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**Pacific Northwest  
National Laboratory**

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## Characterization of Direct Push Vadose Zone Sediments from the T and TY Waste Management Areas

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June 2007

Prepared for the U.S. Department of Energy  
under Contract DE-AC05-76RL01830



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Pacific Northwest National Laboratory  
Richland, Washington 99352



## Executive Summary

The overall goals of the Tank Farm Vadose Zone Project, led by CH2M HILL Hanford Group, Inc., are: 1) to define risks from past and future single-shell tank farm activities, 2) to identify and evaluate the efficacy of interim measures, and 3) to aid, via collection of geochemical information and data, the future decisions that must be made by the U.S. Department of Energy (DOE) regarding the near-term operations, future waste retrieval, and final closure activities for the single-shell tank Waste Management Areas (WMAs). For a more complete discussion of the goals of the Tank Farm Vadose Zone Project, see the overall work plan, *Phase 1 RCRA Facility Investigation/Corrective Measures Study Work Plan for the Single-Shell Tank Waste Management Areas* (DOE 1999). Specific details on the rationale for activities performed at WMAs T and TX-TY are found in Crumpler (2002). To meet these goals, CH2M HILL Hanford Group, Inc., asked scientists from Pacific Northwest National Laboratory (PNNL) to perform detailed analyses of vadose zone sediment collected within the T and TY Tank Farms. Specifically, this report contains all the geologic, geochemical, and selected physicochemical characterization data compiled on vadose zone sediment recovered from direct push samples collected near tanks 241-TY-105 and 241-TY-106 in the TY single-shell tank farm and near tanks 241-T-101 and 241-T-104 in the T single-shell tank farm. Additionally, this report compiles data from direct push samples collected north of the T Tank Farm in support of interim measures.

A geochemical investigation in the vicinity of tanks 241-TY-105 and 241-TY-106 was performed using pairs of direct push probe holes. A total of 31 direct pushes were driven within the TY Tank Farm; 25 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 241-TY-105, which was estimated to have leaked 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 241-TY-106, which was estimated to have leaked 20,000 gal of TBP-uranium recovery waste to the vadose zone in 1959 (UPR-W-153).

Additionally, this report contains 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 a leak from tank 241-T-101. Deaton (DOE 1992) postulated that a leak from tank 241-T-101 resulted in a loss of 28,390 liters (7,500 gallons) of tank waste to the subsurface. This event was the basis for placing tank 241-T-101 on the list of assumed/known leakers. It has been estimated that 1230 Ci of cesium-137, 0.0434 Ci of cobalt-60, and 0.382 Ci of technetium-99 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 241-T-101 and 241-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 1.5 feet 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 successfully driven for the purpose of collecting vadose zone sediment samples.

A core log was generated for both sets of samples (T and TY direct push campaigns, respectively) and a visual geologic evaluation of all sediment samples was performed at the time of liner processing. Aliquots of sediment from the liners were analyzed and characterized in the laboratory for the following parameters: moisture content, gamma-emitting radionuclides, one-to-one 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, technetium-99 and uranium-238, along with other trace metals, were determined in acid and water extracts using inductively coupled plasma-mass spectrometry (ICP-MS). All of the parameters were elevated in at least some of the samples analyzed as part of this study.

The distribution of the 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. The depth profiles for the divalent alkaline earth cations (calcium, magnesium, and strontium) versus sodium show depleted alkaline earth cation concentrations in the shallow Hanford formation sediments at both locations to depths of up to 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 the contamination has been present for a sufficiently long period of time to facilitate the migration of more mobile contaminants (i.e., nitrate and technetium-99) 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, there is no question that the vadose zone surrounding tank 241-TY-106 has been contaminated by tank-related waste. The direct observance of elevated soil pH and cesium-137 in close proximity to tank 241-TY-106 indicates that the tank or infrastructure associated with the tank is responsible for the contamination. The poor sediment recovery associated with the direct push technique has made it difficult to estimate the lateral spread of the contamination, while the capabilities of the direct push technique has made it impossible to determine the vertical extent of the contamination. However, based on characterization of the three probe holes that were emplaced south of tank 241-TY-106, it does not appear that a significant amount of lateral migration has occurred at the depths 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 the confirmation of this hypothesis.

The vadose zone south tank 241-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 on the sediment. The lack of 1) elevated soil pH or 2) detection 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 241-TY-105. The lack of direct evidence of a point source waste signature near tank 241-TY-105 does not mean that the tank did not leak; rather, the vadose zone sediment collected as part of this investigation was not sufficient to either confirm or rebut the supposition that a leak from tank 241-TY-105 led to UPR 200-W-152.

After evaluating all the characterization and analytical data associated with the T Tank Farm direct push campaign, there is no question that the vadose zone in the vicinity of tank 241-T-101 has been contaminated by tank-related waste. The direct observance of elevated soil pH, porewater-corrected electrical conductivity, nitrate, technetium-99, elevated water-extractable sodium, and fission product isotopes of europium as well as cesium-137 in close proximity to tank 241-T-101 indicate that the tank or infrastructure associated with the tank is responsible for the contamination. The sparse sample coverage associated with the direct push technique has made it difficult to estimate the lateral spread of the contamination, while the nature of the direct push technique has made it impossible to determine the vertical extent of the contamination. However, based on characterization of the probe holes that were emplaced to the southeast of tank 241-T-101, it appears that waste from tank 241-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, the lack of depth-discrete samples does not enable the confirmation of this hypothesis.

The vadose zone directly northeast of tank 241-T-104 also has been 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 does not exist to determine if the contamination observed in this region is a result of a loss from tank 241-T-104 or if it is a result of lateral spreading of waste from tank 241-T-101.



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# Contents

Executive Summary .....	iii
Acknowledgements .....	vii
Acronyms and Abbreviations .....	xv
Units of Measure .....	xvi
1.0 Introduction .....	1.1
2.0 Geology .....	2.1
2.1 Characterization and Sampling Methods .....	2.6
2.2 Interpreted Geology Related to Direct-Push Samples .....	2.12
3.0 Geochemical Methods and Materials .....	3.1
3.1 Sample Inventory .....	3.1
3.1.1 TY Tank Farm Direct Push Samples .....	3.1
3.1.2 T Tank Farm Direct Push Samples .....	3.1
3.2 Approach .....	3.1
3.3 Materials and Methods .....	3.3
3.3.1 Moisture Content .....	3.3
3.3.2 1:1 Sediment:Water Extracts .....	3.3
3.3.3 Technetium-99 Extraction and Analysis .....	3.5
3.3.4 Stable Ruthenium Analysis .....	3.6
4.0 Results and Discussion .....	4.1
4.1 Vadose Zone Sediment from the TY Tank Farm Direct Push Samples .....	4.1
4.1.1 Moisture Content .....	4.1
4.1.2 1:1 Sediment:Water Extracts .....	4.2
4.1.3 Vadose Zone Porewater Chemical Composition .....	4.11
4.1.4 8 M Nitric Acid-Extractable Amounts of Selected Elements in the TY Tank Farm Direct Push Sediments .....	4.18
4.1.5 Radionuclide Content in Vadose Zone Sediment from the TY Tank Farm Direct Push Holes .....	4.20
4.1.6 Total Carbon, Calcium Carbonate, and Organic Carbon Content of Vadose Zone Sediment from the TY Tank Farm Direct Push Holes .....	4.22
4.2 Vadose Zone Sediment from the T Tank Farm Direct Push Samples .....	4.22
4.2.1 Moisture Content .....	4.22
4.2.2 1:1 Sediment:Water Extracts .....	4.22
4.2.3 Vadose Zone Porewater Chemical Composition .....	4.37
4.2.4 8 M Nitric Acid-Extractable Amounts of Selected Elements in the TY Tank Farm Direct Push Sediments .....	4.42
4.2.5 Radionuclide Content in Vadose Zone Sediment from the TY Tank Farm Direct Push Holes .....	4.46
4.2.6 Total Carbon, Calcium Carbonate, and Organic Carbon Content of Vadose Zone Sediment from the TY Tank Farm Direct Push Holes .....	4.49

4.3	Tier II Sample Investigations .....	4.49
4.3.1	Technetium-99 Extraction and Analysis .....	4.50
4.3.2	Stable Ruthenium Isotopic Analysis .....	4.55
4.3.3	Estimating Recharge Using 1:1 Sediment:Water Extract Chloride Data .....	4.61
5.0	Summary and Observations.....	5.1
5.1	T and TX-TY Tank Farms Physical Geology Model .....	5.1
5.2	TY Tank Farm Characterization Activities and Data.....	5.1
5.2.1	Sampling Summary at the TY Tank Farm .....	5.1
5.2.2	Moisture Content.....	5.2
5.2.3	Contamination Profile around tanks 241-TY-105 and 241-TY-106 .....	5.2
5.2.4	Source of Contamination around Tanks 241-TY-105 and 241-TY-106 .....	5.3
5.3	T Tank Farm Characterization Activities and Data.....	5.4
5.3.1	Sampling Summary at the T Tank Farm .....	5.4
5.3.2	Moisture Content.....	5.4
5.3.3	Contamination Profile around Tank 241-T-101 .....	5.5
5.3.4	Tier II Activities Associated with the T Tank Farm Direct Push Samples .....	5.6
5.3.5	Source of Contamination around tanks 241-T-101 and 241-T-104 .....	5.9
5.4	Detailed Characterization to Elucidate Controlling Geochemical Processes at the T and TY Tank Farms .....	5.10
6.0	Interim Measures Support .....	6.1
7.0	References .....	7.1
Appendix A – Photographs of Core and Grab Samples from the Direct Push Boreholes in the Vicinity of Single-Shell Tanks 241-TY-105 and 241-TY-106.....		A.1
Appendix B – Logs of Core and Grab Samples from the Direct Push Boreholes in the Vicinity of Single-Shell Tanks 241-TY-105 and 241-TY-106 .....		B.1
Appendix C – Photographs of Core and Grab Samples from the Direct Push Boreholes in the Vicinity of Single Shell Tanks 241-T-101 and 241-T-104.....		C.1
Appendix D – Logs of Core and Grab Samples from the Direct Push Boreholes in the Vicinity of Single Shell Tanks 241-T-101 and 241-T-104 .....		D.1
Appendix E – Photographs of Core and Grab Samples from the Interim Measures Direct Push Boreholes Collected North of the T Tank Farm .....		E.1
Appendix F – Logs of Core and Grab Samples from the Interim Measures Direct Push Boreholes Emplaced North of the T Tank Farm.....		F.1

## Figures

2.1	Generalized, Composite Stratigraphy for the Late-Cenozoic Sediments Overlying the Columbia River Basalt Group at the T-TY Tank Farm.....	2.2
2.2	Borehole and Cross Section Location Map.....	2.4
2.3	Hydrogeologic Cross Section Through the T and TY Tank Farms.....	2.5
2.4	Locations of Direct Push holes in Vicinity of the T Tank Farm .....	2.7
2.5	Locations of Direct-Push holes in Vicinity of the TY Tank Farm.....	2.8

4.1	Moisture Content Data for the TY Tank Farm Direct Push Samples.....	4.2
4.2	pH for 1:1 Sediment:Water Extracts and Dilution-Corrected EC Values from TY Tank Farm .....	4.4
4.3	1:1 Sediment:Water-Extractable Nitrate and Sulfate Data from the TY Tank Farm Direct Push Samples .....	4.7
4.4	1:1 Sediment:Water-Extractable Chloride and Fluoride Data from the TY Tank Farm Direct Push Samples .....	4.8
4.5	1:1 Sediment:Water-Extractable Sodium and Calcium Data from the TY Tank Farm Direct Push Samples .....	4.9
4.6	1:1 Sediment:Water-Extractable and 8M Nitric Acid Extractable Uranium-238 Data from the TY Tank Farm Direct Push Samples.....	4.13
4.7	1:1 Sediment:Water-Extractable Alkalinity Data from the TY Tank Farm Direct Push Samples .....	4.17
4.8	Gamma Energy Analysis Data from the TY Tank Farm Direct Push Samples .....	4.21
4.9	Moisture Content Data for the T Tank Farm Direct Push Samples .....	4.25
4.10	pH for 1:1 Sediment:Water Extracts and Dilution-Corrected EC Values from T Tank Farm ..	4.26
4.11	1:1 Sediment:Water-Extractable Nitrate and Sulfate data from the T Tank Farm Direct Push Samples .....	4.29
4.12	1:1 Sediment:Water-Extractable Chloride and Fluoride Data from the T Tank Farm Direct Push Samples .....	4.30
4.13	1:1 Sediment:Water-Extractable Sodium and Calcium data from the T Tank Farm Direct Push Samples .....	4.32
4.14	1:1 Sediment:Water-Extractable and 8M Nitric Acid Extractable Technetium-99 data from the T Tank Farm Direct Push Samples.....	4.35
4.15	1:1 Sediment:Water-Extractable and 8M Nitric Acid Extractable Uranium-238 data from the T Tank Farm Direct Push Samples.....	4.36
4.16	1:1 Sediment:Water-Extractable Alkalinity Data from the T Tank Farm Direct Push Samples .....	4.41
4.17	Gamma Energy Analysis Data from the T Tank Farm Direct Push Samples .....	4.47
4.18	Gamma Energy Analysis Data from the T Tank Farm Direct Push Samples .....	4.48
4.19	Ruthenium Isotopic Data from the T Tank Farm Direct Push Samples and Samples from Borehole C4104 .....	4.56
4.20	Photograph of Fine-Grained Upper Cold Creek Unit Sediment Recovered from 81.0 to 81.5 ft bgs in Probe Hole C5374.....	4.57
4.21	Photograph of Fine-Grained Upper Cold Creek Unit Sediment Recovered from 80.5 to 81.0 ft bgs in Probe Hole C5374.....	4.58
4.22	Photograph of Fine-Grained Upper Cold Creek Unit Sediment Recovered from 80.0 to 80.5 ft bgs in Probe Hole C5374.....	4.59
4.23	Photograph of Sediment Recovered from 75.1 to 75.7 ft bgs in Borehole C4104.....	4.60
4.24	Photograph of Sediment Recovered from 80.1 to 80.7 ft bgs in Borehole C4104.....	4.60

