chemicals																		
F⁻	0	0	0	0	0	1	0	0	0	0.05	0	1	0	0	1	0.05	0	1
Cr(VI)	0.2	0	3	0	0	8	0.4	0	8	0	0	10	0.2	0	3	0	0	8
Hg(II)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NO₃⁻, NO₂⁻	0	0	0	0	0	0.1	0	0	0	0	0	0.1	0	0	0.1	0	0	0.1
Pb(II)	3	0	10	10	3	100	0	0	30	30	10	300	3	0	10	10	3	100
U(VI) – all isotopes	0.1	0	2	0.2	0.2	0.4	0.3	0	3	2.5	0.6	15	0.3	0	30	2.5	0.6	30
Radionuclides																		
²⁴¹Am(III)	3	0	50	600	200	2000	10	0	150	600	200	2000	10	0	150	600	200	2000
¹⁴C(IV)	5	0	50	1	0	100	5	0	50	1	0	100	5	0	50	1	0	100
⁶⁰Co(II,III)	0	0	10	0	0	10	0	0	30	0	0	30	0	0	30	0	0	30
¹³⁷Cs	1	0	10	100	10	1000	1	0	30	100	30	3000	1	0	10	100	10	1000
Eu(III) – all isotopes	1	0	10	10	3	100	3	0	30	30	10	300	3	0	30	30	10	300
³H	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
¹²⁹I	0	0	0.2	0.2	0	2	0	0	0	0.2	0	2	0	0	0	0.2	0	2
⁶³Ni	0	0	10	3	1	20	0	0	30	10	3	60	0	0	30	10	3	60
²³⁷Np(V)	0	0	5	10	2	30	0	0	15	10	2	50	0	0	15	10	2	50
Pu – all isotopes	3	0	50	600	200	2000	5	0	150	600	200	2000	3	0	50	600	200	2000
²²⁶Ra(II)	1	0.2	20	10	5	20	3	0.6	60	10	5	60	3	0.6	60	10	5	60
⁷⁹Se(VI,IV)	0	0	3	0.1	0	3	0	0	3	0.3	0	10	0	0	3	0.1	0	3
¹²⁶Sn(IV)	0	0	10	0.5	0	20	0	0	30	1.5	0	60	0	0	30	1.5	0	60
⁹⁰Sr	1	0.2	20	10	5	20	3	0.6	60	10	5	100	3	0.6	60	10	5	100
⁹⁹Tc(VII)	0	0	1	0	0	5	0	0	1	0	0	5	0	0	1	0	0	5

For gravel-size sediments, modify sand-size K_d values using Equations (2.3) and (2.4) in Section 2.4.
See Appendix A for references and selection rationale.

3.8   BC Cribs – Trench B-26

Although the BC cribs area south of 200E does not contain tank farms, a detailed characterization of one vadose zone borehole placed through this inactive facility was performed by the Vadose Zone Characterization Project. There was interest in this facility because the waste disposed to trench B-26 was ferrocyanide strontium-cesium recovery wastes that were also stored in some SSTs. Fluor Hanford, Inc. provided grab samples for geochemical characterization. Grab samples were collected every 0.762 m from depths starting right below the bottom of the trench (5.5 m bgs) down to the water table (103 m bgs). Selected sediments from this borehole (C4191) were characterized for most of the analytes typically measured for the SST contaminated sediments using the same procedures and test method-ologies that are documented in the borehole characterization reports (e.g., Serne et al. [2002a, 2002b, 2002c, 2002d, 2002e, 2002f; 2004a, 2004b]).

3.8.1   Geology of the BC Cribs Area

The geology of the BC cribs area, which is south of the 200E area, is not discussed in the RFI SST geology data package by Reidel and Chamness (2007). However, they do describe the statigraphy at the nearby IDF, which should be similar to that below the BC cribs. The description of well 299-E13-10 in Figure 6.6 of Reidel and Chamness (2007) is most similar to the geological description of borehole C4191 by RJ Serne (Reidel 2007[6]). A plot of the measured concentrations of ^{99}Tc, uranium, and nitrate as a function of depth is shown in Figure 3.33 along with the corresponding geologic stratigraphy (far left of figure). The sediments are mainly sand with some gravel with silt near the water table. In the younger sediments (Hanford formation), there are up to 15 very thin lenses of fine sand or silt within the sands. The water table was contacted at 103 m bgs in Ringold Formation Unit E gravel.

3.8.2   Geochemical Characterization of Sediments from C4191 Borehole

No formal reports describing the characterization studies completed on the C4191 vadose zone sediments have been prepared to date, but the data are in an Excel$^©$ file and available in the RMIS electronic database (Serne and Mann 2004). The analytical data indicate that, despite a relatively large volume (4.73 million L [1.25 million gal]) disposal to trench B-26, the mobile contaminants ^{99}Tc and nitrate were found to remain predominantly in the sediments between the depths of 26 to 43 m bgs, as shown in Figure 3.33. The C4191 sediments also contained elevated concentrations of sulfate, phosphate, uranium, and sodium. The elevated concentrations of uranium, phosphate and ^{137}Cs were found to extend from the bottom of the trench to 9, 15 and 4 m bgs, respectively. No measurements of actinides or ^{90}Sr were made. The sediments also showed the ion-exchange front where Na$^+$ dominates the sediment exchange sites down to a depth of 30.8 m bgs and the natural divalent cations Mg^{2+} and Ca^{2+} in the pore water are dominant between 43 and 48.5 m bgs. The sediments between 30.8 and 43 m bgs are a transition zone where sodium dominates but not all the naturally occurring divalent cations have been flushed out by the sodium. The most striking finding at C4191 was the fact that mobile contaminants (those that do not appreciably interact with the sediment and can thus be considered tracers for the water migration itself) had not migrated much below 43 m bgs despite the volume of liquid disposed (4.73×10^6 L). The volume of liquid disposed to B-26 trench was more than an order of magnitude larger than the largest known SST leak (i.e., T-106 at 4.35×10^5 L). At T-106 (see Section 3.6.3), the mobile contaminants do not appear to have migrated any deeper than 37 m bgs but the geology is quite different at WMA T than at the BC cribs area. Much greater vertical migration was expected at the BC cribs for such a large disposal volume.

3.8.3   Estimated K$_d$ Values for Key Contaminants at BC Cribs Trench B-26

The B-26 trench is one of 26 liquid waste disposal sites that were used to dispose various wastes from isotope recovery activities at B, T, and U Plant during the 1950s. Figure 3.34 shows the facilities and the volumes of liquids and the total mass of nitrate, one of the major waste constituents, that were disposed of in each facility based upon data from an earlier version of the Soil Inventory Model (Simpson et al. 2001). The current version has slightly different values for volume disposed and total nitrate inventories but the relative relationships between the 26 inactive facilities remains the same. Trench B-26 was a specific retention trench that received liquid wastes for a few months in late 1956 and early 1957. The chemical

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[6] Reidel SP. 2007. Personal communication from SP Reidel (PNNL [retired]) to RJ Serne (PNNL), April 2, 2007, Richland, Washington.

composition of the waste is shown in Table 3.22 based on data available in Corbin et al. (2005). The waste stream is dominated by sodium, nitrate, sulfate, fluoride, and trace amounts of calcium, phosphate, uranium, and chloride.
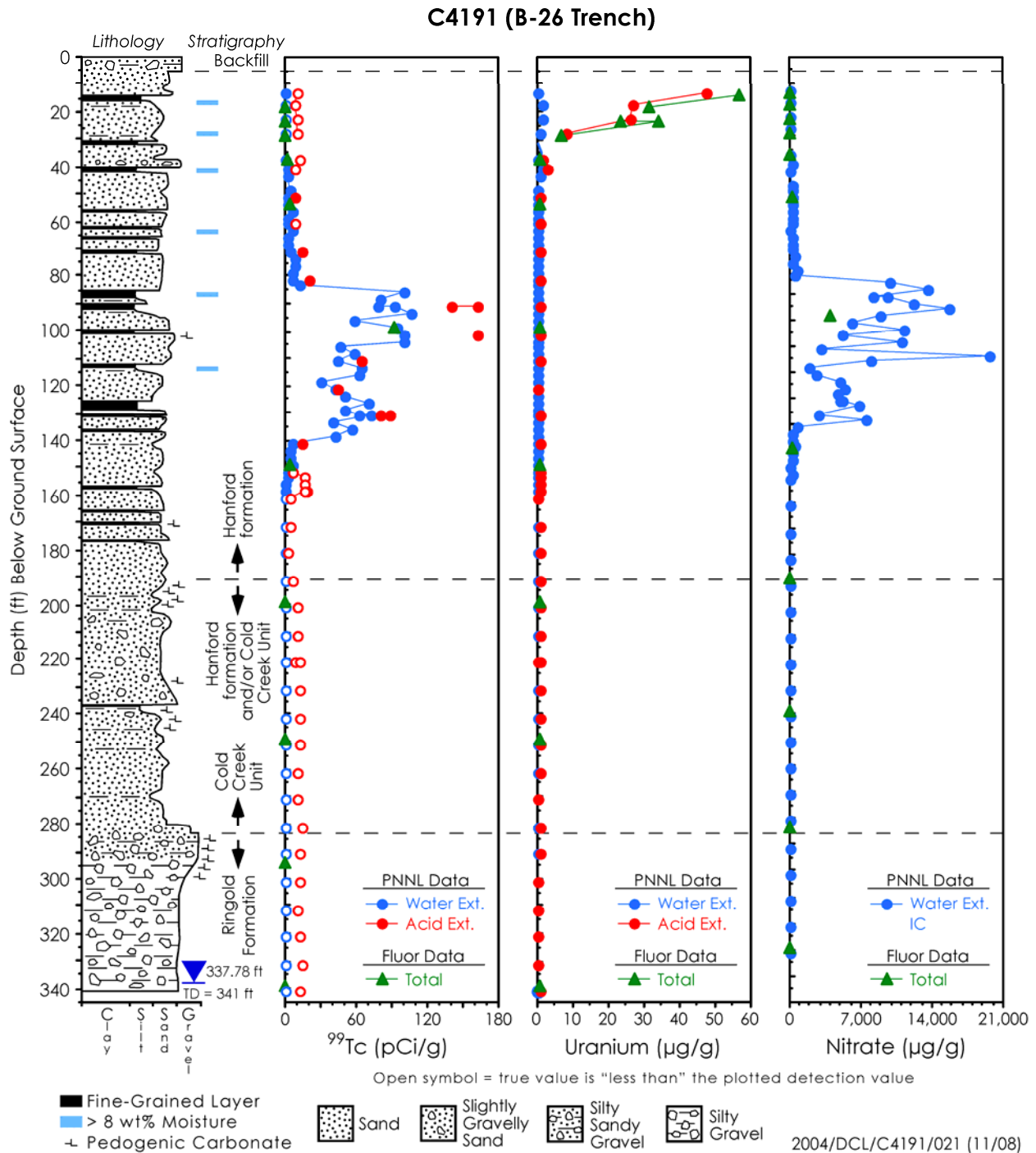
Figure 3.33. Geologic Stratigraphy of the Sediments in Borehole C4191 along with the Measured Concentrations (µg/g sediment) of ^{99}Tc, Uranium, and Nitrate as a Function of Depth
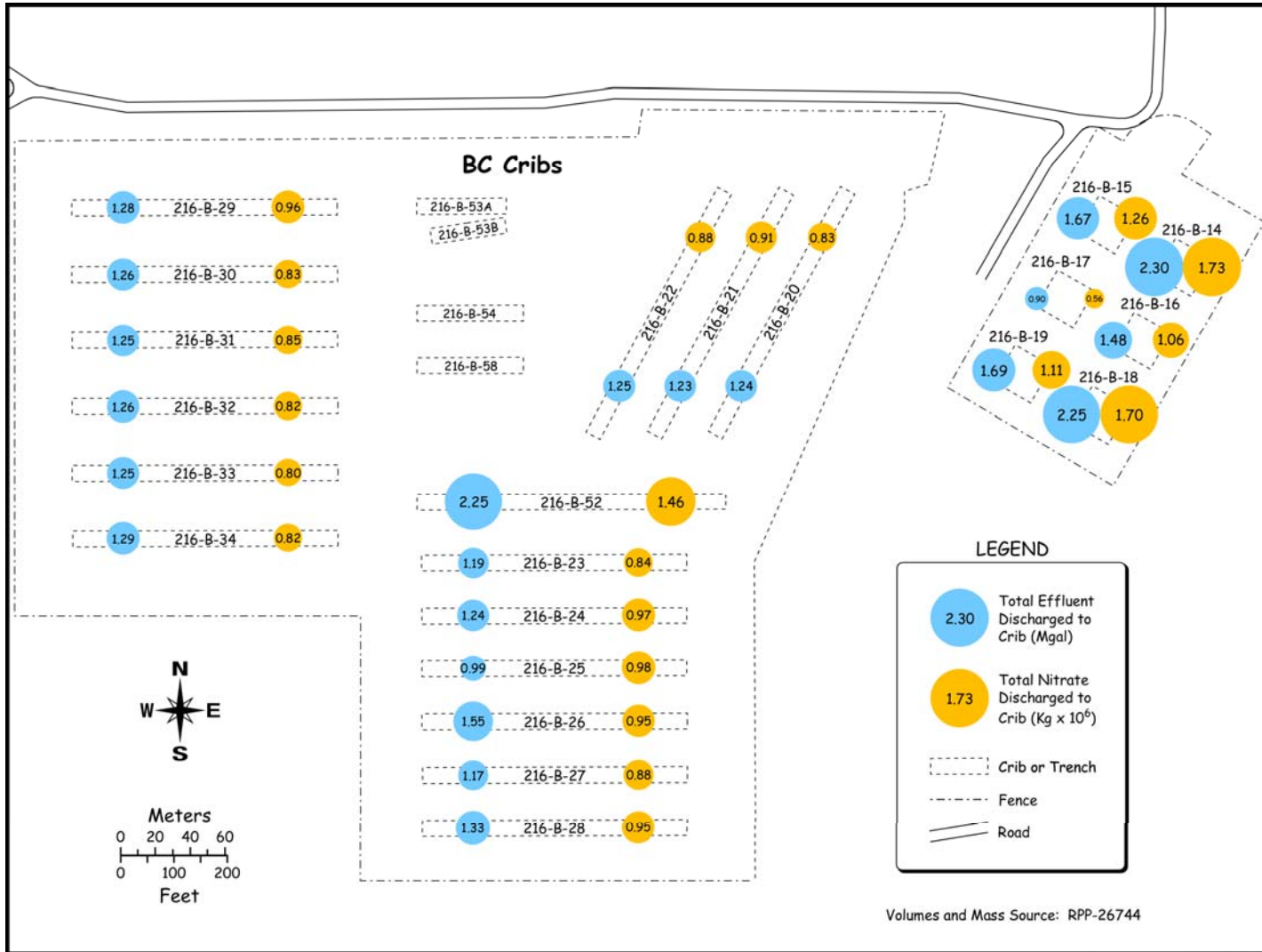
Figure 3.34. Volume of Waste (Mgal = 3.79 x 10⁶ L) and Total Mass of Nitrate Disposed (kg) for Each Crib and Trench (Trench B-26 is the third trench from bottom in middle row)