## Tables

2.1	Stratigraphic Terminology for the Vadose Zone Beneath T-TY Tank Farm.....	2.3
2.2	Sampled Direct-Push Boreholes.....	2.9
2.3	Analyzed Samples from the T and TY Tank Farms.....	2.10
3.1	Sample Inventory from the TY Tank Farm Direct Push Probe Holes .....	3.2
3.2	Sample Inventory from the T Tank Farm Direct Push Probe Holes .....	3.2
4.1	Gravimetric Moisture Content of Samples Obtained from the TY Tank Farm Direct Push Probe Holes .....	4.1
4.2	pH for 1:1 Sediment:Water Extracts and Dilution-Corrected EC Values from TY Tank Farm Core and Grab Samples .....	4.3
4.3	Water-Extractable Anions in the TY Tank Farm Core and Grab Samples .....	4.6
4.4	Water-Extractable Major Cations in the TY Tank Farm Core and Grab Samples.....	4.6
4.5	Water-Extractable Cations in the TY Tank Farm Core and Grab Samples .....	4.11
4.6	Water-Extractable Mobile Metals in the TY Tank Farm Core and Grab Samples .....	4.12
4.7	Calculated Pore Water Anion Concentrations in the TY Tank Farm Core and Grab Samples	4.15
4.8	Calculated Pore Water Cation Concentrations in the TY Tank Farm Direct Push Core and Grab Samples .....	4.15
4.9	Calculated Pore Water Metal Concentrations in the TY Tank Farm Direct Push Core and Grab Samples .....	4.16
4.10	Calculated Pore Water Mobile Metal Concentrations of Key Contaminants of Concern in the TY Tank Farm Direct Push Core and Grab Samples .....	4.16
4.11	Acid-Extractable Cations in the TY Tank Farm Direct Push Core and Grab Samples.....	4.18
4.12	Acid-Leachable Cations in the TY Tank Farm Core and Grab Samples .....	4.19
4.13	Acid-Extractable Mobile Metals in the TY Tank Farm Direct Push Core and Grab Samples.	4.19
4.14	Gamma Emitting Radionuclides in the TY Tank Farm Direct Push Sediments .....	4.20
4.15	Carbon Content of the TY Tank Farm Vadose Zone Samples.....	4.23
4.16	Gravimetric Moisture Content of Samples Obtained from the T Tank Farm Direct Push Probe Holes .....	4.23
4.17	pH for 1:1 Sediment:Water Extracts and Dilution-Corrected EC Values from T Tank Farm Core and Grab Samples.....	4.24
4.18	Water-Extractable Anions in the T Tank Farm Core and Grab Samples .....	4.28
4.19	Water-Extractable Major Cations in the T Tank Farm Core and Grab Samples.....	4.31
4.20	Water-Extractable Cations in the T Tank Farm Core and Grab Samples .....	4.33
4.21	Water-Extractable Mobile Metals in the T Tank Farm Core and Grab Samples .....	4.34
4.22	Calculated Pore Water Anion Concentrations in the T Tank Farm Core and Grab Samples...	4.38
4.23	Calculated Pore Water Cation Concentrations in the T Tank Farm Direct Push Core and Grab Samples .....	4.39
4.24	Calculated Pore Water Mobile Metal Concentrations of Key Contaminants of Concern in the T Tank Farm Direct Push Core and Grab Samples .....	4.40
4.25	Acid-Extractable Cations in the T Tank Farm Direct Push Core and Grab Samples.....	4.43
4.26	Acid-Leachable Cations in the T Tank Farm Core Samples .....	4.44
4.27	Acid-Extractable Mobile Metals in the T Tank Farm Direct Push Core and Grab Samples ...	4.45
4.28	Gamma Emitting Radionuclides in the T Tank Farm Direct Push Sediments .....	4.46
4.29	Carbon Content of the T Tank Farm Vadose Zone Samples .....	4.49

4.30	Water Extractable Technetium-99 Concentrations in the T Tank Farm Vadose Zone Samples .....	4.50
4.31	Water Extractable Technetium-99 Concentrations in the T Tank Farm Vadose Zone Samples After Resin Treatment .....	4.51
4.32	Acid Extractable Technetium-99 Concentrations in the T Tank Farm Vadose Zone .....	4.52
4.33	Acid Extractable Technetium-99 Concentrations in the T Tank Farm Vadose Zone After Resin Treatment .....	4.52
4.34	Microwave Digestible Technetium-99 Concentrations in the T Tank Farm Vadose Zone.....	4.54
4.35	Microwave Digestible Technetium-99 Concentrations in the T Tank Farm Vadose Zone After Resin Treatment.....	4.54
5.1	Maximum Pore Water Concentrations in Sediments from the Hanford Formation Unit.....	5.11
6.1	Sample Inventory from the T Tank Farm Interim Measures Samples .....	6.1
6.2	Gravimetric Moisture Content of Samples Obtained from the T Tank Farm Interim Measures Activites .....	6.1
6.3	Sediment:Water Extractable Nitrate Data for Samples Obtained from the T Tank Farm Interim Measures Activities .....	6.1
6.4	1:1 Sediment:Water Extractable Technetium-99 Data for Samples Obtained from the T Tank Farm Interim Measures Activities .....	6.2



## Acronyms and Abbreviations

%RSD	percent relative standard deviation
ASA	American Society of Agronomy
ASTM	American Society for Testing and Materials
bgs	below ground surface
CMB	chloride mass balance
DOE	U.S. Department of Energy
EC	electrical conductivity
EPA	U.S. Environmental Protection Agency
GEA	gamma energy analysis
H1	Hanford formation – H1 unit
H2	Hanford formation – H2 unit
HCl	hydrochloric acid
HF	hydrofluoric acid
HNO <sub>3</sub>	nitric acid
HPGe	high-purity germanium
IC	ion chromatography or ion chromatograph
ICP-MS	inductively coupled plasma-mass spectrometer
ICP-OES	inductively coupled plasma-optical emission spectroscopy
ILAW	Integrated Low Activity Waste
Kd	distribution coefficient, or sorption partition coefficient, in units of mL/g
MC	moisture content
MCL	maximum contamination level
mS	millisiemen
NDIR	non-dispersive infrared
NIST	National Institute of Standards and Technology
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
QC	quality control
RCRA	Resource Conservation and Recovery Act of 1976
REDOX	Reduction Oxidation Process (the second fuel reprocessing process used at the Hanford Site to extract plutonium)
Rtf	Ringold Formation sand
Rwi	Ringold fluvial gravel
TBP	Tributyl phosphate
UFA	unsaturated flow apparatus (ultracentrifuge for squeezing pore water out of sediment)
UPR	unplanned release
USGS	U.S. Geological Survey
WMA	waste management area

## Units of Measure

%	percent
Bgs	below ground surface
°C	temperature in degrees Celsius [ $T(^{\circ}\text{C}) = T(\text{K}) - 273.15$ ]
Ci	curie
cm	centimeter
ft	foot
g	gram
g	acceleration due to gravity
in.	inch
$\mu$	micro (prefix, $10^{-6}$ )
$\mu\text{Ci}$	microcurie
$\mu\text{eq}$	microequivalent
$\mu\text{g}$	microgram
$\mu\text{m}$	micrometer
m	meter
M	molarity, mol/L
meq/L	milli-equivalent per liter
mg	milligram
mL	milliliter
mm	millimeter
mM	millimolar
mN	millinormal
mol	mole
mS	milliSiemen
N	Normal
nCi	nanocurie
ng	nanogram
pCi	picocurie
wt%	weight percent

## 1.0 Introduction

The overall goals of the Tank Farm Vadose Zone Project, led by CH2M HILL Hanford Group, Inc., are 1) to define risks from past and future single-shell tank farm activities, 2) to identify and evaluate the efficacy of interim measures, and 3) to aid, via collection of geochemical information and data, the future decisions that must be made by the U.S. Department of Energy (DOE) regarding the near-term operations, future waste retrieval, and final closure activities for the single-shell tank Waste Management Areas (WMAs). For a more complete discussion of the goals of the Tank Farm Vadose Zone Project, see the overall work plan, *Phase 1 RCRA Facility Investigation/Corrective Measures Study Work Plan for the Single-Shell Tank Waste Management Areas* (DOE 1999). Specific details on the rationale for activities performed at WMAs T and TX-TY are found in Crumpler (2002). To meet these goals, CH2M HILL Hanford Group, Inc., asked scientists from Pacific Northwest National Laboratory (PNNL) to perform detailed analyses of vadose zone sediment collected within the T and TY Tank Farms (Serne et al. 2004a,b). Upon completion of these activities, additional sampling was performed in the T and TY Tank Farms to further investigate potential leak events.

This report contains all the geochemical and selected physical characterization data collected on vadose zone sediment recovered from five direct push characterization holes emplaced to investigate vadose zone contamination associated with leaks from tanks 241-TY-105 (UPR-200-W-152) and 241-TY-106 (UPR-200-W-153). Tank 241-TY-105 is estimated to have leaked 35,000 gal of tributyl phosphate (TBP) waste from the uranium recovery process to the vadose zone in 1960 (Wood et al. 2001). Wood et al. (2001) conceptualized the 241-TY-105 tank leak as having occurred either at the tank bottom or from a shallow depth somewhere in the vicinity of drywell 52-05-07. Cesium-137 contamination in drywell 52-05-07 occurred at a depth consistent with the bottom of tank 241-TY-105. Wood et al. (2001) and Myers (2005) estimated that the leaked fluid migrated horizontally to the north and southwest of tank 241-TY-105 once it had penetrated deeper than the tank bottom. Wood et al. (2001) further hypothesized that the waste could have flowed to the south, east, and southeast, but the lack of drywells in the region prevented confirmation of this migration pathway. Cobalt-60 from the 241-TY-105 tank leak has migrated vertically at this location and was observed at concentrations in excess of 10 pCi/g at the bottom of drywell 52-03-06. Tank 241-TY-106 is estimated to have leaked 20,000 gal of TBP-uranium recovery waste to the vadose zone in 1959. Although several drywells in the vicinity of tank 241-TY-106 contain measurable quantities of cesium-137 and/or cobalt-60, their relatively low concentrations indicate that the contaminant inventory in the vadose zone around tank 241-TY-106 is quite small (Wood et al. 2001). A location map highlighting the area of interest is presented in Section 2 (Figure 2.1).

Additionally, this report contains 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 241-T-101. Deaton (DOE 1992) postulated that a leak from tank 241-T-101 occurred in 1992, resulting in a loss of 28,390 liters (7,500 gallons) of tank waste to the subsurface. This event was the basis for placing tank 241-T-101 on the list of assumed/known leakers. It has been estimated that 1230 Ci of cesium-137, 0.0434 Ci of cobalt-60, and 0.382 Ci of technetium-99 were lost to the vadose zone as a result of the 1992 leak event (Wood et al. 2001). Wood et al. (2001) conceptualized the vadose zone contamination near tank 241-T-101 having occurred from leakage from a waste transfer or cascade line rather than a tank

wall breach. Cesium-137 contamination in drywell 50-01-04 occurred at a depth beginning at approximately 25 feet below ground surface and extending intermittently to the terminus depth of the drywell (125 feet below ground surface). Wood et al. (2001) and Myers (2005) estimated that the leaked fluid migrated to the south and can be found in drywell 50-01-06. A location map highlighting the area of interest is presented in Section 2 (Figure 2.1).