Table 3.22. Chemical Composition of Waste Stream Disposed in B-26 Trench (from Corbin et al. 2005)

Waste Type	Concentration (mol/L)
	PFeCN2
Na^+	3.95E+00
Ca^{2+}	3.76E-03
K^+	1.71E-02
UO_2^{2+}	1.30E-04
NH_4^+	7.76E-09
Cr	3.31E-03
Mn	0.00E+00
Fe	1.88E-03
Ni	1.82E-03
Bi	1.69E-03
NO_3^-	3.21E+00
NO_2^-	7.09E-04
CO_3^{2-}	3.75E-03
PO_4^{3-}	7.06E-02
SO_4^{2-}	1.24E-01
Cl^-	7.87E-02
F^-	2.17E-01
OH^-	Unknown
$Al(OH)_4^-$	0.00E+00
Organics	0.00E+00

   K_d value estimates for key contaminants in the high and intermediate impact zones of the BC cribs are shown in Table 3.23. Sediment outside this intermediate impact zone should exhibit sorption properties similar to uncontaminated sediments contacting uncontaminated pore waters and have K_d values as given in Table 3.4.

Table 3.23. K_d Values for Impacted Sediments at BC Cribs (K_d units are mL/g)

| | Sand-Size Sediments | | | | | |
| | High Impact | | | Intermediate Impact | | |
	Best	Min	Max	Best	Min	Max
Chemicals						
F⁻	0	0	0	0	0	1
Cr(VI)	1	0	3	0	0	3
Hg(II)	0	0	0	0	0	0
NO_3^-, NO_2^-	0	0	0	0	0	0.1
Pb	3	0	10	10	3	100
U(VI) – all isotopes	20	1	50	1	1	50
Radionuclides						
²⁴¹Am	20	1	50	600	200	2000
¹⁴C	5	0	50	1	0	100
⁶⁰Co(II,III)	0	0	10	0	0	10
¹³⁷Cs	30	10	50	100	10	1000
Eu – all isotopes	20	1	50	10	3	100
³H	0	0	0	0	0	0
¹²⁹I	0	0	0.2	0.2	0	2
⁶³Ni	0	0	10	3	1	20
²³⁷Np(V)	0	0	5	10	2	30
Pu – all isotopes	20	1	50	600	200	2000
²²⁶Ra	1	0.2	20	10	5	20
⁷⁹Se(VI,IV)	0	0	3	0.1	0	3
¹²⁶Sn(IV)	0	0	10	0.5	0	20
⁹⁰Sr	1	0.2	20	10	5	100
⁹⁹Tc(VII)	0.1	0	1	0.1	0	3

For gravel-size sediments, modify sand-size K_d values using Equations (2.3) and (2.4) in Section 2.4.
See Appendix A for references and selection rationale.

4.0   Conclusions

The primary purpose of this data package is to summarize the laboratory characterization data generated during Phase 1 of the RCRA Corrective Action Program in support of the Tank Farm Vadose Zone Program by PNNL's Vadose Zone Characterization Project. Much has been learned during the initial investigations of the Tank Farm Vadose Zone Program. Key geochemistry discoveries include the following:

- Geologic layering of the vadose zone sediments has an important impact on the direction and rate of migration of the waste liquids and dissolved contaminants

- The zone of caustic attack, due to the high pH tank waste, can be determined by measuring the pH of the soil

- A front of naturally occurring calcium and magnesium that have been removed from the sediment exchange sites precedes the tank waste plume containing elevated sodium, thus aiding in determining the leading edge of the plume containing mobile contaminants of concern, and

- Using a 1:1 sediment/water extraction technique, dissolved inorganic constituents in pore water can be determined in sediment that is too dry to easily extract the pore water and measure its composition.

Results from the Vadose Zone Characterization Project have revealed that mobile contaminants, such as ^{99}Tc and nitrate, migrate much differently in the subsurface than previously believed. Conventional thinking was that once mobile contaminants entered the subsurface, they migrated in a nearly vertical path through the soil column. However, it has been shown that geologic layering of the vadose zone sediments has an important impact on the direction and rate of migration of the waste liquids and dissolved contaminants. Detailed sampling and characterization of both contaminated and uncontaminated vadose zone sediments has demonstrated the importance of thin lenses, which are often a few millimeters to a few centimeters in thickness, of fine-grained sediments in the various Hanford formation sediment types. These fine-grained lenses have been shown to cause significant horizontal spreading of leaked fluids within the vadose zone. As a result of findings such as these, characterization campaigns now target fine-grained lenses as optimal sampling points to locate contaminants.

Another discovery from the laboratory studies has been the observation that the zone of caustic attack, due to the high pH tank waste, can be determined by measuring the pH of the soil. Because tank waste is generally considered caustic (in excess of 1M free hydroxide), it is quite common to find elevated soil pHs (between 8.5 and 10) in the vadose zone adjacent to the point of waste release. However, natural minerals present in the sediment act to neutralize the elevated pH tank waste. As such, the total area exhibiting elevated soil pH is always considerably smaller than the footprint that has been contaminated by more mobile constituents, such as nitrate or [99]Tc. Soil pH has therefore become one of the key parameters used to identify waste discharge locations in the vadose zone.

Calcium and magnesium are the two dominant cations present in ion-exchange sites in Hanford sediments. When waste solutions containing high concentrations of dissolved sodium (in excess of 4 M) contact the sediment, the sodium exchanges with the calcium and magnesium, creating an ion-exchange front. In this scenario, a front or wall of naturally present calcium and magnesium that have been removed from the sediment exchange sites precede the tank waste plume containing the elevated sodium.

Although the ion-exchange front will not necessarily define the total vertical impact of tank waste contamination, it can be used to target the most appropriate depths to look for mobile contaminants.

The Vadose Zone Characterization Project continues to evolve to better meet the needs of the Tank Farm Vadose Zone Program. A significant amount of work has been performed to characterize contamination found in the vadose zone within and around the SST farms. However, little success has been achieved at linking contamination found in the groundwater with that found in the vadose zone. This lack of success is due to the complex flow paths for pore water and multiple sources for contamination. As mentioned previously, fluid releases from SSTs and their supporting infrastructure are not the only potential sources of contamination in the Hanford Site Central Plateau region. Because the SST farms are located close to waste disposal sites (i.e., cribs and/or trenches), it is imperative to determine the source(s) of contamination in the groundwater. Historically, this has been difficult because the characteristics of the waste plume change significantly as it migrates through the sediments. However, innovative approaches, such as analyses of certain stable and radioactive isotope concentrations and signatures are now being used. These studies employ advanced analytical techniques and instrumentation to enable better "fingerprinting" of contaminant plumes, making identification of contaminant source terms plausible (Brown et al. 2006b, Cantrell et al. 2007). While the use of "fingerprinting" at the Hanford Site is still relatively new, it has the potential to provide significant support in defining the current and future risks associated with contamination currently residing in the vadose zone.

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Appendix

Rationale for K_d Value Choices for Key Contaminants

Appendix

Rationale for K_d Value Choices for Key Contaminants

This appendix contains tables that provide the rationale and supporting references for the K_d values elected for the key contaminants listed for each WMA for the two impacted zones and sediments not impacted by tank wastes. The series of tables in this appendix are based on those in the main text. However, for each strata and each impact zone of each contaminant, a comment column has been added to document either the source (tables in borehole reports, IDF data package [Krupka et al. 2004], or Last et al. 2006) of the K_d values, or the reasoning used to select the K_d value. The latter includes use of generic non-Hanford Site literature with citation, chemical analogy to another element for which Hanford Site data are available, or simply a conservative estimate based on expert opinion.

Table A.1. K_d Values for Sand-Size Sediments – No Impact Zone (Table 3.4 Main Text)

Table 3.4 Main Text	Sand-Size Sediments – No Impact Zone				
	Best	Minimum	Maximum	Comments	Reference
Chemicals					
F $^-$	0.1	0	3	No Hanford-specific data	Fluher et al. (1982) and Peek and Volk (1984)
Cr(VI)	0	0	0.3	Adequate Hanford data	Last et al. (2006)
Hg(II)	150	72	673	No Hanford-specific data	Del Debbio (1991)
NO_3^-, NO_2^-	0	0	0	Hanford field observations	Assumed based on any borehole characterization report (e.g., Serne et al. 2002e)
Pb(II)	50	10	500	Pb is strongly sorbed	Rhoads et al. (1992)
U(VI)	0.8	0.2	4	Adequate Hanford data	Last et al. (2006)
Radionuclides					
[241]Am(III)	300	60	2000	Based on IDF data package	Krupka et al. (2004)
[14]C	5	0	100	Based on IDF data package	Krupka et al. (2004)
[60]Co(II,III)	10	0	2000	Assumed organic or CN chelate exists for low values	Krupka et al. (2004) for maximum value
[137]Cs	2000	200	10000	Adequate Hanford data	Last et al. (2006)
Eu(III)-isotopes	300	60	2000	Adequate Hanford data	Krupka et al. (2004)
[3]H	0	0	0	Hanford field observations	Last et al. (2006)
[129]I	0.2	0	2	Adequate Hanford data	Last et al. (2006)
[63]Ni	300	50	2500	Some Hanford data	Krupka et al. (2004)
[237]Np(V)	10	2	30	Some Hanford data	Last et al. (2006)
Pu(all)-isotopes	600	200	2000	Some Hanford data	Last et al. (2006)
[226]Ra	20	10	50	Based on IDF data package	Krupka et al. (2004)
[79]Se(VI,IV)	5	3	10	Adequate Hanford data	Last et al. (2006)
[126]Sn(IV)	50	50	250	Based on IDF data package	Krupka et al. (2004)
[90]Sr	20	10	50	Adequate Hanford data	Last et al. (2006)
[99]Tc(VII)	0	0	0.1	Adequate Hanford data	Last et al. (2006)

Table A.2. K_d Values for Silt-Size Sediments – No Impact Zone (Table 3.4 Main Text)

Table 3.4 Main Text	Silt-Size Sediments – No Impact Zone				
	Best	Minimum	Maximum	Comments	Reference
Chemicals					
F $^-$	0.2	0	3	No Hanford-specific data	Fluher et al. (1982) and Peek and Volk (1984)
Cr(VI)	0	0	0.6	Assumed sorption is 2X sand values	Last et al. (2006)
Hg(II)	150	118	1900	No Hanford-specific data	Del Debbio (1991)
NO_3^-, NO_2^-	0	0	0	Hanford field observations	Assumed based on any borehole characterization report (e.g., Serne et al. 2002e)
Pb(II)	100	30	2000	Pb is strongly sorbed	Rhoads et al. (1992)
U(VI)	1.5	0.2	20	Assumed sorption is 2X sand values	Last et al. (2006)
Radionuclides					
^{241}Am(III)	300	200	4000	Based on IDF data package; assumed silt sorption is 2X sand values	Krupka et al. (2004)
^{14}C	5	0	100	Based on IDF data package	Krupka et al. (2004)
^{60}Co(II,III)	10	0	2000	Assumed organic or CN chelate exists for low values	Krupka et al. (2004) for maximum value
^{137}Cs	2000	600	10000	Assumed sorption is 3X sand values	Last et al. (2006)
Eu(III)-isotopes	300	200	4000	Based on IDF data package; assumed silt sorption is 2X sand values	Krupka et al. (2004)
^{3}H	0	0	0	Hanford field observations	Last et al. (2006)
^{129}I	0.2	0	5	Assumed maximum value is 2.5X sand maximum value	Last et al. (2006)
^{63}Ni	300	50	2500	Some Hanford data	Krupka et al. (2004)
^{237}Np(V)	20	5	60	Assumed sorption is 2X sand values	Last et al. (2006)
Pu(all)-isotopes	600	200	4000	Assumed sorption is 2X sand values	Last et al. (2006)
^{226}Ra	40	20	200	Assumed sorption is 2X sand values	Krupka et al. (2004)
^{79}Se(VI,IV)	5	3	30	Assumed sorption maximum is 2X sand maximum	Last et al. (2006)
^{126}Sn(IV)	100	50	250	Assumed best value is 2X best sand value	Krupka et al. (2004)
^{90}Sr	40	20	200	Assumed sorption is 2X sand values	Last et al. (2006)
^{99}Tc(VII)	0	0	0.2	Assumed sorption is 2X sand values	Last et al. (2006)

Table A.3. K_d Values for Carbonate-Dominated Sediments – No Impact Zone (Table 3.4 Main Text)

Table 3.4 Main Text	Carbonate-Dominated Sediments – No Impact Zone				
	Best	Minimum	Maximum	Comments	Reference
Chemicals					
F^-	0	0	1	No Hanford-specific data; less sorption in calcareous sediments	Fluher et al. (1982) and Peek and Volk (1984)
Cr(VI)	0	0	0.3	Assumed calcite has no impact; same as sand values	Last et al. (2006)
Hg(II)	150	72	673	No Hanford-specific data	Del Debbio (1991)
NO_3^-, NO_2^-	0	0	0	Hanford field observations	Assumed based on any borehole characterization report (e.g., Serne et al. 2002e)
Pb(II)	50	10	500	Assumed calcite has no impact; same as sand values	Rhoads et al. (1992)
U(VI)	4	3	20	Adequate Hanford data	Last et al. (2006)
Radionuclides					
[241]Am(III)	150	60	2000	Assumed aqueous complexes decrease sorption	Krupka et al. (2004)
[14]C	15	5	250	Calcite increases sorption	Martin (1996)
[60]Co(II,III)	15	3	2000	Assumed calcite increases sorption	Krupka et al. (2004) for maximum value
[137]Cs	2000	200	10000	Assumed no impact versus sand	Last et al. (2006)
Eu(III)-isotopes	150	60	2000	Assumed aqueous complexes decrease sorption	Krupka et al. (2004)
[3]H	0	0	0	Hanford field observations	Last et al. (2006)
[129]I	0.2	0	2	Assumed no impact versus sand	Last et al. (2006)
[63]Ni	300	50	2500	Assumed no impact versus sand	Krupka et al. (2004)
[237]Np(V)	10	2	30	Assumed no impact versus sand	Last et al. (2006)
Pu(all)-isotopes	300	200	2000	Assumed aqueous complexes decrease sorption	Last et al. (2006)
[226]Ra	40	20	200	Assumed divalent cations adsorbed better to calcite than sand	Krupka et al. (2004)
[79]Se(VI,IV)	5	3	30	Assumed no impact versus sand	Last et al. (2006)
[126]Sn(IV)	50	50	250	Assumed no impact versus sand	Krupka et al. (2004)
[90]Sr	40	20	200	Assumed divalent cations adsorbed better to calcite than sand	Last et al. (2006)
[99]Tc(VII)	0	0	0.1	Assumed no impact versus sand	Last et al. (2006)

Table A.4. K_d Values for Sand-Dominated Sediments at Waste Management Area A-AX for High and Intermediate Impact Zones (Table 3.3 Main Text)

Table 3.3 Main Text A-AX WMA	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
Chemicals								
F $^-$	0	0	0	0	0	1	Assumed no sorption except on fine-grained sediment	Expert opinion; no data or references for A-AX Farm
Cr(VI)	0.05	0	3	0	0	3	Caustic condition leads to slight retardation based on SX boreholes	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates
NO$_3^-$, NO$_2^-$	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f)
Pb(II)	3	0	10	10	3	100	No data available for these conditions, but Pb is not mobile under alkaline conditions	Expert opinion; no data or references for A-AX Farm
U(VI)	0.1	0	1	0.8	0.2	4	Expert opinion; no data or references for A-AX Farm; based on BX-102 and TX-104 field results	Serne et al. (2004b, 2002c)
Radionuclides								
[241]Am(III)	3	0	50	600	200	2000	No data available for A-AX Farm; Am shows very low mobility at T-106	Serne et al. (2004a)
[14]C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters	Expert opinion; no data or references for A-AX Farm

Table 3.3 Main Text A-AX WMA	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
[60]Co(II,III)	0	0	10	0	0	10	[60]Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones	Expert opinion; no data or references for A-AX Farm; used WMA T (Serne et al. 2004b)
[137]Cs	1	0	10	100	10	1000	Cs at SX has K_d values from 0 to 10+ in high impact zone and then reach values up to high 100's in moderate salt; lowered high impact versus Last et al. (2006) but honored the intermediate impact zone	Expert opinion; no data for A-AX Farm; used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact
Eu(III)-isotopes	1	0	10	10	3	100	Eu in high impact zone often found in sediment likely as chelate; intermediate zone effectively captures all Eu	Expert opinion; no data for A-AX Farm; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone
[3]H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
[129]I	0	0	0.2	0.2	0	2	At SX-108 [129]I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone

Table 3.3 Main Text A-AX WMA	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{63}Ni	0	0	10	3	1	20	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA	Expert opinion (assumed adsorption similar to Co)
^{237}Np(V)	0	0	5	10	2	30	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used values from IDF for sand	No data for A-AX; used T WMA; Serne et al. (2004b) and IDF (Krupka et al. 2004)
Pu(all)-isotopes	3	0	50	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for high impact; used Last et al. (2006) values for intermediate zone	No data for A-AX; used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b, 2004b)
^{226}Ra	1	0.2	20	10	5	20	No Ra studies for SST Vadose Zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones	No data for A-AX; used Sr similarity and Last et al. (2006)
^{79}Se(VI,IV)	0	0	3	0.1	0	3	^{79}Se not studied at SST WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments	No data for A-AX; used Kaplan et al. (1998a, 1998b) and expert opinion

Table 3.3 Main Text A-AX WMA	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
[126]Sn(IV)	0	0	10	0.5	0	20	No study for Sn so allowed no sorption in high impact zone; tin is not soluble at neutral-to-high pH values based on (Serne et al. 1993) so allowed slight sorption in intermediate impact zone; if [126]Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for A-AX; used Serne et al. (1993) and expert opinion
[90]Sr	1	0.2	20	10	5	20	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at B-110, there was some mobility for a few tens of meters below tank; at T-106, there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones	No data for A-AX; used Serne et al. (2002a), Last et al. (2006), and expert opinion
[99]Tc(VII)	0	0	0.2	0	0	1	At SX, T and other sites, Tc seems completely mobile through high and intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata	No data for A-AX; used Serne et al. (2002b, 2004a, 2004b), Last et al. (2006), and expert opinion

Table A.5. K_d Values for Silt-Dominated Sediments in Waste Management Area A-AX for High and Intermediate Impact Zones (Table 3.3 Main Text)

Table 3.3 Main Text A-AX WMA	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Chemicals								
F$^-$	0	0	0	0.05	0	1	Assumed no sorption except on fine-grained sediment	Expert opinion; no data or references for A-AX Farm
Cr(VI)	0.1	0	3	0	0	10	Caustic condition leads to slight retardation based on SX bore-holes; silts given a bit larger impact based on more ferrous reduction	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO$_3^-$, NO$_2^-$	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f)
Pb(II)	0	0	30	30	10	300	No data available for these conditions, but Pb is not mobile under alkaline conditions	Expert opinion; no data or references for A-AX Farm
U(VI)	0.3	0	3	2.5	0.6	15	Expert opinion; no data or references for A-AX Farm; based on BX-102 and TX-104 field results	Serne et al. (2004b, 2002c)
Radionuclides								
^{241}Am(III)	10	0	150	600	200	2000	No data available for A-AX Farm; Am shows very low mobility at T-106	Serne et al. (2004a)

Table 3.3 Main Text A-AX WMA	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{14}C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters	Expert opinion; no data or references for A-AX Farm
^{60}Co(II,III)	0	0	30	0	0	30	^{60}Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones	Expert opinion; no data or references for A-AX Farm; used WMA T (Serne et al. 2004b)
^{137}Cs	1	0	30	100	30	3000	Cs at SX has K_d values from 0 to 10+ in high impact zone and then reach values up to high 100's in moderate salt; lowered high impact versus Last (2006) but honored the intermediate impact zone; silt 3X increase over sand	Expert opinion; no data for A-AX Farm; used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact
Eu(III)-isotopes	3	0	30	30	10	300	Eu in high impact zone often found in sediment likely as chelate; intermediate zone effectively captures all Eu; allowed 3X silt impacts assuming adsorption is as important as pH effects	Expert opinion; no data for A-AX Farm; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes

Table 3.3 Main Text A-AX WMA	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{129}I	0	0	0	0.2	0	2	At SX-108, ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone and made no silt correction based on no "sorption sensitivity to surface area"	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone
^{63}Ni	0	0	30	10	3	60	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA	Expert opinion (assumed adsorption similar to Co)
^{237}Np(V)	0	0	15	10	2	50	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used values from IDF for sand; assumed silt impacts maximum value only	No data for A-AX so used T WMA; Serne et al. (2004b) and IDF (Krupka et al. 2004).
Pu(all)-isotopes	5	0	150	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for high impact; used Last values for intermediate zone; silt impact values ~3X sand	No data for A-AX so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b, 2004b)