This report is divided into sections that describe the geochemical characterization methods employed and the results of analysis of the T and TY Tank Farm direct push core samples. English units are used in this report for descriptions and discussions of drilling activities and samples because that is the system of units used by drillers to measure and report depths. To convert feet to meters, multiply by 0.3048; to convert inches to centimeters, multiply by 2.54. The metric system is used in this report for all other purposes.

## 2.0 Geology

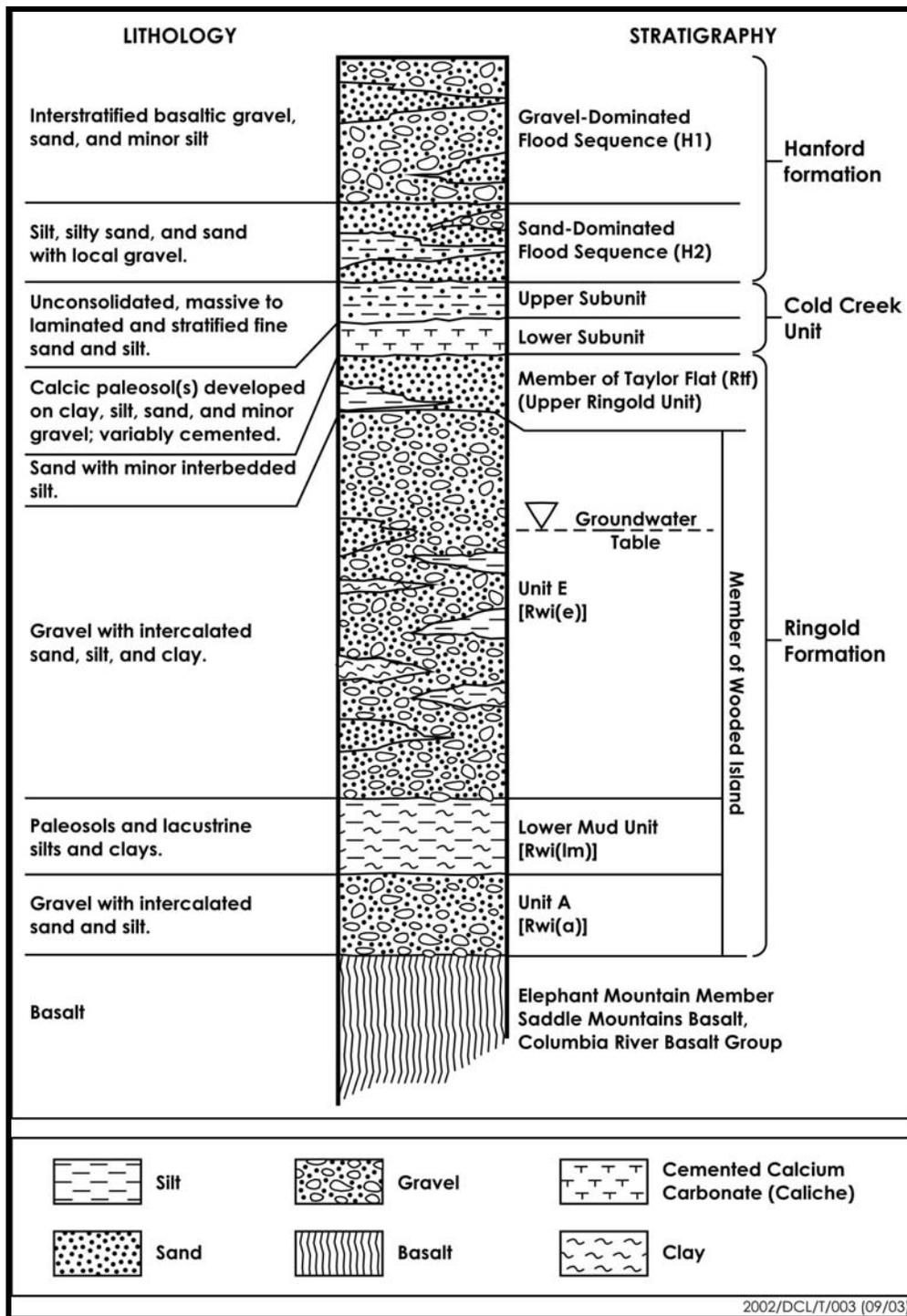
The regional geologic setting and site-specific geology in the vicinity of the T-TX-TY Tank Farm has been covered extensively in a number of previous reports (Price and Fecht 1976; Brown et al. 1979; Tallman et al. 1979; Last et al. 1989; Connelly et al. 1992; Freeman-Pollard et al. 1994; Wood et al. 2001; Lindsey et al. 2001; Williams et al. 2002; DOE/GJO 1998, 1999; Reidel and Chamness 2007).

In general, the geology of the vadose zone beneath the T and TY Tank Farms includes four stratigraphic units. From youngest to oldest these include 1) recent deposits of eolian sand or backfill material, 2) Ice-Age flood deposits of the Hanford formation, 3) the Cold Creek unit, formerly known as the Plio-Pleistocene unit (DOE 2002), and 4) the Ringold Formation. The varying character of these units is compared in Figure 2.1 and Table 2.1.

Figure 2.2 shows the location of T and TY Tank Farms where the direct-push samples reported in this document were collected. The general geology and stratigraphy of the T and TY Tank Farms is illustrated along cross section A-A' (Figure 2.3).

Recent surficial deposits at the T and TY Tank Farms usually consist of a meter or less of recent windblown sand. In the Tank Farms there may be up to 50 ft of backfill material used to bury and fill around the underground storage tanks (Figure 2.3). Below this is up to 80 ft of mostly sand and gravel, deposited onto the giant Cold Creek bar, which formed during repeated Pleistocene cataclysmic floods (Bjornstad 2006). The upper part of the Hanford formation is dominated with gravel (H1 unit) while the lower part is predominantly sand (H2 unit), although there is a considerable amount of internal heterogeneity.

Beneath the Hanford formation is the Cold Creek unit, which consists of an upper fine sand to silt unit and a lower unit of variably cemented caliche, representing a buried paleosol sequence. Combined, the Cold Creek unit may be up to 40 ft thick and its upper surface has a pronounced dip to the south. Below the Cold Creek unit is a discontinuous layer of Ringold Formation sand (Rtf) underlain by a thick sequence of variably cemented Ringold fluvial gravel (Rwi).



**Figure 2.1.** Generalized, Composite Stratigraphy for the Late-Cenozoic Sediments Overlying the Columbia River Basalt Group at the T-TY Tank Farm (modified after Wood et al. 2001)

**Table 2.1.** Stratigraphic Terminology for the Vadose Zone Beneath T-TY Tank Farm

Stratigraphic Symbol	Formation	Facies / Subunit	Description	Genesis
Backfill	NA	Backfill	<b>Gravel-dominated sequence</b> 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 1976; Wood et al. 2001).	Anthropogenic
H1	Hanford formation	Unit H1 (Gravel-dominated facies association)	<b>Gravel-dominated flood sequence</b> 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 Qfg 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. (2001), and gravel-dominated facies association of DOE (2002). The majority of this unit was excavated out and is missing from beneath T Tank Farm.	Cataclysmic flood deposits (high-energy)
H2		Unit H2 (Sand-dominated facies association)	<b>Sand-dominated flood sequence</b> composed of mostly horizontal to tabular cross-bedded sand to pebbly 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. (2001), the sandy sequence of Last et al. (1989) and Lindsey et al. (1992), and Qfs documented by Reidel and Fecht (1994), and sand-dominated facies described in DOE (2002). The H2 unit was subdivided into a lower and upper subunit by Sobczyk (2001).	Cataclysmic flood deposits (moderate energy)
CCU <sub>u</sub>	Cold Creek unit	Upper subunit	<b>Silty sequence</b> consisting of massive to interstratified, well sorted silt and fine sand. Uncemented but may be moderately to strongly calcareous from detrital CaCO <sub>3</sub> . Equivalent to the “early Palouse soil” (Brown 1970; Tallman et al. 1979; DOE 1988; and DOE-GJO 1997) and the Hanford Formation/Plio-Pleistocene deposits (H/PP) of Wood et al. (2001). Also equivalent to the upper Plio-Pleistocene unit (Lindsey et al. 2001; Sobczyk 2001) and the fine-grained, laminated to massive [CCUf(lam-msv)] lithofacies of the Cold Creek unit (DOE 2002). Same as PPU of Lindsey et al. (2001).	Post-Ringold Fm. eolian and/or overbank alluvial deposits
CCU <sub>l</sub>		Lower subunit	<b>Calcic paleosol sequence</b> , 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 <sub>3</sub> , originally referred to as “caliche” (Brown 1959). Since then the name has evolved from the Plio-Pleistocene unit (Bjornstad 1984, 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. (2001), and the coarse- to fine-grained, CaCO <sub>3</sub> -cemented lithofacies [CCUc-f(calc)] of the Cold Creek unit (DOE 2002). Same as PPc of Lindsey et al. (2001).	Calcic paleosols developed on eroded Ringold or post-Ringold Fm. eolian and/or fluvial deposits

Table 2.1. (contd)

Stratigraphic Symbol	Formation	Facies / Subunit	Description	Genesis
Rtf	Ringold Formation	Member of Taylor Flat	<b>Fine-grained Ringold Formation sequence</b> consisting of interstratified, well bedded fine to coarse sand to silt. Equivalent to the upper Ringold unit (DOE 1988).	Ancestral Columbia River System fluvial channel, crevasse splay, and/or overbank deposits
Rwi		Member of Wooded Island	<b>Coarse-grained Ringold Formation sequence</b> , consisting of mostly moderately sorted, quartzitic sandy gravel to silty sandy gravel. Equivalent to middle Ringold unit (DOE 1988) and the Ringold Unit E gravels (Wood et al. 2001; Lindsey et al. 2001) .	Ancestral Columbia River System fluvial, braided-stream deposits