Table 3.3 Main Text A-AX WMA	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
[226]Ra	3	0.6	60	10	5	60	No Ra studies for SST Vadose Zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones; also used the 3X silt correction	No data for A-AX; used Sr similarity and Last et al. (2006)
[79]Se(VI,IV)	0	0	3	0.3	0	10	[79]Se not studied at SST WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments; used 3X increase for silt	No data for A-AX; used Kaplan et al. (1998a, 1998b) and expert opinion
[126]Sn(IV)	0	0	30	1.5	0	60	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; if [126]Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for A-AX; used Serne et al. (1993) and expert opinion
[90]Sr	3	0.6	60	10	5	60	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at B-110, there was some mobility for a few tens of meters below tank; at T-106, there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones; used 3X increase for silt because Sr adsorption is quite sensitive to surface area	No data for A-AX; used Serne et al. (2002a), Last et al. (2006), and expert opinion

Table A.5. (contd)

Table 3.3 Main Text A-AX WMA	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{99}Tc(VII)	0	0	0.2	0	0	5	At SX, T and other sites, Tc seems completely mobile through high and intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata	No data for A-AX; used Serne et al. (2002b, 2004a, 2004b), Last et al. (2006), and expert opinion

Table A.6. K_d Values for Sand-Size Sediments at Waste Management Area B-BX-BY for High and Intermediate Impact Zones
(Table 3.7 Main Text)

Table 3.7 Main Text B-BX-BY	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Chemicals								
F⁻	0	0	0	0	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	0.05	0	3	0	0	3	Caustic condition leads to slight retardation based on SX boreholes	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO₃⁻, NO₂⁻	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f)
Pb(II)	3	0	10	10	3	100	No data available for these conditions, but Pb is not mobile under alkaline conditions	Expert opinion; no data or references for B-BX-BY Farms
U(VI)	0.1	0	2	0.2	0.2	0.4	High impact based on BX-102, where U quite mobile but not zero (differs from Last et al. [2006] and A-AX values); used BX-102 for intermediate zone	Serne et al. (2002c)

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Table 3.7 Main Text B-BX-BY	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Radionuclides								
[241]Am(III)	3	0	50	600	200	2000	No data available for B-BX-BY Farms; Am shows very low mobility at T-106; intermediate zone based on Am not being sensitive to salt but rather pH; neutral pH high sorption; used values from IDF	Serne et al. (2004a) and Krupka et al. (2004)
[14]C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters	Expert opinion; no data or references for B-BX-BY Farms
[60]Co(II,III)	0	0	10	0	0	10	[60]Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones	Expert opinion; no data or references for B-BX-BY Farms; used WMA T (Serne et al. 2004b)
[137]Cs	1	0	10	100	10	1000	Cs at SX has K_d values from 0 to 10+ in high impact zone and then reach values up to high 100's in moderate salt; lowered high impact versus Last et al. (2006) but honored the intermediate impact zone	Expert opinion; no data for B-BX-BY Farms; used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact
Eu(III)-isotopes	1	0	10	10	3	100	Eu in high impact zone often found in sediment likely as chelate; intermediate zone effectively captures all Eu	Expert opinion; no data for B-BX-BY Farms; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone

Table A.6. (contd)

Table 3.7 Main Text B-BX-BY	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
^{129}I	0	0	0.2	0.2	0	2	At SX-108, ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone
^{63}Ni	0	0	10	3	1	20	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA	Expert opinion (assumed adsorption similar to Co)
^{237}Np(V)	0	0	5	10	2	30	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used values from IDF for sand	No data for B-BX-BY so used T WMA; Serne et al. (2004b) and IDF (Krupka et al. 2004).

Table A.6. (contd)

Table 3.7 Main Text B-BX-BY	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Pu(all)-isotopes	3	0	50	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for high impact; used Last et al. (2006) values for intermediate zone	No data for B-BX-BY Farms so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b, 2004b)
[226]Ra	1	0.2	20	10	5	20	No Ra studies for SST vadose zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones	No data for B-BX-BY Farms so used Sr similarity and Last et al. (2006)
[79]Se(VI,IV)	0	0	3	0.1	0	3	[79]Se not studied at SST WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments	No data for B-BX-BY Farms; used Kaplan et al. (1998a, 1998b) and expert opinion
[126]Sn(IV)	0	0	10	0.5	0	20	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; if [126]Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for B-BX-BY Farms; used Serne et al. (1993) and expert opinion

Table A.6. (contd)

Table 3.7 Main Text B-BX-BY	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{90}Sr	1	0.2	20	10	5	20	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at B-110 there was some mobility for a few tens of meters below tank; at T-106, there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones	Serne et al. (2002a), Last et al. (2006), and expert opinion
^{99}Tc(VII)	0	0	0.2	0	0	1	At SX, T and other sites Tc seems completely mobile through high and intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata	Little useful Tc data at B and BX; used Serne et al. (2002b, 2004a, 2004b), Last et al. (2006), and expert opinion

Table A.7. K_d Values for Silt-Dominated Sediments at Waste Management Area B-BX-BY for High and Intermediate Impact Zones (Table 3.7 Main Text)

Table 3.7 Main Text B-BX-BY	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Chemicals								
F $^-$	0	0	0	0.05	0	1	Assumed no sorption except on fine-grained sediment	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	0.1	0	3	0	0	10	Caustic condition leads to slight retardation based on SX boreholes; silts given a bit larger impact based on more ferrous reduction	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO$_3^-$, NO$_2^-$	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f)
Pb(II)	0	0	30	30	10	300	No data available for these conditions, but Pb is not mobile under alkaline conditions	Expert opinion; no data or references for B-BX-BY Farms
U(VI)	0.3	0	3	2.5	0.6	15	Based on BX-102 and TX-104 field results	Serne et al. (2002c)
Radionuclides								
[241]Am(III)	10	0	150	600	200	2000	No data available for B-BX-BY Farms; Am shows very low mobility at T-106	Serne et al. (2004a) and Krupka et al. (2004)

Table A.7. (contd)

Table 3.7 Main Text B-BX-BY	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{14}C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters	Expert opinion; no data or references for B-BX-BY Farms
^{60}Co(II,III)	0	0	30	0	0	30	^{60}Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones	Expert opinion; no data or references for B-BX-BY Farms; used WMA T (Serne et al. 2004b)
^{137}Cs	1	0	30	100	30	3000	Cs at SX has K_d values from 0 to 10+ in high impact zone and then reach values up to high 100's in moderate salt; lowered high impact versus Last et al. (2006) but honored the intermediate impact zone; silt 3X increase over sand	Expert opinion; no data for B-BX-BY Farms; used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact
Eu(III)-isotopes	3	0	30	30	10	300	Eu in high impact zone often found in sediment likely as chelate; intermediate zone effectively captures all Eu; allowed 3X silt impacts assuming adsorption is as important as pH effects	Expert opinion; no data for B-BX-BY Farms; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes

Table 3.7 Main Text B-BX-BY	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{129}I	0	0	0	0.2	0	2	At SX-108, ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone and made no silt correction based on no "sorption sensitivity to surface area"	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone
^{63}Ni	0	0	30	10	3	60	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA	Expert opinion (assumed adsorption similar to Co)
^{237}Np(V)	0	0	15	10	2	50	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used values from IDF for sand; assumed silt impacts maximum value only	No data for B-BX-BY so used T WMA; Serne et al. (2004b) and IDF (Krupka et al. 2004)
Pu(all)-isotopes	5	0	150	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for High Impact; used Last et al. (2006) values for intermediate zone; silt impact values ~3X sand	No data for B-BX-BY Farms so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b, 2004b)

Table 3.7 Main Text B-BX-BY	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{226}Ra	3	0.6	60	10	5	60	No Ra studies for SST Vadose Zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones; used the 3X silt correction too	No data for B-BX-BY Farms so used Sr similarity and Last et al. (2006)
^{79}Se(VI,IV)	0	0	3	0.3	0	10	^{79}Se not studied at SST WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments; used 3X increase for silt	No data for B-BX-BY Farms; used Kaplan et al. (1998a, 1998b) and expert opinion
^{126}Sn(IV)	0	0	30	1.5	0	60	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; if ^{126}Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for B-BX-BY Farms; used Serne et al. (1993) and expert opinion
^{90}Sr	3	0.6	60	10	5	100	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at B-110 there was some mobility for a few tens of meters below tank; at T-106, there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones; used 3X increase for silt because Sr adsorption is quite sensitive to surface area	Serne et al. (2002a), Last et al. (2006), and expert opinion

Table A.7. (contd)

Table 3.7 Main Text B-BX-BY	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{99}Tc(VII)	0	0	0.2	0	0	5	At SX, T and other sites Tc seems completely mobile through High and Intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata	Little useful Tc data at B and BX; used Serne et al. (2002b, 2004a, 2004b), Last et al. (2006) and expert opinion

Table A.8. K_d Values for Sand-Dominated Sediments at Waste Management Area C for High and Intermediate Impact Zones (Table 3.9 Main Text)

Table 3.9 Main Text WMA C	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Chemicals								
F $^-$	0	0	0	0	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	1	0	3	0	0	3	Caustic condition leads to slight retardation based on SX boreholes	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO$_3$$^-$, NO$_2$$^-$	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f) and Brown et al. (2006)
Pb(II)	3	0	10	10	3	100	No data available for these conditions, but Pb is not mobile under alkaline conditions	Expert opinion; no data or references for C Farm
U(VI)	1	0.5	5	2	2	20	High and intermediate impact values based on C4297 in situ desorption K_d values (differ from Last et al. [2006] and other SST values)	Brown et al. (2006)

Table 3.9 Main Text WMA C	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
Radionuclides								
^{241}Am(III)	3	1	50	600	200	2000	No data available for C Farm; assumed high impact zone conservatively modeled with moderate K_d; intermediate zones comes from IDF and are based on Am not being sensitive to salt but rather pH; neutral pH high sorption	Krupka et al. (2004)
^{14}C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters; stayed "loyal" in part with Last et al. (2006) minimum-maximum ranges	Expert opinion; no data or references for C Tank Farm; minimum and maximum values from Last et al. (2006)
^{60}Co(II,III)	0	0	10	0	0	10	^{60}Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones; Field logging data at C Tank Farm suggests similar mobility	Expert opinion; no data or references for B-BX-BY Farms; used WMA T (Serne et al. 2004b)
^{137}Cs	10	10	50	100	10	1000	Cs at C WMA appears immobile even in high impact zone; at other SST boreholes K_d reaches values up to high 100's in moderate salt; same best value as Last et al. (2006) for high impact; Last et al. (2006) values honored the intermediate impact zone	Expert opinion; no in-situ desorption K_d data for C Farm; used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact

Table A.8. (contd)

Table 3.9 Main Text WMA C	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Eu(III)-isotopes	3	1	50	10	3	100	Eu in high impact zone assumed to be similar to Am; assumed that intermediate zone effectively captures all Eu	Expert opinion; no data for C Farm; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
^{129}I	0	0	0.2	0.2	0	2	At SX-108, ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone
^{63}Ni	0	0	10	3	1	20	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA	Expert opinion (assumed adsorption similar to Co)
^{237}Np(V)	0	0	5	10	2	30	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used values from IDF for sand	No data for C WMA so used T WMA; Serne et al. (2004b) and IDF (Krupka et al. 2004)

Table 3.9 Main Text WMA C	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Pu(all)-isotopes	3	1	50	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for High Impact; used Last et al. (2006) values for intermediate zone	No data for C Farm so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs –Serne et al. (2002b and 2004b)
^{226}Ra	1	0.2	20	10	5	20	No Ra studies for SST Vadose Zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones	No data for C Farm so used Sr similarity and Last et al. (2006)
^{79}Se(VI,IV)	0	0	3	0.1	0	3	^{79}Se not studied at SST WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments	No data for C Farm; used Kaplan et al. (1998a, 1998b) and expert opinion
^{126}Sn(IV)	0	0	10	0.5	0	20	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; if ^{126}Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for C Farm; used Serne et al. (1993) and expert opinion

Table A.8. (contd)

| Table 3.9 Main Text WMA C | Sand-Size Sediments – Tank Waste Impacted | | | | | | | |
| | High Impact | | | Intermediate Impact | | | | |
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{90}Sr	1	0.2	20	10	5	100	Have no data for C WMA; used Last et al. (2006) values for high impact zone; used B-110 for moderate zone	Serne et al. (2002a), Last et al. (2006), and expert opinion
^{99}Tc(VII)	0.1	0	1	0.1	0	3	At C and other sites, Tc seems completely mobile through High and Intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from C4297 borehole to give a better maximum range for different strata	Used Brown et al. (2006), Last et al. (2006), and expert opinion

Table A.9. K_d Values for Sand-Dominated Sediments at Waste Management Area S-SX for High and Intermediate Impact Zones (Table 3.13 Main Text)

Table 3.13 Main Text S-SX WMA	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Chemicals								
F $^-$	0	0	0	0	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	0.2	0	3	0	0	8	Caustic condition leads to slight retardation based on SX boreholes	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO$_3^-$, NO$_2^-$	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f)
Pb(II)	3	0	10	10	3	100	No data available for these conditions, but Pb is not mobile under alkaline conditions	Expert opinion; no data or references for S-SX Farms
U(VI)	0.1	0	10	0.8	0.2	17	High impact based on BX-102, where U quite mobile but not zero (differs from Last et al. (2006) and A-AX and C WMA values); used BX-102 for intermediate zone	Serne et al. (2002c)

Table 3.13 Main Text S-SX WMA	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Radionuclides								
^{241}Am(III)	3	0	50	600	200	2000	No data available for S-SX Farms; Am shows very low mobility at T-106; intermediate zone based on Am not being sensitive to salt but rather pH; neutral pH high sorption; used values from IDF	Serne et al. (2004a) and Krupka et al. (2004)
^{14}C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters	Expert opinion; no data or references for S-SX Farms
^{60}Co(II,III)	0	0	10	0	0	10	^{60}Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones	Expert opinion; no data or references for S-SX Farms; used WMA T (Serne et al. 2004b)
^{137}Cs	1	0	10	100	10	1000	Cs at SX has K_d values from 0 to 10+ in high impact zone and then reach values up to high 100's in moderate salt; lowered high impact versus Last (2006) but honored Last et al. (2006) for the intermediate impact zone	Used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact
Eu(III)-isotopes	1	0	10	10	3	100	Eu in high impact zone often found in sediment likely as chelate; intermediate zone effectively captures all Eu	Expert opinion; no data for S-SX Farms; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone

Table 3.13 Main Text S-SX WMA	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
^{129}I	0	0	0.2	0.2	0	2	At SX-108 ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone
^{63}Ni	0	0	10	3	1	20	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA	Expert opinion (assumed adsorption similar to Co)
^{237}Np(V)	0	0	5	10	2	30	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used values from IDF for sand	Used SX-108 and T WMA; Serne et al. (2002b, 2002f, 2004b) and IDF (Krupka et al. 2004)
Pu(all)-isotopes	3	0	50	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for high impact; used Last et al. (2006) values for intermediate zone	Water extract data for SX Farms below detection (Serne et al. 2002b, 2002f) so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b and 2004b)

Table 3.13 Main Text S-SX WMA	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
[226]Ra	1	0.2	20	10	5	20	No Ra studies for SST Vadose Zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones	No data for S-SX Farms so used Sr similarity and Last et al. (2006)
[79]Se(VI,IV)	0	0	3	0.1	0	3	[79]Se not studied at SST WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments	SX-108 (Serne et al. 2002f; Evans et al. 2002) shows Se fairly mobile but less so than nitrate/^{99}Tc; used Kaplan et al. (1998a, 1998b) and expert opinion
[126]Sn(IV)	0	0	10	0.5	0	20	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; if [126]Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for S-SX Farms; used Serne et al. (1993) and expert opinion
[90]Sr	1	0.2	20	10	5	20	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at B-110, there was some mobility for a few tens of meters below tank; at T-106, there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones	No ^{90}Sr at SX at detectable values so used Serne et al. (2002a), Last et al. (2006), and expert opinion
[99]Tc(VII)	0	0	1	0	0	5	At SX, T and other sites, Tc seems completely mobile through High and Intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata	Used in situ desorption K_d values from Serne et al. (2002b, 2002e, 2002f) and Last et al. (2006)

Table A.10. K_d Values for Waste Management Area S-SX Silt-Dominated Sediments for High and Intermediate Impact Zones (Table 3.13 Main Text)

Table 3.13 Main Text S-SX WMA	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Chemicals								
F⁻	0	0	0	0.05	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	0.4	0	8	0	0	10	Caustic condition leads to slight retardation based on SX boreholes	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO₃⁻, NO₂⁻	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f)
Pb(II)	0	0	30	30	10	300	No data available for these conditions, but Pb is not mobile under alkaline conditions; silts given 3X sand values	Expert opinion; no data or references for S-SX Farms
U(VI)	0.3	0	3	2.5	0.6	15	High impact based on BX-102, where U quite mobile but not zero (differs from Last et al. (2006) and A-AX and C WMA values); used BX-102 for intermediate zone; silts given 3X sand values	Serne et al. (2002c)

Table 3.13 Main Text S-SX WMA	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Radionuclides								
[241]Am(III)	10	0	150	600	200	2000	No data available for S-SX Farms; Am shows very low mobility at T-106; intermediate zone based on Am not being sensitive to salt but rather pH; neutral pH high sorption; used values from IDF; silts given 3X sand values	Serne et al. (2004a) and Krupka et al. (2004)
[14]C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters; did not increase for silt because not surface area sensitive or generally salt impacted	Expert opinion; no data or references for S-SX Farms
[60]Co(II,III)	0	0	30	0	0	30	[60]Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones	Expert opinion; no data or references for S-SX Farms; used WMA T (Serne et al. 2004b)
[137]Cs	1	0	30	100	30	3000	Cs at SX has K_d values from 0 to 10+ in high impact zone and then reach values up to high 100's in moderate salt; lowered high impact versus Last et al. (2006) but honored Last et al. (2006) for the intermediate impact zone; silt impacts yield 3X increase over sand	Used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact

Table 3.13 Main Text S-SX WMA	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Eu(III)-isotopes	3	0	30	30	10	300	Eu in high impact zone often found in sediment likely as chelate; allowed 3X silt impacts assuming adsorption is as important as pH effects	Expert opinion; no data for S-SX Farms; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
^{129}I	0	0	0	0.2	0	2	At SX-108 ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone; no silt correction based on no "sorption sensitivity to surface area"	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone
^{63}Ni	0	0	30	10	3	60	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA	Expert opinion (assumed adsorption similar to Co)
^{237}Np(V)	0	0	15	10	2	50	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used values from IDF for sand; silt impact is not as prevalent but does affect maximum K_d values	Used SX-108 and T WMA; Serne et al. (2002b, 2002f and 2004b) and IDF (Krupka et al. 2004)

Table 3.13 Main Text S-SX WMA	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Pu(all)-isotopes	5	0	150	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for High Impact; used Last et al. (2006) values for intermediate zone; silt impact values ~3X sand	Water extract data for SX Farms below detection (Serne et al. 2002b, 2002f) so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b and 2004b)
^{226}Ra	3	0.6	60	10	5	60	No Ra studies for SST vadose zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones; used the 3X sand values for silt	No data for S-SX Farms so used Sr similarity and Last et al. (2006)
^{79}Se(VI,IV)	0	0	3	0.3	0	10	^{79}Se not studied at SST WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments; used 3X increase for silt	SX-108 (Serne et al. 2002f, Evans et al. 2002) shows Se fairly mobile but less so than Nitrate/^{99}Tc used Kaplan et al. (1998a, 1998b) and expert opinion
^{126}Sn(IV)	0	0	30	1.5	0	60	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; if ^{126}Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for S-SX Farms; used Serne et al. (1993) and expert opinion

Table A.10. (contd)

Table 3.13 Main Text S-SX WMA	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
[90]Sr	3	0.6	60	10	5	100	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at B-110 there was some mobility for a few tens of meters below tank; at T-106 there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones; used 3X increase over sand values for silt	No ^{90}Sr at SX at detectable values so used Serne et al. (2002a), Last et al. (2006), and expert opinion
[99]Tc(VII)	0	0	1	0	0	5	At SX, T and other sites Tc seems completely mobile through High and Intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata	Used in situ desorption K_d values from Serne et al. (2002b, 2002e, 2002f) and Last et al. (2006)

Table A.11. K_d Values for Waste Management Area S-SX Carbonate-Dominated Sediments for High and Intermediate Impact Zones (Table 3.13 Main Text)

Table 3.13 Main Text S-SX WMA	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Chemicals								
F⁻	0	0	1	0.05	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	0.2	0	3	0	0	8	Caustic condition leads to slight retardation based on SX boreholes; carbonate rich sediment K_d values same as sand	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	Conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO₃⁻, NO₂⁻	0	0	0.1	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f)
Pb(II)	3	0	10	10	3	100	No data available for these conditions, but Pb is not mobile under alkaline conditions; silts given 3X sand values	Expert opinion; no data or references for S-SX Farms
U(VI)	0.3	0	30	2.5	0.6	30	High impact based on BX-102, where U quite mobile but not zero; used TX-104 carbonate sediment data from S&T	Serne et al. (2002c) and Appendix D of RPP (2005)

Table A.11. (contd)

Table 3.13 Main Text S-SX WMA	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Radionuclides								
[241]Am(III)	10	0	150	600	200	2000	No data available for S-SX Farms; Am shows very low mobility at T-106; intermediate zone based on Am not being sensitive to salt but rather pH; neutral pH high sorption; used values from IDF; for carbonate dominated assumed same as silt because some affinity of Am to carbonate solids	Serne et al. (2004a) and Krupka et al. (2004)
[14]C	5	0	50	1	0	100	No ^{14}C data available but carbonates interact at high pH via precipitation; did not increase for silt because not surface area sensitive or generally salt impacted; assumed carbonate sediments exchange ^{14}C for ^{12}C so use silt values; stayed "loyal" in part with Last et al. (2006) minimum-maximum ranges	Expert opinion; no data or references for S-SX Farms
[60]Co(II,III)	0	0	30	0	0	30	[60]Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones	Expert opinion; no data or references for S-SX Farms; used WMA T (Serne et al. 2004b)

Table 3.13 Main Text S-SX WMA	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{137}Cs	1	0	10	100	10	1000	Cs at SX has K_d values from 0 to 10+ in high impact zone and then reach values up to high 100's in moderate salt; lowered high impact versus Last (2006) but honored Last et al. (2006) for the intermediate impact zone; used silt values for carbonate rich sediments	Used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact
Eu(III)-isotopes	3	0	30	30	10	300	Eu in high impact zone often found in sediment likely as chelate; used silt values for carbonate dominated sediments (assumed some sorption to carbonates)	Expert opinion; no data for S-SX Farms; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
^{129}I	0	0	0	0.2	0	2	At SX-108, ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone; carbonate dominated sediments same as sand	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone

Table 3.13 Main Text S-SX WMA	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
[63]Ni	0	0	30	10	3	60	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA; used silt values for carbonate dominated sediments (assumed some sorption to carbonates)	Expert opinion (assumed adsorption similar to Co)
[237]Np(V)	0	0	15	10	2	50	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used silt values for carbonate dominated sediments (assumed some sorption to carbonates)	Used SX-108 and T WMA; Serne et al. (2002b, 2002f, 2004b) and IDF (Krupka et al. 2004)
Pu(all)-isotopes	3	0	50	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for high impact; used Last et al. (2006) values for intermediate zone; used sand values for carbonate rich sediments to be conservative	Water extract data for SX Farms below detection (Serne et al. 2002b,f) so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b, 2004b)
[226]Ra	3	0.6	60	10	5	60	No Ra studies for SST Vadose Zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones	No data for S-SX Farms so used Sr similarity and Last et al. (2006)