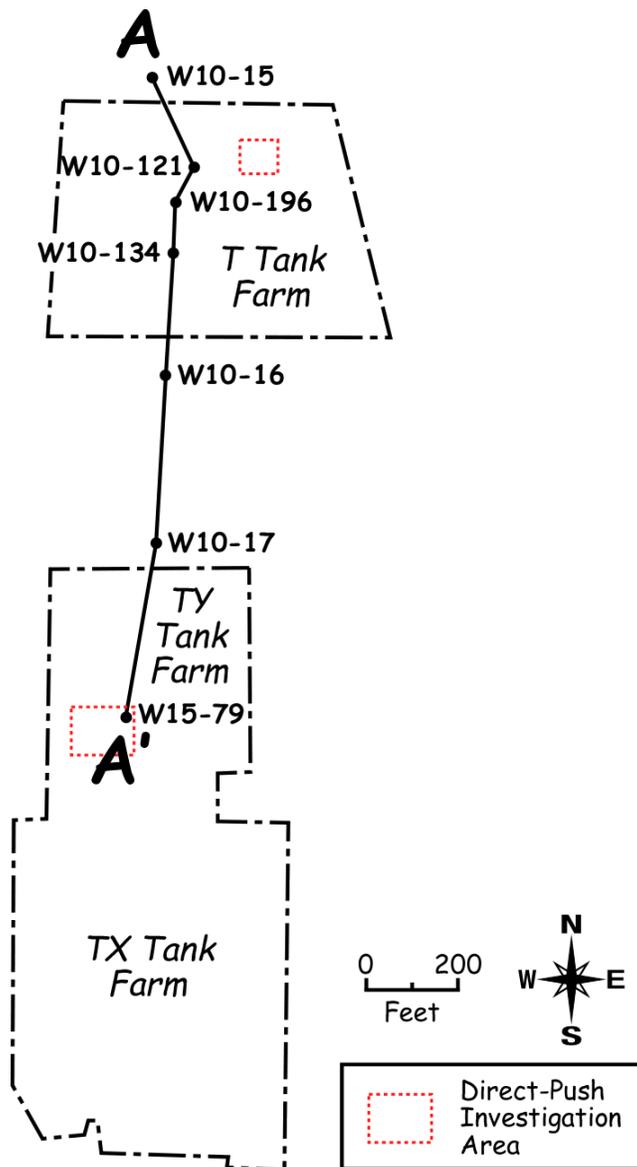
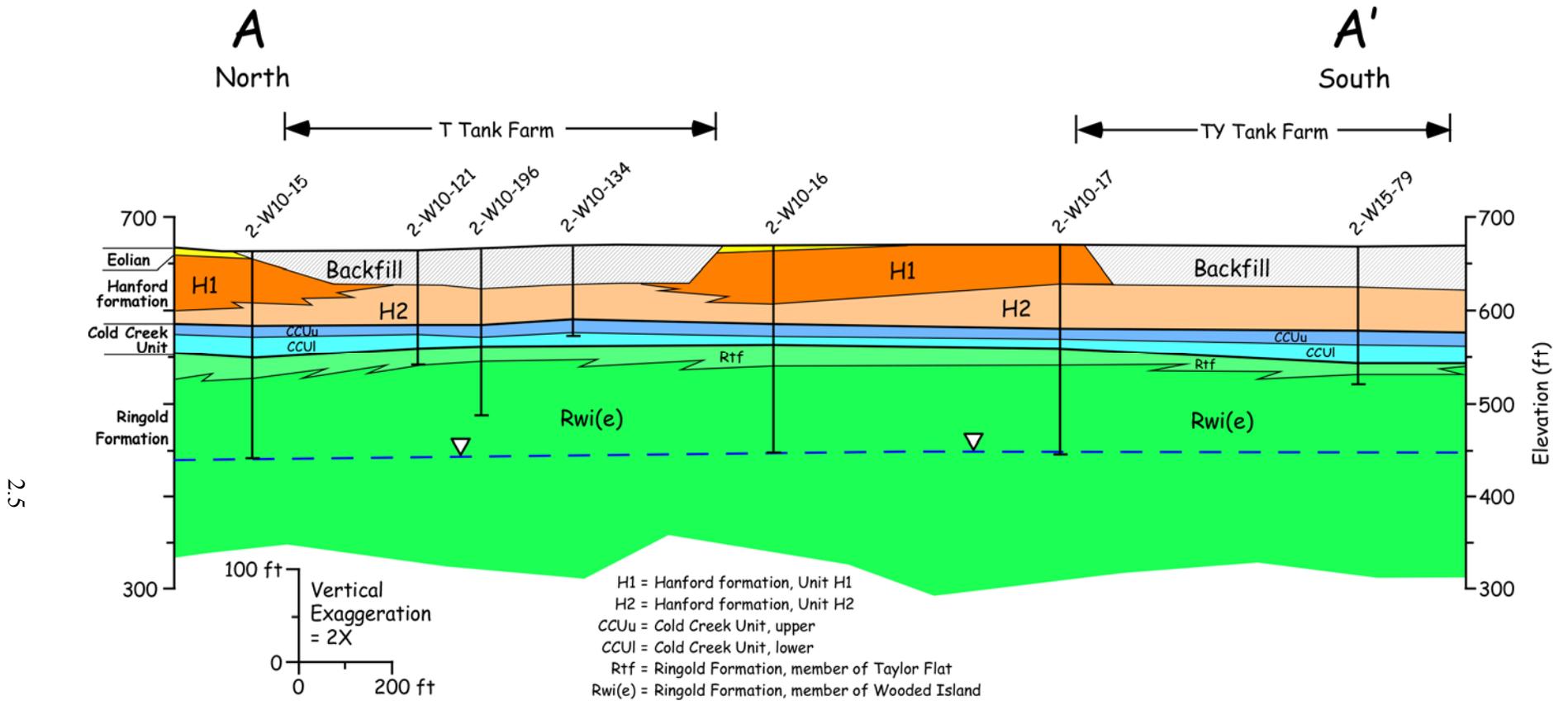


Figure 2.2. Borehole and Cross Section Location Map. Cross section A-A' is shown in Figure 2.3.



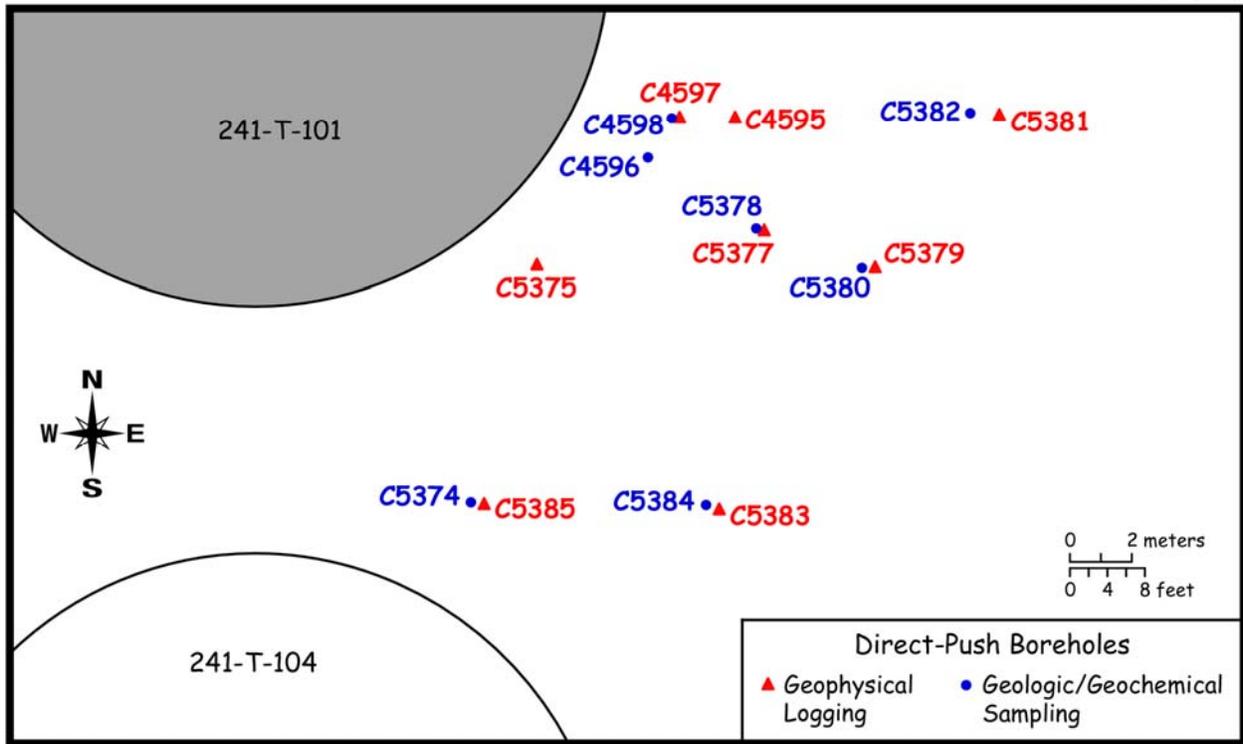
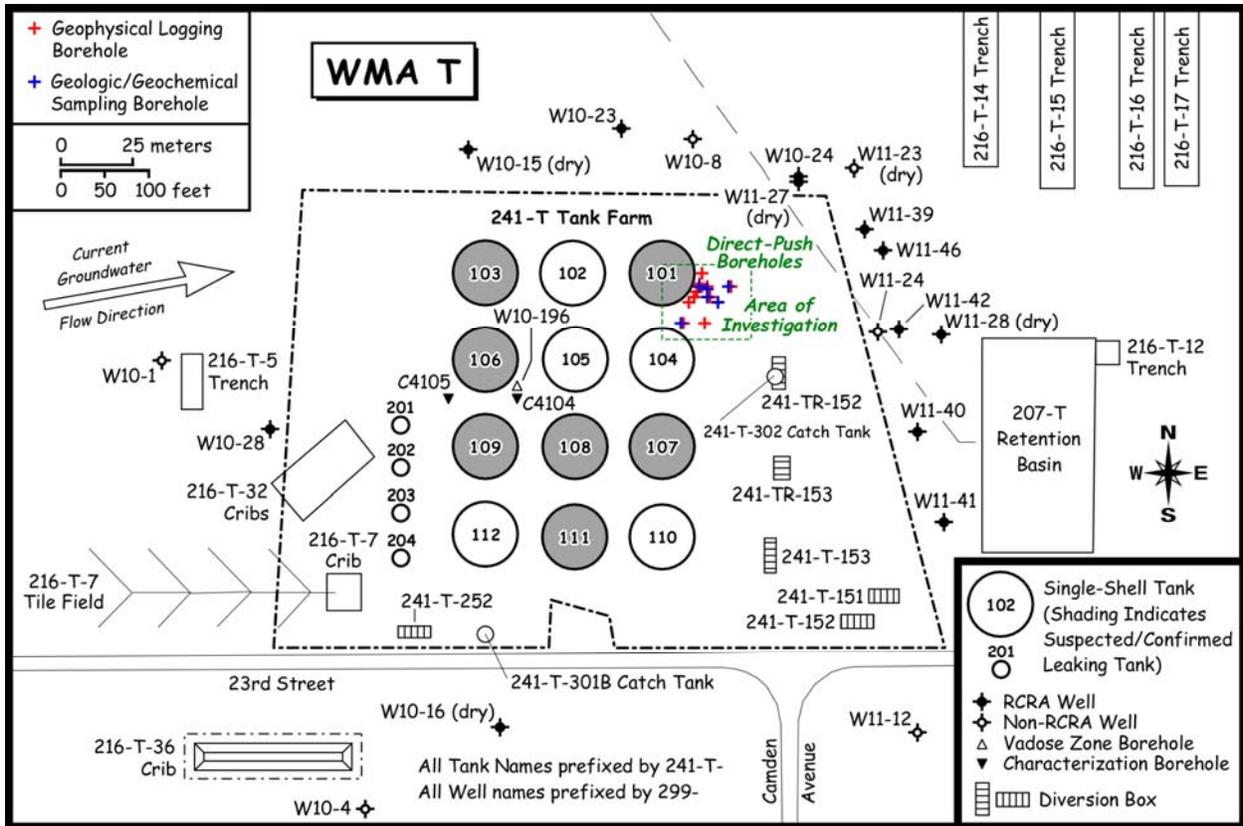
**Figure 2.3.** Hydrogeologic Cross Section Through the T and TY Tank Farms. See Figure 2.2 for location of cross section.

## 2.1 Characterization and Sampling Methods

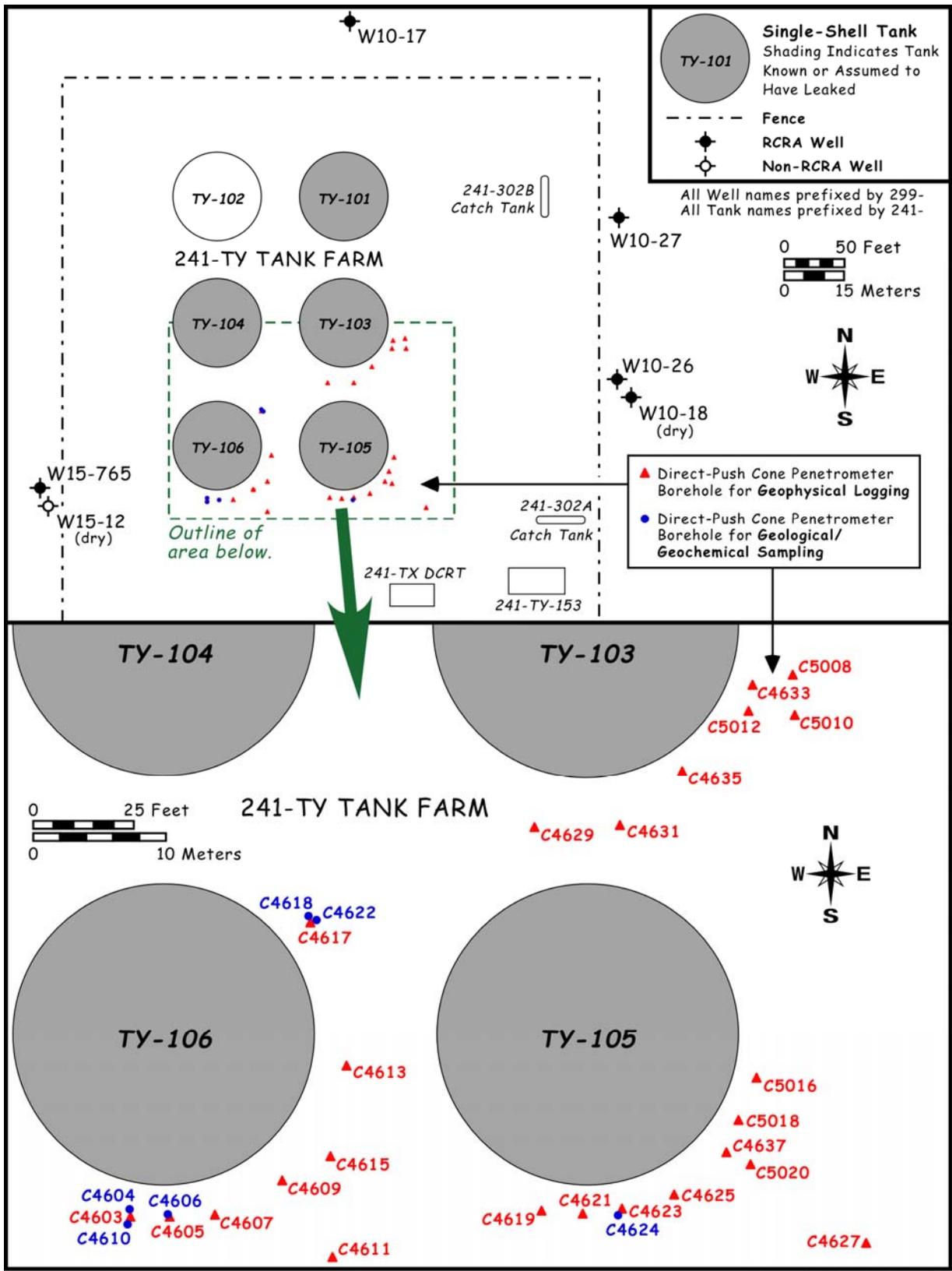
This document reports on the geologic/geochemical characterization of 11 recent vadose-zone, cone-penetrometer probe (direct push) holes drilled in the vicinity of the T and TY Tank Farms. Six of the holes were drilled in the T Tank Farm (Figure 2.4); the other five were drilled in the TY Tank Farm (Figure 2.5). Direct-push holes were drilled in two stages. First, 24 direct-push holes were advanced up to 85 ft below ground surface for geophysical logging to target intervals for collection of core samples to be used for geological/geochemical characterization. Downhole geophysical logs measured gamma activity using up to three different detectors: 1) NaI (scintillation), 2) Geiger-Mueller (gross gamma), and 3) spectral gamma (Randall and Price 2006). Out of the 24 holes geophysically logged at the TY Tank Farm, only about 40% showed any significant gamma activity in the deep subsurface. Five direct push holes displayed a single gamma spike, usually at about 45 ft depth below ground surface (bgs). Five other holes displayed multiple gamma spikes in the deep subsurface at  $\geq 45$  ft depth bgs.