Table 3.13 Main Text S-SX WMA	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
[79]Se(VI,IV)	0	0	3	0.1	0	3	[79]Se not studied at SST WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments; for carbonate dominated sediments used sand values	SX-108 (Serne et al. 2002f; Evans et al. 2002) shows Se fairly mobile but less so than Nitrate/^{99}Tc used Kaplan et al. (1998a, 1998b) and expert opinion
[126]Sn(IV)	0	0	30	1.5	0	60	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH so allowed slight sorption in intermediate impact zone; used 3X increase for silt and carbonate dominated sediments	No data for S-SX Farms; used Serne et al. (1993) and expert opinion
[90]Sr	3	0.6	60	10	5	100	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at B-110; there was some mobility for a few tens of meters below tank; at T-106 there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones; used 3X increase for carbonate because Sr is sequestered by carbonates	No ^{90}Sr at SX at detectable values so used Serne et al. (2002a), Last et al. (2006) and expert opinion

Table A.11. (contd)

Table 3.13 Main Text S-SX WMA	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{99}Tc(VII)	0	0	1	0	0	5	At SX, T and other sites Tc seems completely mobile through High and Intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata; assumed no differences in adsorption for carbonate rich sediments	Used in situ desorption K_d values from Serne et al. (2002b, 2002e, 2002f) and Last et al. (2006)

Table A.12. K_d Values for Sand-Dominated Sediments at Waste Management Area T-TX-TY for High and Intermediate Impact Zones (Table 3.16 Main Text)

Table 3.16 Main Text WMA T-TX-TY	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Chemicals								
F⁻	0	0	0	0	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	0.2	0	3	0	0	8	Caustic condition leads to slight retardation based on SX boreholes; carbonate rich sediment K_d values same as sand	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO₃⁻, NO₂⁻	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f; 2004a, 2004b)
Pb(II)	3	0	10	10	3	100	No data available for these conditions, but Pb is not mobile under alkaline conditions	Expert opinion; no data or references for T-TX-TY Farms
U(VI)	0.2	0.06	0.6	0.8	0.2	17	High impact based on TX-104, where U quite mobile but not zero (differs from Last et al. (2006) and A-AX values); used BX-102 for intermediate zone	Serne et al. (2004a, 2002c)

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Table 3.16 Main Text WMA T-TX-TY	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
Radionuclides								
^{241}Am(III)	3	0	50	600	200	2000	Am shows very low mobility at T-106; intermediate zone based on Am not being sensitive to salt but rather pH; neutral pH high sorption; used values from IDF	Serne et al. (2004a) and Krupka et al. (2004)
^{14}C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters	Expert opinion; no data or references for T-TX-TY Farms
^{60}Co(II,III)	0	0	10	0	0	10	^{60}Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones	Used WMA T (Serne et al. 2004b)
^{137}Cs	1	0	10	100	10	1000	Cs at SX has K_d values from 0 to 10+ in high impact zone and then reach values up to high 100's in moderate salt; lowered high impact versus Last (2006) but honored Last et al. (2006) for the intermediate impact zone	Used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact; low mobility of ^{137}Cs at T-106 (Serne et al. 2004b)
Eu(III)-isotopes	1	0	10	10	3	100	Eu in high impact zone often found in sediment likely as chelate; intermediate zone effectively captures all Eu	Expert opinion; no data for S-SX Farms; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone

Table A.12. (contd)

Table 3.16 Main Text WMA T-TX-TY	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
^{129}I	0	0	0.2	0.2	0	2	At SX-108, ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone; no data for T or TX Farms	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone
^{63}Ni	0	0	10	3	1	20	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA	Expert opinion (assumed adsorption similar to Co)
^{237}Np(V)	0	0	5	10	2	30	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used values from IDF for sand	Used SX-108 and T WMA; Serne et al. (2002b, 2002f, 2004b) and IDF (Krupka et al. 2004)

Table 3.16 Main Text WMA T-TX-TY	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
Pu(all)-isotopes	3	0	50	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for high impact; used Last et al. (2006) values for intermediate zone	Water extract data for T Farm below detection (Serne et al. 2004b) so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b, 2004b)
[226]Ra	1	0.2	20	10	5	20	No Ra studies for SST vadose zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones	No data for T-TX-TY Farms so used Sr similarity and Last et al. (2006)
[79]Se(VI,IV)	0	0	3	0.1	0	3	[79]Se not studied at T or TX WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments	SX-108 (Serne et al. 2002f; Evans et al. 2002) shows Se fairly mobile but less so than nitrate and ^{99}Tc used Kaplan et al. (1998a, 1998b) and expert opinion
[126]Sn(IV)	0	0	10	0.5	0	20	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; if [126]Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for T-TX-TY Farms; used Serne et al. (1993) and expert opinion

Table A.12. (contd)

Table 3.16 Main Text WMA T-TX-TY	Sand-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{90}Sr	1	0.2	20	10	5	20	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at T-106, there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones	No water extractable ^{90}Sr at T-106 so high K_d – Serne et al. (2004b), used Last et al. (2006), and expert opinion
^{99}Tc(VII)	0	0	1	0	0	1	At T and TX and other sites Tc seems completely mobile through high and intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata	Used in situ desorption K_d values from Serne et al. (2004a, 2004b) and Last et al. (2006)

Table A.13. K_d Values for Waste Management Area T-TX-TY Silt-Dominated Sediments for High and Intermediate Impact Zones (Table 3.16 Main Text)

Table 3.16 Main Text WMA T-TX-TY	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
Chemicals								
F⁻	0	0	0	0.05	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	0.4	0	8	0	0	10	Caustic condition leads to slight retardation based on SX boreholes; carbonate rich sediment K_d values same as sand	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO₃⁻, NO₂⁻	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f; 2004a, 2004b)
Pb(II)	0	0	30	30	10	300	No data available for these conditions, but Pb is not mobile under alkaline conditions; silt K_d values given 3X sand values	Expert opinion; no data or references for T-TX-TY Farms

Table A.13. (contd)

Table 3.16 Main Text WMA T-TX-TY	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
U(VI)	0.3	0	3	2.5	0.6	15	High impact based on TX-104, where U quite mobile but not zero (differs from Last et al. [2006] and A-AX values); used BX-102 for intermediate zone; silt K_d values given 3X sand values	Serne et al. (2004a, 2002c)
Radionuclides								
^{241}Am(III)	10	0	150	600	200	2000	Am shows very low mobility at T-106; silt K_d values given 3X sand values; intermediate zone based on Am not being sensitive to salt but rather pH; neutral pH high sorption; used values from IDF	Serne et al. (2004a) and Krupka et al. (2004)
^{14}C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters; did not increase for silt because not surface area sensitive or generally salt impacted	Expert opinion; no data or references for T-TX-TY Farms
^{60}Co(II,III)	0	0	30	0	0	30	^{60}Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones	Used WMA T (Serne et al. 2004b)

Table 3.16 Main Text WMA T-TX-TY	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{137}Cs	1	0	30	100	30	3000	Low mobility of ^{137}Cs at T-106; silt K_d values given 3X sand values; lowered high impact versus Last (2006) but honored Last et al. (2006) for the intermediate impact zone	Used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact; low mobility of ^{137}Cs at T-106 (Serne et al. 2004b)
Eu(III)-isotopes	3	0	30	30	10	300	Eu in high impact zone often found in sediment likely as chelate; intermediate zone effectively captures all Eu; silt K_d values given 3X sand values	Expert opinion; no data for S-SX Farms; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
^{129}I	0	0	0	0.2	0	2	At SX-108, ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone; no data for T or TX Farms; made no silt correction based on no "sorption sensitivity to surface area"	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone

Table 3.16 Main Text WMA T-TX-TY	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
[63]Ni	0	0	30	10	3	60	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA	Expert opinion (assumed adsorption similar to Co)
[237]Np(V)	0	0	15	10	2	50	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; silt impact is not as prevalent but does affect maximum values	Used SX-108 and T WMA; Serne et al. (2002b, 2002f, 2004b) and IDF (Krupka et al. 2004)
Pu(all)-isotopes	5	0	150	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for high impact; used Last et al. (2006) values for intermediate zone; silt K_d values given 3X sand values	Water extract data for T Farm below detection (Serne et al. 2004b) so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b, 2004b)
[226]Ra	3	0.6	60	10	5	60	No Ra studies for SST Vadose Zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones; silt K_d values given 3X sand values	No data for T-TX-TY Farms so used Sr similarity and Last et al. (2006)

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Table 3.16 Main Text WMA T-TX-TY	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{79}Se(VI,IV)	0	0	3	0.3	0	10	^{79}Se not studied at T or TX WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments; silt K_d values given 3X sand values	SX-108 (Serne et al. 2002f; Evans et al. 2002) shows Se fairly mobile but less so than Nitrate/^{99}Tc used Kaplan et al. (1998a, 1998b) and expert opinion
^{126}Sn(IV)	0	0	30	1.5	0	60	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; silt K_d values given 3X sand values	No data for T-TX-TY Farms; used Serne et al. (1993) and expert opinion
^{90}Sr	3	0.6	60	10	5	100	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at T-106 there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones; silt K_d values given 3X sand values	No water extractable ^{90}Sr at T-106 so high K_d – Serne et al. (2004b); used Last et al. (2006) and expert opinion

Table A.13. (contd)

Table 3.16 Main Text WMA T-TX-TY	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{99}Tc(VII)	0	0	1	0	0	0.3	At T and TX and other sites, Tc seems completely mobile through High and Intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata	Used in situ desorption K_d values from Serne et al. (2004a, 2004b) and Last et al. (2006)

Table A.14. K_d Values for Waste Management Area T-TX-TY Carbonate-Dominated Sediments for High and Intermediate Impact Zones (Table 3.16 Main Text)

Table 3.16 Main Text WMA T-TX-TY	Carbonate-Dominated Sediments						Tank Waste Impacted	
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
Chemicals								
F $^-$	0	0	1	0.05	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	0.2	0	3	0	0	8	Caustic condition leads to slight retardation based on SX boreholes; carbonate rich sediment K_d values same as sand	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO$_3^-$, NO$_2^-$	0	0	0.1	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f; 2004a, 2004b)
Pb(II)	3	0	10	10	3	100	No data available for these conditions, but Pb is not mobile under alkaline conditions; carbonate K_d values given 3X sand values	Expert opinion; no data or references for T-TX-TY Farms

Table 3.16 Main Text WMA T-TX-TY	Carbonate-Dominated Sediments						Tank Waste Impacted	
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
U(VI)	0.3	0	30	2.5	0.6	30	High impact based on TX-104, where U quite mobile but not zero (differs from Last et al. (2006) and A-AX values); used BX-102 for intermediate zone; used TX-104 carbonate sediment data from S&T	Serne et al. (2004a, 2002c); Appendix D of RPP (2005); Zacahara et al. (2007a, 2007b)
Radionuclides								
^{241}Am(III)	10	0	150	600	200	2000	Am shows very low mobility at T-106; intermediate zone based on Am not being sensitive to salt but rather pH; neutral pH high sorption; used values from IDF; for carbonate dominated assumed same as silt because some affinity of Am to carbonate solids	Serne et al. (2004a) and Krupka et al. (2004)
^{14}C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters; assumed carbonate sediments exchange ^{14}C for ^{12}C so use silt values; stayed "loyal" in part with Last et al. (2006) minimum-maximum ranges	Expert opinion; no data or references for T-TX-TY Farms

Table A.14. (contd)

Table 3.16 Main Text WMA T-TX-TY	Carbonate-Dominated Sediments						Tank Waste Impacted	
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{60}Co(II,III)	0	0	30	0	0	30	^{60}Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones; carbonate sediment K_d values same as silt	Used WMA T (Serne et al. 2004b)
^{137}Cs	1	0	10	100	10	1000	Lowered high impact versus Last (2006) but honored Last et al. (2006) for the intermediate impact zone; carbonate sediment K_d values same as silt	Used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact; low mobility of ^{137}Cs at T-106 (Serne et al. 2004b)
Eu(III)-isotopes	3	0	30	30	10	300	Eu in high impact zone often found in sediment likely as chelate; intermediate zone effectively captures all Eu; used silt K_d values for carbonate dominated sediments (assumed some sorption to carbonates)	Expert opinion; no data for S-SX Farms; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes

Table 3.16 Main Text WMA T-TX-TY	Carbonate-Dominated Sediments						Tank Waste Impacted	
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{129}I	0	0	0	0.2	0	2	At SX-108 ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone; no data for T or TX Farms; carbonate sediment K_d values same as silt	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone
^{63}Ni	0	0	30	10	3	60	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA; carbonate sediment K_d values same as silt	Expert opinion (assumed adsorption similar to Co)
^{237}Np(V)	0	0	15	10	2	50	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; carbonate sediment K_d values same as silt	Used SX-108 and T WMA; Serne et al. (2002b, 2002f, 2004b) and IDF (Krupka et al. 2004)
Pu(all)-isotopes	3	0	50	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for high impact; used Last et al. (2006) values for intermediate zone; used sand K_d values for carbonate rich sediments to be conservative	Water extract data for T Farm below detection (Serne et al. 2004b) so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b, 2004b)

Table 3.16 Main Text WMA T-TX-TY	Carbonate-Dominated Sediments						Tank Waste Impacted	
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
[226]Ra	3	0.6	60	10	5	60	No Ra studies for SST vadose zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones; used silt values for carbonate dominated sediments except for maximum value which was 3X silt (assumed some sorption to carbonates)	No data for T-TX-TY Farms so used Sr similarity and Last et al. (2006)
[79]Se(VI,IV)	0	0	3	0.1	0	3	[79]Se not studied at T or TX WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments; used sand values for carbonate rich sediments to be conservative	SX-108 (Serne et al. 2002f; Evans et al. 2002) shows Se fairly mobile but less so than nitrate and ^{99}Tc; used Kaplan et al. (1998a, 1998b) and expert opinion
[126]Sn(IV)	0	0	30	1.5	0	60	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; if [126]Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for T-TX-TY Farms; used Serne et al. (1993) and expert opinion; used silt values for carbonate dominated sediments (assumed some sorption to carbonates)

Table A.14. (contd)

Table 3.16 Main Text WMA T-TX-TY	Carbonate-Dominated Sediments						Tank Waste Impacted	
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
[90]Sr	3	0.6	60	10	5	100	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at T-106 there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones; used 3X sand K_d values for carbonate rich sediments; ^{90}Sr is sequestered by carbonates	No water extractable ^{90}Sr at T-106 so high K_d – Serne et al. (2004b), used Last et al. (2006) and expert opinion
[99]Tc(VII)	0	0	1	0	0	1	At T and TX and other sites Tc seems completely mobile through high and intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata; assumed no differences from sand K_d values for carbonate rich sediments	Used in situ desorption K_d values from Serne et al. (2004a, 2004b) and Last et al. (2006)

Table A.15. K_d Values for Waste Management Area U Sand-Dominated Sediments for High and Intermediate Impact Zones
(Table 3.20 Main Text)

Table 3.20 Main Text WMA U	Sand-Size Sediments –Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
Chemicals								
F $^-$	0	0	0	0	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	0.2	0	3	0	0	8	Caustic condition leads to slight retardation based on SX boreholes; carbonate rich sediment K_d values same as sand	Values from Serne et al. (2002b); and Brown et al. (2007) mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO$_3^-$, NO$_2^-$	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f; 2004a, 2004b)
Pb(II)	3	0	10	10	3	100	No data available for these conditions, but Pb is not mobile under alkaline conditions	Expert opinion; no data or references for U Farm

Table A.15. (contd)

Table 3.20 Main Text WMA U	Sand-Size Sediments –Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
U(VI)	0.1	0	2	0.2	0.2	0.7	High impact based on TX-104, where U quite mobile but not zero (differs from Last et al. (2006) and A-AX values); used combination of BX-102 and U Farm direct push for intermediate zone; U-104 was same BiPO4 waste as BX-102	Serne et al. (2004a, 2002c) and Brown et al. (2007)
Radionuclides								
[241]Am(III)	3	0	50	600	200	2000	Am shows very low mobility at T-106; intermediate zone based on Am not being sensitive to salt but rather pH; neutral pH high sorption; used values from IDF	Serne et al. (2004a) and Krupka et al. (2004)
[14]C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters	Expert opinion; no data or references for U Farm
[60]Co(II,III)	0	0	10	0	0	10	[60]Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones	No studies at WMA U so used WMA T (Serne et al. 2004b)

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Table 3.20 Main Text WMA U	Sand-Size Sediments –Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{137}Cs	1	0	10	100	10	1000	Cs at SX has K_d values from 0 to 10+ in high impact zone and then reach values up to high 100's in moderate salt; lowered high impact versus Last et al. (2006) but honored Last et al. (2006) for the intermediate impact zone	No studies at U; used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact; low mobility of ^{137}Cs at T-106 (Serne et al. 2004b)
Eu(III)-isotopes	1	0	10	10	3	100	Eu in high impact zone often found in sediment likely as chelate; intermediate zone effectively captures all Eu	Expert opinion; no data for U Farm; so used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
^{129}I	0	0	0.2	0.2	0	2	At SX-108 ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone; no data for T or TX Farms	No studies at U Farm so expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone

Table 3.20 Main Text WMA U	Sand-Size Sediments –Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{63}Ni	0	0	10	3	1	20	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA	Expert opinion (assumed adsorption similar to Co)
^{237}Np(V)	0	0	5	10	2	30	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used values from IDF for sand	Used SX-108 and T WMA; Serne et al. (2002b, 2002f, 2004b) and IDF (Krupka et al. 2004)
Pu(all)-isotopes	3	0	50	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for high impact; used Last et al. (2006) values for intermediate zone	No studies at U Farm so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b, 2004b)
^{226}Ra	1	0.2	20	10	5	20	No Ra studies for SST vadose zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones	No data for U Farm so used Sr similarity and Last et al. (2006)

Table A.15. (contd)

Table 3.20 Main Text WMA U	Sand-Size Sediments –Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
[79]Se(VI,IV)	0	0	3	0.1	0	3	[79]Se not studied at T or TX WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments	SX-108 (Serne et al. 2002f; Evans et al. 2002) shows Se fairly mobile but less so than Nitrate/^{99}Tc used Kaplan et al. (1998a, 1998b) and expert opinion
[126]Sn(IV)	0	0	10	0.5	0	20	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; if [126]Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for U Farm; used Serne et al. (1993) and expert opinion
[90]Sr	1	0.2	20	10	5	20	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at T-106 there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones	No studies at U Farm; used Last et al. (2006) and expert opinion

Table A.15. (contd)

| Table 3.20 Main Text WMA U | Sand-Size Sediments –Tank Waste Impacted | | | | | | | |
| | High Impact | | | Intermediate Impact | | | | |
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{99}Tc(VII)	0	0	1	0	0	5	At T and TX and other sites, Tc seems completely mobile through high and intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata; very recent data from U Farm direct push (the data is considered to reflect intermediate impact zone) show K_d varies from 0.02 to 0.3 with an average of 0.03 for three data points with best analytical pedigree	Used in situ desorption K_d values from Serne et al. (2004a, 2004b), Last et al. (2006) and considered the new U Farm direct push data set (5 data) in Brown et al. (2007) Table 4.40

Table A.16. K_d Values for Waste Management Area U Silt-Dominated Sediments for High and Intermediate Impact Zones
(Table 3.20 Main Text)

Table 3.20 Main Text WMA U	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Chemicals								
F$^-$	0	0	0	0.05	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	0.4	0	8	0	0	10	Caustic condition leads to slight retardation based on SX boreholes; silt K_d values given ~2 to 3X sand values	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO$_3^-$, NO$_2^-$	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f; 2004a, 2004b)
Pb(II)	0	0	30	30	10	300	No data available for these conditions, but Pb is not mobile under alkaline conditions; silt K_d values given 3X sand values	Expert opinion; no data or references for U Farm

A.67

Table A.16. (contd)

Table 3.20 Main Text WMA U	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
U(VI)	0.3	0	3	2.5	0.6	15	High impact based on TX-104, where U quite mobile but not zero (differs from Last et al. (2006) and A-AX values); used BX-102 for intermediate zone; U-104 leak was BiPO4 waste same as BX-102; silt K_d values given 3X sand values	Serne et al. (2004a, 2002c)
Radionuclides								
^{241}Am(III)	10	0	150	600	200	2000	Am shows very low mobility at T-106; intermediate zone based on Am not being sensitive to salt but rather pH; neutral pH high sorption; used values from IDF; silt K_d values given 3X sand values	No sediment studies at U; used Serne et al. (2004a) and Krupka et al. (2004)
^{14}C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters; made no silt correction based on no "sorption sensitivity to surface area"	Expert opinion; no data or references for U Farm
^{60}Co(II,III)	0	0	30	0	0	30	^{60}Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones; silt K_d values given 3X sand values	No studies at WMA U so used WMA T (Serne et al. 2004b)

Table 3.20 Main Text WMA U	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{137}Cs	1	0	30	100	30	3000	Cs at SX has K_d values from 0 to 10+ in high impact zone and then reach values up to high 100's in moderate salt; lowered high impact versus Last et al. (2006) but honored Last et al. (2006) for the intermediate impact zone; silt K_d values given 3X sand values	No studies at U so used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact; low mobility of ^{137}Cs at T-106 (Serne et al. 2004b)
Eu(III)-isotopes	3	0	30	30	10	300	Eu in high impact zone often found in sediment likely as chelate; intermediate zone effectively captures all Eu; silt K_d values given 3X sand values	Expert opinion; no data for U Farm; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
^{129}I	0	0	0	0.2	0	2	At SX-108, ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone; made no silt correction based on no "sorption sensitivity to surface area"	No studies at U Farm so used expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone

Table A.16. (contd)

Table 3.20 Main Text WMA U	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
[63]Ni	0	0	30	10	3	60	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA; silt K_d values given ~2 to 3X sand values	Expert opinion (assumed adsorption similar to Co)
[237]Np(V)	0	0	15	10	2	50	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used values from IDF for sand; silt impact is not as prevalent but does affect maximum values	Used SX-108 and T WMA; Serne et al. (2002b, 2002f, 2004b) and IDF (Krupka et al. 2004)
Pu(all)-isotopes	5	0	150	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for high impact; used Last et al. (2006) values for intermediate zone; silt K_d values given ~3X sand values	No studies at U Farm so used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b, 2004b)

| Table 3.20 Main Text WMA U | Silt-Size Sediments – Tank Waste Impacted | | | | | | | |
| | High Impact | | | Intermediate Impact | | | | |
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
^{226}Ra	3	0.6	60	10	5	60	No Ra studies for SST vadose zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones; silt K_d values given ~3X sand values	No data for U Farm so used Sr similarity and Last et al. (2006)
^{79}Se(VI,IV)	0	0	3	0.3	0	10	^{79}Se not studied at T or TX WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments; silt K_d values given ~3X sand values	SX-108 (Serne et al. 2002f; Evans et al. 2002) shows Se fairly mobile but less so than nitrate and ^{99}Tc; used Kaplan et al. (1998a, 1998b) and expert opinion
^{126}Sn(IV)	0	0	30	1.5	0	60	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; silt K_d values given 3X sand values; if ^{126}Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for U Farm; used Serne et al. (1993) and expert opinion
^{90}Sr	3	0.6	60	10	5	100	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at T-106 there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones; silt K_d values given 3X sand values	No studies at U Farm; used Last et al. (2006) and expert opinion

Table A.16. (contd)

Table 3.20 Main Text WMA U	Silt-Size Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{99}Tc(VII)	0	0	1	0	0	5	At T and TX and other sites, Tc seems completely mobile through high and intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata; made no silt correction based on no "sorption sensitivity to surface area"	No sediment studies at U Farm; used in situ desorption K_d values from Serne et al. (2004a, 2004b) and Last et al. (2006)