A second direct-push campaign was used to place holes near locations that showed elevated gamma activity in the first campaign for the purpose of collecting core samples. Core samples were collected from these secondary holes for geologic/geochemical characterization. In most holes, including all probe holes in the TY Tank Farm, only a single depth interval ( $\leq 2$  ft) was sampled (Table 2.2); core recovery ranged from 15% to 110%. Multiple intervals were core sampled in one of the holes in the T Tank Farm (C5378). From each interval, up to three continuous core segments were collected in 1.5-inch-diameter by 6-inch-long stainless-steel liners, and grab samples were also collected from the shoe at the base of some core intervals (Table 2.3).

In the laboratory, immediately upon extruding the cores from their liners, moisture samples were collected and high-resolution color photographs were obtained for each core or grab sample (Appendices A and C). Next, standard descriptions of grain size, sorting, color, structure, consolidation, moisture content, mineralogy, and reaction with hydrochloric acid were entered onto geologic core logs (Appendices B and D). Cores were also sub-sampled for laboratory characterization of physical and chemical properties at that time.



**Figure 2.4.** Locations of Direct Push holes in Vicinity of the T Tank Farm



2007/DCL/TY/009 (05/16)

Figure 2.5. Locations of Direct-Push holes in Vicinity of the TY Tank Farm

**Table 2.2. Sampled Direct-Push Boreholes**

Sampled Direct Push Borehole	Easting	Northing	Elevation at Ground Surface (m above mean sea level)	Date Received	Date Opened	Lab Number	Sampled Depths ft bgs	Total Length Intact Core (ft)
<b>241-T Tank Farm</b>								
C4596	566853.5	136759.1	206.834	8/25/2006	12/5/06	B1KC36	47.0-49.2	2.2
C4598	566851.4	136759.7	206.552	8/18/2006	12/5/06	B1KC35	43-44	0.6
C5374	566844.9	136747.2	206.369	11/3/2006	12/5/06	B1KC40	80-82	2.0
C5378	566854.2	136756.1	206.885	10/25/06	12/5/06	B1KC37	45-46.2	1.0
C5378	566854.2	136756.1	206.885	10/27/06	12/5/06	B1KC38	62-64	2.0
C5384	566852.5	136747.1	206.704	10/27/06	12/5/06	B1KC39	44.2-46	1.8
C5380	566857.6	136754.8	207.139	11/16/06	12/5/06	B1LB08	50-52	2.0
C5382	566.861.1	136759.9	207.341	11/16/06	12/5/06	B1LB07	78-79.5	1.5
<b>241-TY Tank Farm</b>								
C4604	566739.5	136370.8	205.631	11/3/05	12/20/05	S06001-1	44.5-45.4	0.3
C4606	566742.3	136370.4	205.653	11/3/05	12/20/05	S06001-4	44.4-46.0	1.6
C4610	566739.3	136369.7	205.590	11/3/05	12/20/05	S06001-3	43.7-44.5	0.8
C4618	566753.0	136393.0	No sediment retrieved from borehole					
C4622	566776.3	136392.7	205.653	11/11/05	12/20/05	S06001-5	43.4-43.7	0.3
C4624	566766.3	136370.4	205.780	11/3/05	12/20/05	S06001-2	42.0-43.1	1.1

**Table 2.3.** Analyzed Samples from the T and TY Tank Farms

Sampled Direct-Push Borehole	Lab #	Sample Type	Depth ft gs	Mid Depth ft bgs	Lithology	Stratigraphic Unit	Lab Moisture	Core Moisture	Comments
<b>TY Tank Farm</b>									
C4604	S06001-1A	core	44.5-45.4	44.95	Silty sandy gravel	Hanford fm.	5.09%	dry	pulverized
C4604	S06001-1	grab	shoe	~45.3	Silty sandy gravel	Hanford fm.	5.45%	moist	
C4624	S06001-2B	core	42.0-42.2	42.10	Silty sandy gravel, calcareous	Hanford fm.	5.64%	sl. moist	
C4624	S06001-2A	core	42.2-42.8	42.50	Silty sandy gravel, calcareous	Hanford fm.	8.29%	sl. moist	
C4624	S06001-2	grab	42.8-43.3	43.05	Silty sandy gravel, calcareous	Hanford fm.	5.24%	sl. moist	
C4610	S06001-3A	core	43.67-43.92	43.80	Silty sandy gravel	Hanford fm.	5.50%	sl. moist	
C4610	S06001-3	grab	43.92-44.5	44.21	Gravelly sand	Hanford fm.	6.18%	moist	
C4606	S06001-4C	core	44.33-44.42	44.38	Silty sandy gravel	Hanford fm.	4.26%	sl. moist	
C4606	S06001-4B	core	44.42-44.92	44.67	Silty sandy gravel	Hanford fm.	5.89%	moist	
C4606	S06001-4A	core	44.92-45.42	45.17	Silty gravelly sand	Hanford fm.	6.44%	moist	
C4606	S06001-4A DUP	core	44.92-45.42	45.17	Silty gravelly sand	Hanford fm.	6.57%	moist	
C4606	S06001-4	grab	45.42-46.0	45.71	Slightly gravelly sand	Hanford fm.	9.73%	moist	
C4622	S06001-5	grab	43.5-43.8	43.65	Silty sandy gravel, calcareous	Hanford fm.	4.53%	sl. moist	
<b>T Tank Farm</b>									
C4598	B1KC35A	core	43.5-44.0	43.8	Slightly pebbly sand, lt gray	Hanford fm.	3.97%	dry	
C4598	B1KC35B	core	43.0-43.5	43.3	Slightly pebbly muddy sand	Hanford fm.	4.30%	dry	slough?
C4596	B1KC36	grab	48.5-49.2	48.9	Med-crs sand	Hanford fm.	3.50%	sl. moist	High rad interval
C4596	B1KC36A	core	48.0-48.5	48.3	Fn-crs sand	Hanford fm.	6.37%	sl. moist	
C4596	B1KC36B	core	47.5-48.0	47.8	Med-crs sand	Hanford fm.	4.21%	sl. moist	
C4596	B1KC36C	core	47.0-47.5	47.3	Med-crs sand	Hanford fm.	4.57%	sl. moist	
C5378	B1KC37A	core	46.0-46.5	46.3	Crs sand	Hanford fm.	2.58%	sl. moist	Upper interval from C5378
C5378	B1KC37B	core	45.5-46.0	45.8	Med sand	Hanford fm.	5.87%	sl. moist	
C5378	B1KC37C	core	45.0-45.5	45.3	Med sand	Hanford fm.	11.7%	sl. moist	

**Table 2.3. (contd)**

Sampled Direct-Push Borehole	Lab #	Sample Type	Depth ft gs	Mid Depth ft bgs	Lithology	Stratigraphic Unit	Lab Moisture	Core Moisture	Comments
C5378	B1KC38	grab	63.5-64.0	63.8	Crs sand, basaltic	Hanford fm.	4.40%	sl. moist	Lower interval from C5378
C5378	B1KC38A	core	63.0-63.5	63.3	Gravelly sand, basaltic	Hanford fm.	5.18%	sl. moist	
C5378	B1KC38B	core	62.5-63.0	62.8	Gravelly sand, basaltic	Hanford fm.	5.48%	sl. moist	
C5378	B1KC38C	core	62.0-62.5	62.3	Gravelly sand, basaltic	Hanford fm.	6.51%	sl. moist	
C5384	B1KC39	grab	45.5-46.0	45.8	Med-crs sand, lt gray	Hanford fm.	4.66%	sl. moist	Hole # changed from C5380
C5384	B1KC39A	core	45.0-45.5	45.3	Fn-crs sand, yellowish	Hanford fm.	3.56%	sl. moist	Hole # changed from C5380
C5384	B1KC39B	core	44.5-45.0	44.8	Med-crs sand, lt gray	Hanford fm.	4.54%	sl. moist	Hole # changed from C5380
C5384	B1KC39C	core	44.0-44.5	44.3	Med-crs sand, lt gray	Hanford fm.	6.10%	sl. moist	Hole # changed from C5380
C5380	B1LB08	grab	51.5-52.0	51.8	Gravelly sand	Hanford fm.	5.65%	sl. moist	
C5380	B1LB08A	core	51.0-51.5	51.3	Med-crs sand	Hanford fm.	8.33%	sl. moist	
C5380	B1LB08B	core	50.5-51.0	50.8	Med-crs sand	Hanford fm.	9.14%	sl. moist	
C5380	B1LB08C	core	50.0-50.5	50.3	Med-crs sand	Hanford fm.	8.27%	sl. moist	
C5374	B1KC40	grab	81.5-82.0	81.8	Fn-med sand, pale yellow, laminated	Upper Cold Creek unit	8.35%	sl. moist	
C5374	B1KC40A	core	81.0-81.5	81.3	Fn sandy silt, yel. brn, calcareous	Upper Cold Creek unit	16.6%	moist	
C5374	B1KC40B	core	80.5-81.0	80.8	Silty fn sand, yel. brn, calcareous	Upper Cold Creek unit	18.2%	moist	
C5374	B1KC40C	core	80.0-80.5	80.3	Silty fn sand, yel. brn, calcareous	Upper Cold Creek unit	14.9%	moist	
C5382	B1LB07A	core	79.0-79.5	79.3	Pale yellow silty sand, laminated, calcareous	Upper Cold Creek unit	22.7%	moist	
C5382	B1LB07B	core	78.5-79.0	78.8	Pale yellow silty sand, laminated, calcareous	Upper Cold Creek unit	14.9%	moist	
C5382	B1LB07C	core	78.0-78.5	78.3	Med-crs sand	Hanford formation?	5.98%	sl. moist	

fm = formation; Fn = fine; crs = course

## 2.2 Interpreted Geology Related to Direct-Push Samples

All the samples from the TY Tank Farm came from a depth between 43.5 and 45.5 ft bgs within the gravel-dominated H1 unit of the Hanford formation. Samples from the T Tank Farm, on the other hand, came from a wider interval (43-82 ft bgs), which appears to include both gravel (H1)- and sand-dominated (H2) units of the Hanford formation, as well as the upper Cold Creek subunit.

All the new direct push holes in the TY Tank Farm penetrated only coarse-grained cataclysmic flood deposits of the Hanford formation, while the deepest samples from the T Tank Farm reached into fine-grained sediments of the upper Cold Creek unit. Except for the discrete core intervals, no direct geologic observations were made available by direct push holes. However, some indirect interpretation of lithology can be made based on the gamma logs.

Based on down-hole geophysical logs, a spike in gamma activity was often associated with the ~45-ft depth and less often at a depth of ~55 ft at the TY Tank Farm. The 45-ft depth lies near the H1/H2 contact and, therefore, may reflect a capillary boundary that exists between highly contrasting lithologies along this boundary. Moisture and contaminants moving through the vadose zone have been shown to collect along highly contrasting lithologic boundaries (Serne et al. 2004a).

Unlike the C-152 direct push characterization study (Brown et al. 2007) in WMA C, which had lots of neutron geophysical log information and showed multiple moisture boundaries, there is much less information, with no moisture (neutron) logs for T and TY probe holes. Therefore, not much can be concluded about the geology penetrated by the T and TY direct push holes.

## **3.0 Geochemical Methods and Materials**

This chapter discusses the methods and philosophy used to characterize the T and TY Tank Farm probe samples and the parameters that were measured and analyzed in the laboratory. It also describes the materials and methods used to conduct analyses of the physical, geochemical, and radio-analytical properties of the sediments.

### **3.1 Sample Inventory**

#### **3.1.1 TY Tank Farm Direct Push Samples**

Samples were numbered using a project-specific prefix, in this case S06001 for the samples collected from the TY Tank Farm, followed by a specific sample identification suffix, such as -1. At the TY Tank Farm, sediment samples were collected from five direct push probe holes (see Figure 2.5). Each direct push sampling campaign resulted in up to three depth-discrete cores (3.8 cm in diameter by approximately 15.2 cm long) and one grab sample consisting of the material captured in the drive shoe. The core samples from each direct probe hole were further identified by the letters A, B, or C, where the A liner (the liner was the stainless steel sleeve that contained the sediment core sample) was always in the deeper position closest to the drive shoe (i.e., the protective end attached to the bottom of the drive casing). All core samples can be delineated from the grab samples by the additional A, B, or C nomenclature following the sample identification suffix, such as S06001-1A (Table 3.1). One laboratory duplicate sample was collected during core opening and is designated by the nomenclature DUP. Recovery of samples was poor, particularly for the core material: the A-sleeve from probe hole C4604 was approximately 1/6 full, the C-sleeve from probe hole C4606 was nearly empty, and the B-sleeve from C4624 and the A-sleeve from C4610 were approximately 1/2 full. For probe hole C4622, only sediment within the shoe was recovered.

#### **3.1.2 T Tank Farm Direct Push Samples**

At the T Tank Farm, sediment samples were collected from seven direct push holes (see Figure 2.4). Each direct push sampling campaign resulted in up to three depth-discrete cores (1.25 inches in diameter by 6 inches long) and one grab sample consisting of the material captured in the drive shoe. Each sample interval collected within the T Tank Farm was numbered using Hanford Environmental Information System (HEIS)-specific sample names. The core samples from each sample interval were further identified by the letters A, B, or C, where the A Liner was always in the deeper position closest to the drive shoe. Three laboratory duplicate samples were collected during core opening and are designated by the nomenclature DUP. Recovery of samples was fairly good in most of the probe holes. The one exception was probe hole C4598, which had no material recovered from the shoe, one full liner, and one partially full liner. Details about the T Tank Farm direct push samples are in Table 3.2.

### **3.2 Approach**

During a past investigation at WMA SX, it was found that changes in sediment type and contaminant concentrations often occurred within a distance of a few inches within a given liner (Serne et al. 2002b). It was concluded that a more methodical scoping approach would be necessary to provide the technical

**Table 3.1.** Sample Inventory from the TY Tank Farm Direct Push Probe Holes

Sample Number	Probe Hole Number	Sample Recovery (%)	Sample Number	Probe Hole Number	Sample Recovery (%)
S06001-1A	C4604	20	S06001-3	C4610	NA
S06001-1	C4604	NA	S06001-4C	C4606	10
S06001-2B	C4624	50	S06001-4B	C4606	100
S06001-2A	C4624	90	S06001-4A	C4606	100
S06001-2	C4624	NA	S06001-4	C4606	NA
S06001-3A	C4610	50	S06001-5	C4622	65
Shaded cells indicate grab samples. NA indicates not applicable.					

**Table 3.2.** Sample Inventory from the T Tank Farm Direct Push Probe Holes

Sample Number	Probe Hole Number	Sample Recovery (%)	Sample Number	Probe Hole Number	Sample Recovery (%)
B1KC35B	C4598	20	B1KC39B	C5384	95
B1KC35A	C4598	90	B1KC39A	C5384	95
B1KC36C	C4596	100	B1KC39	C5384	NA
B1KC36B	C4596	95	B1KC40C	C5374	100
B1KC36A	C4596	100	B1KC40B	C5374	100
B1KC36	C4596	NA	B1KC40A	C5374	100
B1KC37C	C5378	70	B1KC40	C5374	NA
B1KC37B	C5378	95	B1LB07C	C5382	100
B1KC37A	C5378	40	B1LB07B	C5382	100
B1KC38C	C5378	95	B1LB07A	C5382	85
B1KC38B	C5378	95	B1LB08C	C5380	100
B1KC38A	C5378	75	B1LB08B	C5380	100
B1KC38	C5378	NA	B1LB08A	C5380	100
B1KC39C	C5384	100	B1LB08	C5380	NA
Shaded cells indicate grab samples. NA indicates not applicable.					

justification for selecting samples for detailed characterization as defined in the data quality objectives process (DOE 1999). Subsequently, a method was developed to select samples that considered depth, geology (e.g., lithology, grain-size composition, and carbonate content, etc.), individual liner contaminant concentration (e.g., radionuclides, nitrate), moisture content, and overall sample quality. Extraction/leaching procedures were performed and certain key parameters (i.e., moisture content, gamma energy analysis) were measured on sediment from each liner. Grab samples were only utilized as part of this study if sufficient sample material for characterization and analysis was not contained in the core samples.

During the geologic examination of the core samples, the liner contents were sub-sampled for moisture content, gamma-emission radiocounting, 1:1 water extracts (which provide soil pH, electrical conductivity (EC), cation, 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). Sampling preference was always biased towards the finer-grained and/or wetter material contained in each liner. The remaining sediment from each liner was then sealed and placed in cold storage.

### **3.3 Materials and Methods**

During sub-sampling of each core liner, every effort was made to minimize moisture loss and prevent cross contamination between samples. Depending on the sample matrix, very coarse pebbles and larger material (i.e., >32 mm) were avoided during sub-sampling. Larger substrate was excluded to provide moisture contents representative of gamma energy analysis and 1:1 sediment:water extract samples. Therefore, the results from the sub-sample measurements may contain a possible bias toward higher concentrations for some analytes that would be preferentially associated with the smaller sized sediment fractions.

Procedures ASTM D2488-93 (1993) and PNL-MA-567-DO-1 (PNL 1990) were followed for visual descriptions and geological descriptions of all direct push samples. The sediment classification scheme used for geologic identification of the sediment types (used solely for graphing purposes in this report) was based on the modified Folk/Wentworth classification scheme (1968/1922).

#### **3.3.1 Moisture Content**

Gravimetric water contents of the sediment samples from each liner and shoe grab sample were determined using PNNL procedure PNNL-AGG-WC-001 (PNNL 2005). This procedure is based on the American Society for Testing and Materials procedure “Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass” (ASTM D2216-98 [ASTM 1998]). One representative sub-sample of at least 15 to 70 g was used. Sediment aliquots were placed in tared containers, weighed, and dried in an oven at 105°C until constant weight was achieved, which took at least 24 hours. The containers were removed from the oven, sealed, cooled, and weighed. At least two weighings, each after a 24-hour heating period, were performed to ensure that all moisture was removed. All weighings were performed using a calibrated balance. A calibrated weight set was used to verify balance performance before weighing the samples. The gravimetric water content was computed as the percentage change in soil weight before and after oven drying.

#### **3.3.2 1:1 Sediment:Water Extracts**

Water-soluble inorganic constituents were determined using a 1:1 sediment:deionized-water extract method. This method was chosen because the sediment was too dry to easily extract vadose zone pore water. The extracts were prepared by adding an exact weight of deionized water to approximately 60 to 80 g of sediment sub-sampled from each liner or drive shoe grab sample. The weight of deionized water needed was calculated based on the weight of the field-moist samples and their previously determined moisture contents. The sum of the existing moisture (pore water) and the deionized water was fixed at the mass of the dry sediment. An appropriate amount of deionized water was added to screw cap jars containing the sediment samples. The jars were sealed and briefly shaken by hand, then placed on a mechanical orbital shaker for one hour. The samples were allowed to settle, generally overnight, until the supernatant liquid was fairly clear. The supernatant was carefully decanted and separated into unfiltered aliquots for conductivity and pH determinations and into filtered aliquots (passed through 0.45 µm membranes) for anion, cation, alkalinity, and radionuclide analyses. More details can be found in Rhoades (1996) and within Methods of Soils Analysis - Part 3 (ASA 1996).

### **3.3.2.1 pH and Conductivity**

Two approximately 3-mL aliquots of the unfiltered 1:1 sediment:water extract supernatants were used for pH and conductivity measurements. The pH of the extracts was measured with a solid-state pH electrode and a pH meter calibrated with buffers 4, 7, and 10. Electrical conductivity was measured and compared to potassium chloride standards with a range of 0.001 M to 1.0 M.

### **3.3.2.2 Anions**

The 1:1 sediment:water extracts were analyzed for anions using ion chromatography (IC). Fluoride, chloride, nitrite, bromide, nitrate, carbonate, phosphate, and sulfate were separated on a Dionex AS17 column with a gradient elution of 1 mM to 35 mM sodium hydroxide and measured using a conductivity detector. This methodology is based on U.S. Environmental Protection Agency (EPA) Method 300.0A (EPA 1984) with the exception of using the gradient elution of sodium hydroxide. Water extract chromatograms were visually scanned to ensure there were no unidentified peaks caused by other constituents.

### **3.3.2.3 Cations and Trace Metals**

Major cation analysis was performed using an inductively coupled plasma-optical emission spectroscopy (ICP-OES) unit using high-purity calibration standards to generate calibration curves and verify continuing calibration during the analysis run. Multiple dilutions were made of each 1:1 water extract for analysis to investigate and correct for matrix interferences. Details of this method are found in EPA Method 6010B (EPA 2000b). The second instrument used to analyze trace metals, including technetium-99 and uranium-238, was an inductively coupled plasma-mass spectrometer (ICP-MS) using PNNL-AGG-415 method (PNNL 1998). This method is quite similar to EPA Method 6020 (EPA 2000c).

### **3.3.2.4 Alkalinity**

The alkalinity of several of the 1:1 sediment:water extracts was measured using standard titration. The alkalinity procedure is equivalent to the U.S. Geological Survey (USGS) National Field Manual (USGS 2001) method.

### **3.3.2.5 8 M Nitric Acid Extract**

Approximately 20 g of oven-dried sediment was contacted with 8 M nitric acid at a ratio of approximately five parts acid to one part sediment. The slurries were heated to about 80°C for several hours, then the fluid was separated by filtration through 0.45 µm membranes. The acid extracts were analyzed for major cations and trace metals using ICP-OES and ICP-MS techniques, respectively. The acid digestion procedure is based on EPA SW-846 Method 3050B (EPA 2000a).

### **3.3.2.6 Gamma Energy Analysis**

Gamma energy analysis (GEA) was performed on sediment from the direct push liners. All samples for GEA were analyzed using 60% efficient intrinsic germanium gamma detectors. All germanium counters were efficiency calibrated for distinct geometries using mixed gamma standards traceable to the National Institute of Standards and Technology (NIST). Field-moist samples were placed in 150-cm<sup>3</sup> counting containers and analyzed for 100 minutes in a fixed geometry. All spectra were background-

subtracted. Spectral analysis was conducted using libraries containing most mixed fission products, activation products, and natural decay products. Control samples were run throughout the analysis to ensure correct operation of the detectors. The controls contained isotopes with photo peaks spanning the full detector range and were monitored for peak position, counting rate, and full-width half-maximum. Details are found in *Gamma Energy Analysis, Operation, and Instrument Verification using Genie2000™ Support Software* (PNNL 1997).

### **3.3.2.7 Carbon Content of Sediment**

The total carbon concentration in aliquots of sediment from the core liners was measured with a Shimadzu TOC-V CSN instrument with a SSM-5000A Total Organic Carbon Analyzer by combustion at approximately 900°C based on ASTM Method, *Standard Test Methods for Analysis of Metal Bearing Ores and Related Materials by Combustion Infrared Absorption Spectrometry* (ASTM E1915-01, 2001). Samples were placed into pre-combusted, tared, ceramic combustion sample holders and weighed on a calibrated balance. After the combustion sample holders were placed into the furnace introduction tube, an approximately 2-minute waiting period was allowed for the ultra-pure oxygen carrier gas to remove any carbon dioxide introduced to the system from the atmosphere during sample placement. After this sparging process, the sample was moved into the combustion furnace and the combustion was begun. The carrier gas then delivered the sample combustion products to the cell of a non-dispersive infrared (NDIR) gas analyzer where the carbon dioxide was detected and measured. The amount of CO<sub>2</sub> measured is proportional to the total carbon content of the sample. Adequate system performance was confirmed by analyzing known quantities of a calcium carbonate standard.