Table A.17. K_d Values for Waste Management Area U Carbonate-Dominated Sediments for High and Intermediate Impact Zones (Table 3.20 Main Text)

Table 3.20 Main Text WMA U	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
Chemicals								
F⁻	0	0	1	0.05	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	0.2	0	3	0	0	8	Caustic condition leads to slight retardation based on SX boreholes; carbonate rich sediment K_d values same as sand	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO₃⁻, NO₂⁻	0	0	0.1	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f; 2004a, 2004b)
Pb(II)	3	0	10	10	3	100	No data available for these conditions, but Pb is not mobile under alkaline conditions; for carbonate dominated assumed same as silt because some affinity of Pb to carbonate solids	Expert opinion; no data or references for T-TX-TY Farms

Table A.17. (contd)

Table 3.20 Main Text WMA U	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
U(VI)	0.3	0	30	2.5	0.6	30	High impact based on TX-104, where U quite mobile but not zero (differs from Last et al. (2006) and A-AX values); used BX-102 for intermediate zone; used TX-104 carbonate sediment data	Serne et al. (2004a, 2002c) and Appendix D of RPP (2005)
Radionuclides								
[241]Am(III)	10	0	150	600	200	2000	Am shows very low mobility at T-106; intermediate zone based on Am not being sensitive to salt but rather pH; neutral pH high sorption; used values from IDF; for carbonate dominated assumed same as silt because some affinity of Am to carbonate solids	No sediment studies at U so used Serne et al. (2004a) and Krupka et al. (2004)
[14]C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters; assumed carbonate sediments exchange ^{14}C for ^{12}C; stayed loyal in part with Last et al. (2006) minimum-maximum ranges	Expert opinion; no data or references for U Farm
[60]Co(II,III)	0	0	30	0	0	30	[60]Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones; for carbonate dominated assumed same K_d values as silt	No studies at WMA U so used WMA T (Serne et al. 2004b)

Table 3.20 Main Text WMA U	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{137}Cs	1	0	10	100	10	1000	Cs at SX has K_d values from 0 to 10+ in high impact zone and then reach values up to high 100's in moderate salt; lowered high impact versus Last et al. (2006) but honored Last et al. (2006) for the intermediate impact zone; for carbonate dominated, assumed same K_d values as silt	No studies at U so used Serne et al. (2002b, 2002f) for high impact zone and Last et al. (2006) for intermediate impact; low mobility of ^{137}Cs at T-106 (Serne et al. 2004b)
Eu(III)-isotopes	3	0	30	30	10	300	Eu in high impact zone often found in sediment likely as chelate; intermediate zone effectively captures all Eu; used silt K_d values for carbonate dominated sediments (assumed some sorption to carbonates)	Estimated based on expert opinion; no data for U Farm; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
^{129}I	0	0	0	0.2	0	2	At SX-108 ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone; made no carbonate K_d correction based on no "sorption sensitivity to surface area"	No studies at U Farm, so used expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone

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Table 3.20 Main Text WMA U	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
[63]Ni	0	0	30	10	3	60	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA; carbonate sediment K_d values same as silt	Estimated based on expert opinion (assumed adsorption similar to Co)
[237]Np(V)	0	0	15	10	2	50	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used silt values for carbonate dominated sediments (assumed some sorption to carbonates)	Used SX-108 and T WMA from Serne et al. (2002b, 2002f, 2004b) and IDF (Krupka et al. 2004)
Pu(all)-isotopes	3	0	50	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too low; used IDF values for high impact; used Last et al. (2006) values for intermediate zone; used sand K_d values for carbonate rich sediments to be conservative	No studies at U Farm; used IDF (Krupka et al. 2004) for high impact zone and Last et al. (2006) for intermediate zone; field observations of little mobility at SX and T WMAs – Serne et al. (2002b, 2004b)
[226]Ra	3	0.6	60	10	5	60	No Ra studies for SST vadose zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones; for carbonate dominated assumed same K_d values as silt	No data for U Farm; used Sr similarity and Last et al. (2006)

Table 3.20 Main Text WMA U	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
[79]Se(VI,IV)	0	0	3	0.1	0	3	[79]Se not studied at T or TX WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments; assumed no differences in sand K_d values for carbonate rich sediments	SX-108 (Serne et al. 2002f; Evans et al. 2002) shows Se fairly mobile but less so than nitrate and ^{99}Tc; used Kaplan et al. (1998a, 1998b) and expert opinion
[126]Sn(IV)	0	0	30	1.5	0	60	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; for carbonate dominated assumed same K_d values as silt; if [126]Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for U Farm; used Serne et al. (1993) and expert opinion
[90]Sr	3	0.6	60	10	5	100	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at T-106 there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones; for carbonate dominated assumed same K_d values as silt because Sr is sequestered by carbonates	No studies at U Farm; used Last et al. (2006) and expert opinion

Table A.17. (contd)

Table 3.20 Main Text WMA U	Carbonate-Dominated Sediments – Tank Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{99}Tc(VII)	0	0	1	0	0	5	At T and TX and other sites Tc seems completely mobile through High and Intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from the boreholes to give a better maximum range for different strata; made no carbonate correction versus sand K_d values	No sediment studies at U Farm so used in situ desorption K_d values from Serne et al. (2004a, 2004b) and Last et al. (2006)

Table A.18. K_d Values for Sand-Dominated Sediments at BC Cribs for High and Intermediate Impact Zones (Table 3.22 Main Text)

Table 3.22 Main Text BC Cribs	Sand-Size Sediments – Crib Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
Chemicals								
F⁻	0	0	0	0	0	1	Assumed no sorption except on fine-grained sediment; B-110 had high F that was relatively deep in profile	Expert opinion and F deep in sediment profile at B-110 – Serne et al. (2002a)
Cr(VI)	1	0	3	0	0	3	Caustic condition leads to slight retardation based on SX boreholes	Values from Serne et al. (2002b); mechanisms from Ginder-Vogel et al. (2005), He et al. (2005), Qafoku et al. (2003), and Zachara et al. (2003)
Hg(II)	0	0	0	0	0	0	No data available; conservative assumptions used until reach no impact zone where INEL data (Rousseau et al. 2005) is a surrogate to Hanford	Conservative estimates based on expert opinion
NO₃⁻, NO₂⁻	0	0	0	0	0	0.1	Nitrate is generally at the front of vadose zone plumes at all sites studied	Serne et al. (2002a, 2002b, 2002c, 2002d, 2002e, 2002f)
Pb(II)	3	0	10	10	3	100	No data available for these conditions, but Pb is not mobile under alkaline conditions	Expert opinion; no data or references for BC cribs
U(VI)	20	1	50	1	1	50	High impact based on borehole C4191 where U not mobile; U in high salt intermediate zone is quite mobile but not zero (differs from Last et al. (2006) and SST values)	Serne and Mann (2004)

Table A.18. (contd)

Table 3.22 Main Text BC Cribs	Sand-Size Sediments – Crib Waste Impacted							
	High Impact			Intermediate Impact				
	Best	Minimum	Maximum	Best	Minimum	Maximum	Comments	References
Radionuclides								
[241]Am(III)	20	1	50	600	200	2000	Assumed high impact zone similar to U with little movement in high impact zone; intermediate zones comes from IDF and are based on Am not being sensitive to salt but rather pH; neutral pH high sorption	Serne et al. (2004a) and Krupka et al. (2004)
[14]C	5	0	50	1	0	100	No data available for any Tank WMAs; calcite insoluble at high pH in Hanford pore waters	Expert opinion; no data or references for BC cribs
[60]Co(II,III)	0	0	10	0	0	10	[60]Co at T-106 and TX-107 appears mobile in water extracts throughout H2, CCU; likely chelated so honor high mobility throughout both impact zones	Expert opinion; no data or references for BC cribs; used WMA T (Serne et al. 2004b)
[137]Cs	30	10	50	100	10	1000	Cs at BC immobile even in high impact zone; at other SST boreholes K_d reaches values up to high 100's in moderate salt; lowered high impact versus Last et al. (2006) but honored the intermediate impact zone	Serne and Mann (2004) shows low mobility for high impact zone and Last et al. (2006) for intermediate impact
Eu(III)-isotopes	20	1	50	10	3	100	Eu in high impact zone assumed to be similar to U; assumed that intermediate zone effectively captures all Eu	Expert opinion; no data for BC cribs; used Serne et al. (2004b) for high impact zone and expert opinion for intermediate impact zone

Table 3.22 Main Text BC Cribs	Sand-Size Sediments – Crib Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{3}H	0	0	0	0	0	0	Very little tritium data for SST vadose zone sediments but it was found in perched water at BX-102; assumed mobile in all impact zones based on groundwater plumes	Expert opinion and observation of widespread groundwater plumes
^{129}I	0	0	0.2	0.2	0	2	At SX-108 ^{129}I seemed completely mobile through high impact zone, so lowered from Last et al. (2006); honored Last et al. (2006) for intermediate zone	Expert opinion and Serne et al. (2002b) for high impact zone and Last et al. (2006) for intermediate impact zone
^{63}Ni	0	0	10	3	1	20	No Ni data; assumed it is same as ^{60}Co in high impact zone but shows some competitive sorption in intermediate zone because chelate complexes will break apart unlike Co(III)-EDTA	Expert opinion (assumed adsorption similar to Co)
^{237}Np(V)	0	0	5	10	2	30	Only saw faint hits of Np at SX and T-106 and it remained near tank bottoms; could not get a desorption K_d because activity too small; used values from IDF for sand	No data for BC cribs; used T WMA; Serne et al. (2004b) and IDF (Krupka et al. 2004)
Pu(all)-isotopes	20	1	50	600	200	2000	Only saw faint hits of Pu at SX and T-106 and it remained near tank bottoms; used values estimated for U at B-26 crib; used Last et al. (2006) values for intermediate zone	No data for BC cribs so used B-26 U values as chemical analog for high impact zone and Last et al. (2006) for intermediate zone

Table A.18. (contd)

Table 3.22 Main Text BC Cribs	Sand-Size Sediments – Crib Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
[226]Ra	1	0.2	20	10	5	20	No Ra studies for SST vadose zone; used ^{90}Sr data and honored Last et al. (2006) for both impact zones	No data for BC so used Sr similarity and Last et al. (2006)
[79]Se(VI,IV)	0	0	3	0.1	0	3	[79]Se not studied at SST WMAs; estimated no sorption in high impact zones, but allowed some sorption in intermediate zones based on Kaplan sorption versus pH work on IDF sediments	No data for BC cribs; used Kaplan et al. (1998a, 1998b) and expert opinion
[126]Sn(IV)	0	0	10	0.5	0	20	No study for Sn so allowed no sorption in high impact zone; Sn is not soluble at neutral-to-high pH values based on Serne et al. (1993) so allowed slight sorption in intermediate impact zone; if [126]Sn becomes a risk driver, a more realistic appraisal is warranted because Sn should not be mobile	No data for BC cribs used Serne et al. (1993) and expert opinion
[90]Sr	1	0.2	20	10	5	100	Only B-110 and T-106 showed elevated ^{90}Sr in vadose zone; at B-110 there was some mobility for a few tens of meters below tank; at T-106 there was not much movement of ^{90}Sr below tank bottom; used Last et al. (2006) values for both impact zones	Serne et al. (2002a), Last et al. (2006), and expert opinion

Table A.18. (contd)

Table 3.22 Main Text BC Cribs	Sand-Size Sediments – Crib Waste Impacted							
	High Impact			Intermediate Impact			Comments	References
	Best	Minimum	Maximum	Best	Minimum	Maximum		
^{99}Tc(VII)	0.1	0	1	0.1	0	3	At B-26 and other sites Tc seems completely mobile through high and intermediate impact zones; used Last et al. (2006) for best and minimum values and some of the in situ desorption K_d values from B-26 borehole to give a better maximum range for different strata	Used Serne and Mann (2004), Last et al. (2006), and expert opinion

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