Sediment samples were analyzed for inorganic carbon content by placing a sediment aliquot into a ceramic combustion boat. The combustion boat was placed into the sample introduction tube where it was sparged with ultra-pure oxygen for two minutes to remove atmospheric carbon dioxide. A small amount (usually 0.6 ml) of 3 M phosphoric acid was then added to the sample in the combustion boat. The boat was moved into the combustion furnace where it was heated to 200°C. Samples were completely covered by the acid to allow full reaction to occur. Ultra-pure oxygen swept the resulting carbon dioxide through a dehumidifier and scrubber into the cell of a NDIR gas analyzer where the carbon dioxide was detected and measured. The amount of CO<sub>2</sub> measured is proportional to the inorganic carbon content of the sample.

Organic carbon content was determined by the difference between the inorganic carbon and total carbon concentrations.

### **3.3.3 Technetium-99 Extraction and Analysis**

A subset of samples from the direct push probe holes emplaced with the T Tank Farm were selected for a comprehensive investigation of water vs. acid soluble technetium-99. The four deepest samples collected from probe hole C5374 (B1KC40, B1KC40A, B1KC40B, and B1KC40C) as well as one uncontaminated sediment (C3177) were extracted in triplicate using either the 1:1 sediment:water or 8M nitric acid extractions described in the previous section. A third extraction technique, microwave-assisted digestion, was also performed. Using this technique, approximately 300 mg of sediment was placed in a 100-mL Teflon microwave digestion vessel. Following this, 10 mL water, 5 mL of 16-M nitric acid (HNO<sub>3</sub>), 2 mL of 12-M hydrochloric acid (HCl), and 1 mL of 29-M hydrofluoric acid (HF) were added, and the vessel was sealed and placed in a MARS5™ microwave-assisted digestion system (CEM

Corporation, Matthews, NC). The samples were heated at the EPA-recommended temperatures and times. The samples were then allowed to cool, and 0.45 g of powdered boric acid was added to the digestate, which was then shaken by hand. Boric acid reacts with residual HF in the digestate to form a boron complex (preventing the residual HF from etching the sample introduction glassware in the ICP-MS instrument). Although there were no visible solids in the digestate, samples were filtered through a 0.45- $\mu\text{m}$ -pore-size syringe filter prior to analysis.

Recoveries for technetium-99 during the respective extraction processes were evaluated using preparation blanks, blank spikes, and matrix spikes. Preparation blanks were composed of matrix appropriate solutions (i.e., deionized water, 8M HNO<sub>3</sub>, or microwave digestion acids) known to be free of technetium-99. The blank spikes consisted of the same matrix appropriate solutions containing 0.3  $\mu\text{g/L}$  technetium-99, while the matrix spikes consisted of actual samples spiked with 0.3  $\mu\text{g/L}$  technetium-99. These quality control samples, as well as the 1:1 sediment:water extracts, 8M nitric acid extracts, and microwave assisted digestates were analyzed for technetium-99 using ICP-MS.

An aliquot of each filtered extract or digestate (from above) was further processed using TEVA® resin (Eichrom, Darien, IL) and reanalyzed for technetium-99 via ICP-MS. This additional step was performed to ensure that any matrix effects resulting from the extraction or digestion process could be removed prior to analysis of the samples. The samples were prepared for processing by drying 10 mL aliquots of the nitric acid extracts and microwave-digested samples under a heat lamp. Once dried, the samples were brought to 10 mL with 0.1-M HNO<sub>3</sub>. All three types of 10 mL aliquots of the 1:1 sediment:water extracts were acidified with concentrated HNO<sub>3</sub> to a final concentration of 0.1 M. These 10 mL solutions were added to columns containing 2 mL of TEVA® resin that had been previously cleaned/conditioned using 5 mL of a 0.1-M HNO<sub>3</sub> solution. Under these conditions the TEVA® resin selectively captures pertechnetate species but allows most other solutes to pass through the resins. After addition of the samples, the columns were further flushed by flowing 20 mL of a 1-M HNO<sub>3</sub> solution through each column. The technetium-99 trapped in the columns was eluted using 10 mL of a 12-M HNO<sub>3</sub> solution. The eluted solution containing the technetium-99 was collected in a 20-mL glass liquid scintillation vial and evaporated to dryness under a heat lamp. Once the solution was completely evaporated, 5 mL of a 2% HNO<sub>3</sub> solution was added to the vials, and the samples were analyzed for technetium-99 via ICP-MS.

### **3.3.4 Stable Ruthenium Analysis**

A subset of samples from the direct push probe holes emplaced within the T Tank Farm was selected for stable ruthenium isotopic analysis. Aliquots of the 1:1 sediment:water extracts from the four deepest samples collected from probe hole C5374 (B1KC40, B1KC40A, B1KC40B, and B1KC40C) were further processed using ion exchange resin. Specifically, 10 mL aliquots of the water extracts were acidified with HCl to a final concentration of 5% (by volume) and added to columns containing 1 mL of Dowex-1 100-200 mesh anion exchange resin, which should have adsorbed anionic ruthenium species [RuO<sub>4</sub><sup>2-</sup>]. The resin columns had been conditioned with 5% HCl prior to addition of the acidified water extracts. After addition of the extracts, the columns were rinsed with 5 mL of 5% HCl. The columns were then flushed with 10 mL of deionized water. Finally, the ruthenium was eluted from the columns using 10 mL of 8M HNO<sub>3</sub>. All of the eluted ruthenium solutions that passed through the anion exchange columns, including the 5% HCl rinsate, the deionized water rinsate, and the 8M nitric acid rinsate, were analyzed for ruthenium isotopes using ICP-MS after adjusting the nitric acid molarity to 0.3M.

## 4.0 Results and Discussion

This section presents the geochemical and physical characterization data collected on sediment from the direct push holes emplaced within the T and TY Tank Farms. These characterization activities emphasized tests that provided basic characterization data and were key to determining the distribution of mobile contaminants in the vadose zone sediments. Such information on the direct push sediments included moisture content, total and inorganic carbon content, and pH, electrical conductivity (EC), and measurements of major cations, anions, and trace metals (including technetium-99 and uranium-238). Gamma energy analysis (GEA) of the sediments was also performed to search for any detectable man-made gamma-emitting radionuclides.

### 4.1 Vadose Zone Sediment from the TY Tank Farm Direct Push Samples

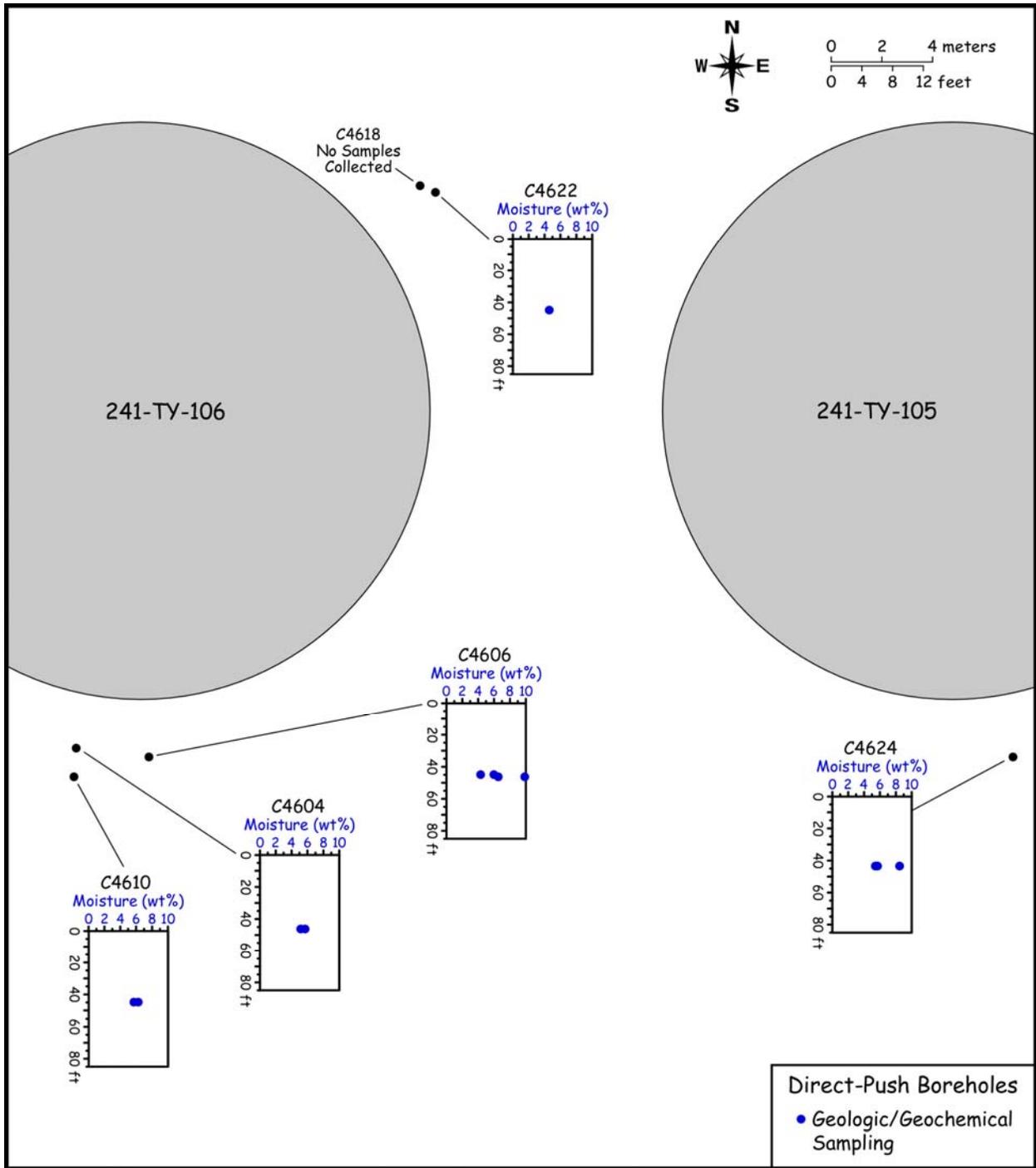
#### 4.1.1 Moisture Content

The moisture contents of the seven core liners and five grab samples collected from the TY direct push holes are presented as a function of depth in Table 4.1 and Figure 4.1. Two samples displayed slightly elevated moisture contents: the A-sleeve of probe hole C4624 (8.29%) and the shoe material from C4606 (9.73%). The A and B liners from probe hole C4624 contained sediment with appreciably different moisture contents (greater than 30% difference), indicating that the contact for the zone of increased moisture was encountered within the 0.8 ft sampling interval. Photographs of the sediment removed from each liner are included in Appendix A of this report. The average gravimetric moisture content of all of the TY direct push samples measured in this study was 6.1 wt%, which was slightly higher than the average moisture content in core samples collected within the Hanford formation H2 unit (3.9%) at the nearby TX Tank Farm characterization borehole (background borehole 299-W10-27 just east of the TY Tank Farm) (Serne et al. 2004b). However, the TY direct samples were collected at the interface between the backfill and Hanford formation; therefore, the elevated moisture measured in these samples could be an artifact of the compaction that occurred at this interface during construction of the tank farm or of the capillary boundary along this discontinuity.

**Table 4.1.** Gravimetric Moisture Content of Samples Obtained from the TY Tank Farm Direct Push Probe Holes

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Moisture (%)
S06001-1A	C4604	44.95	5.09%
S06001-1	C4604	NR	5.45%
S06001-2B	C4624	42.10	5.64%
S06001-2A	C4624	42.50	8.29%
S06001-2	C4624	43.05	5.24%
S06001-3A	C4610	43.80	5.50%
S06001-3	C4610	44.21	6.18%
S06001-4C	C4606	44.38	4.26%
S06001-4B	C4606	44.67	5.89%
S06001-4A	C4606	45.17	6.44%
S06001-4A DUP	C4606	45.17	6.57%
S06001-4	C4606	45.71	9.73%
S06001-5	C4622	43.65	4.53%

NR indicates the information was not recorded on the chain of custody.  
Shaded cells indicate grab samples.



2007/DCL/TY/001 (05/14)

**Figure 4.1.** Moisture Content Data for the TY Tank Farm Direct Push Samples

#### 4.1.2 1:1 Sediment:Water Extracts

The samples from the TY Tank Farm direct push were characterized by performing 1:1 sediment:water extracts. The following tables present the mass of a given constituent leached per gram of sediment as measured in the water extracts. Other tables show dilution-corrected values that represent

concentrations in vadose zone pore water. As discussed in several other Vadose Zone Characterization Project reports, the dilution-corrected 1:1 sediment:water extracts are a reasonable estimate of the actual vadose zone pore water in contaminated sediments, but slightly over predict actual pore water concentrations in uncontaminated sediments (see Serne et al. 2002a, 2002b, 2002c, 2002e, 2002f).

#### 4.1.2.1 pH and Electrical Conductivity

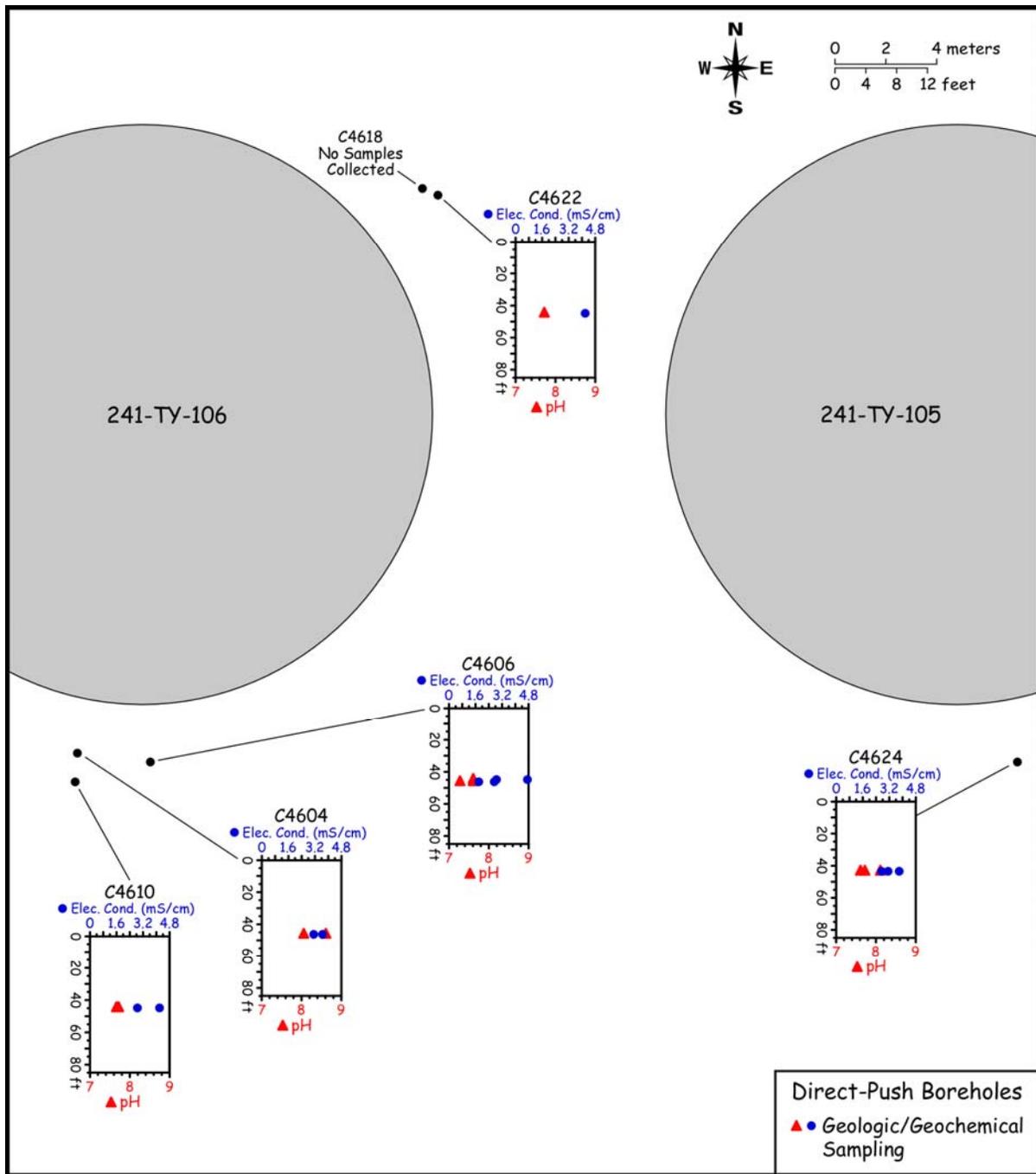
The 1:1 sediment:water extract pH and EC data for the TY Tank Farm core and grab samples are shown in Table 4.2 and Figure 4.2. The pH is tabulated as measured in the 1:1 sediment:water extracts but the EC is corrected for dilution and tabulated as if it was actual pore water. Nearly all of the extract samples tested had pH values in the normal range for Hanford formation sediments (between 7.5 and 8.5). However, one of the core samples, S06001-1A from probe hole C4604, had a slightly elevated pH value of 8.63. In comparison, sample S06001-4C from probe hole C4610 (just south of C4604) had a pH of 7.61. Therefore, it is possible that the elevated pH data for sample S006001-A indicates the presence of caustic tank-related waste from tank 241-TY-106. Previous borehole reports have shown that regions of elevated soil pH are considered to be good indicators of the location of the original leak event or very near-field close to the initial tank waste entry zone (see Serne et al. 2002a, 2002b, 2002c, 2002e, 2002f).

The pore water-corrected EC data for all of the samples from TY Tank Farm were low, with a range of 1.71 to 4.62 mS/cm. The average EC of the grab and core samples was 3.2 mS/cm, which is significantly lower than the average calculated porewater EC (20.4 mS/cm) in samples from the background borehole 299-W10-27 emplaced east of the TY Tank Farm as part of the TX Tank Farm characterization effort. For comparison, two contaminated boreholes located near the TY Tank Farm, C4104 (near T-106) and C3831 (near TX-107), had average pore water-corrected EC values of 14.2 and 8.7 mS/cm, with peak EC values of 33.4 and 43.3, respectively. Therefore, the porewater in the sediment samples collected around the TY Tank Farm appeared to be dilute with respect to the dissolved salts in comparison to contaminated core samples from C3831 (near TX-107) and C4104 (near T-106).

**Table 4.2.** pH for 1:1 Sediment:Water Extracts and Dilution-Corrected EC Values from TY Tank Farm Core and Grab Samples

Sample ID	Probe Hole ID	Mid-Depth ft bgs	pH	Conductivity (mS/cm)
S06001-1A	C4604	44.95	<b>8.63</b>	3.12
S06001-1	C4604	NR	7.98	3.59
S06001-2B	C4624	42.10	8.12	3.68
S06001-2A	C4624	42.50	7.70	2.71
S06001-2	C4624	43.05	7.64	3.13
S06001-3A	C4610	43.80	7.73	4.18
S06001-3	C4610	44.21	7.65	2.75
S06001-4C	C4606	44.38	7.61	4.62
S06001-4B	C4606	44.67	7.59	2.75
S06001-4A	C4606	45.17	7.27	2.66
S06001-4A DUP	C4606	45.17	7.51	2.18
S06001-4	C4606	45.71	7.63	1.71
S06001-5	C4622	43.65	7.70	4.08

Bold values denote elevated concentrations.  
 EC values are dilution corrected and represent pore water concentrations not 1:1 extract values.  
 Shaded cells indicate grab samples.



2007/DCL/TY/002 (05/29)

**Figure 4.2.** pH for 1:1 Sediment:Water Extracts and Dilution-Corrected EC Values from TY Tank Farm

#### 4.1.2.2 Composition of the 1:1 Sediment:Water Extracts from the TY Tank Farm Core and Grab Samples

The water extract values for the major anions, cations, and several trace constituents are discussed in this section. The anion data are tabulated in Table 4.3 and Figures 4.3 through 4.4 in units of mass per gram of dry sediment. Two of the 1:1 sediment:water extracts contained slightly elevated concentrations

of fluoride (greater than 1  $\mu\text{g/g}$ ) compared to the average fluoride concentration of all 12 samples (0.58  $\mu\text{g/g}$ ). The average 1:1 sediment:water extract fluoride value for the TY Tank Farm probe holes was comparable to the average concentration of 0.60  $\mu\text{g/g}$  found in borehole 299-W10-27. The probe holes containing the samples with elevated fluoride were C4610 (A-sleeve) and C4606 (C-sleeve), which are both located at the south end of tank 241-TY-106. The A-sleeve is the first liner placed in the sampler behind the nose cone and represents the deepest core sample collected from the hole. Interestingly, tank 241-TY-103 was the only tank leak within the TY tank farm reported to contain significant fluoride (0.123 M) (Cantrell et al. 2007). Two of the 1:1 sediment:water extracts contained elevated chloride concentrations (greater than 3  $\mu\text{g/g}$ ) compared to the average chloride concentration of all 12 samples (1.38  $\mu\text{g/g}$ ), which was comparable to the average chloride concentration of 0.90  $\mu\text{g/g}$  found in the background borehole (299-W10-27). These two samples were from probe holes C4604 (A-sleeve) and C4624 (A-sleeve), which are located south of tanks 241-TY-106 (C4604) and 241-TY-105 (C4624). Both tanks 241-T-105 and 241-TY-106 held waste containing approximately 0.1M chloride, although the leak at tank TY-105 released approximately twice as much volume ( $1.32\text{E}+05$  L) to the vadose zone than the leak from tank TY-106 ( $7.57\text{E}+04$  L) (Cantrell et al. 2007). Water-extractable nitrate was highest (approximately 6  $\mu\text{g/g}$  of dry sediment) in a sample from probe hole C4606, which is just south of tank 241-TY-106, compared to an average nitrate value for all 12 samples of 2.8  $\mu\text{g/g}$ . The nitrate values for the 1:1 sediment:water extracts for the TY Tank Farm direct push samples were, on average, slightly higher than values found in borehole 299-W10-27 (1.5  $\mu\text{g/g}$ ). All of the tank leaks within the TY tank farm contained in excess of 2M nitrate-nitrite (Cantrell et al. 2007). The A-sleeve 1:1 sediment:water extract from probe hole C4604 (located just south of 241-TY-106) contained elevated sulfate (greater than 90  $\mu\text{g/g}$ ), compared to the average of all 12 samples (24  $\mu\text{g/g}$ ). The average sulfate concentration for the 1:1 sediment:water extracts from the TY Tank Farm direct push was approximately a factor of two higher than the average concentration from background borehole 299-W10-27 (11  $\mu\text{g/g}$ ). The majority of the samples did not contain quantifiable amounts of water-extractable phosphate.

The water-extractable major cations in the TY Tank Farm probe hole sediments are tabulated in Table 4.4 and Figure 4.5 in units of mass per gram of sediment on a dry weight basis. The A-sleeve from push hole C4604 (located south of tank 241-TY-106) contained elevated levels of several water-extractable cations. Specifically, the calcium concentration (82  $\mu\text{g/g}$ ) in the A-sleeve from C4604 was significantly higher than the average calcium concentration of all the samples measured (15  $\mu\text{g/g}$ ); potassium (21  $\mu\text{g/g}$ ) was elevated compared to the average potassium concentration of all the samples measured (6.4  $\mu\text{g/g}$ ); strontium (0.3  $\mu\text{g/g}$ ), was a factor of five higher than the average strontium concentration of all the samples measured (0.06  $\mu\text{g/g}$ ) and sodium (79  $\mu\text{g/g}$ ) was elevated compared to the average sodium concentration of all the samples measured (26  $\mu\text{g/g}$ ). All of the TY farm tank leaks contained in excess of 4M sodium and insignificant concentrations of calcium, magnesium, and potassium (Cantrell et al. 2007). It was surprising to find elevated calcium, magnesium, and sodium together in the same sample, since the sodium would typically drive the divalent cations off the exchange sites. The concentrations of these cations from the A-sleeve material of push hole C4604 were significantly higher than those found in the shoe material from the same push hole. Further, this disparity was consistent with the pH and EC measurements from these two samples and was likely an artifact of sampling limitations (i.e., poor recovery in combination with slough). Conversely, water-extractable magnesium was low for the A-sleeve (0.01  $\mu\text{g/g}$ ) and shoe (0.6  $\mu\text{g/g}$ ) materials from push hole C4604, as well as for the B-sleeve (0.6  $\mu\text{g/g}$ ) material from push hole C4624. The A-sleeve material from push hole C4624 contained an elevated concentration of magnesium (2.4  $\mu\text{g/g}$ ), as did the shoe material for push hole C4606 (2.2  $\mu\text{g/g}$ ). With the exception of the A-liner sample from direct push hole C4604, sodium was the dominant water extractable cation in the Sediment:water extract samples; however, the

A-liner from push hole C4604 still contained significantly elevated water-extractable sodium. Based on these data, there are signs of cation exchange by high sodium containing tank waste in all of the probe holes emplaced around tank 241-TY-106.

**Table 4.3.** Water-Extractable Anions in the TY Tank Farm Core and Grab Samples ( $\mu\text{g/g}$  dry sediment)

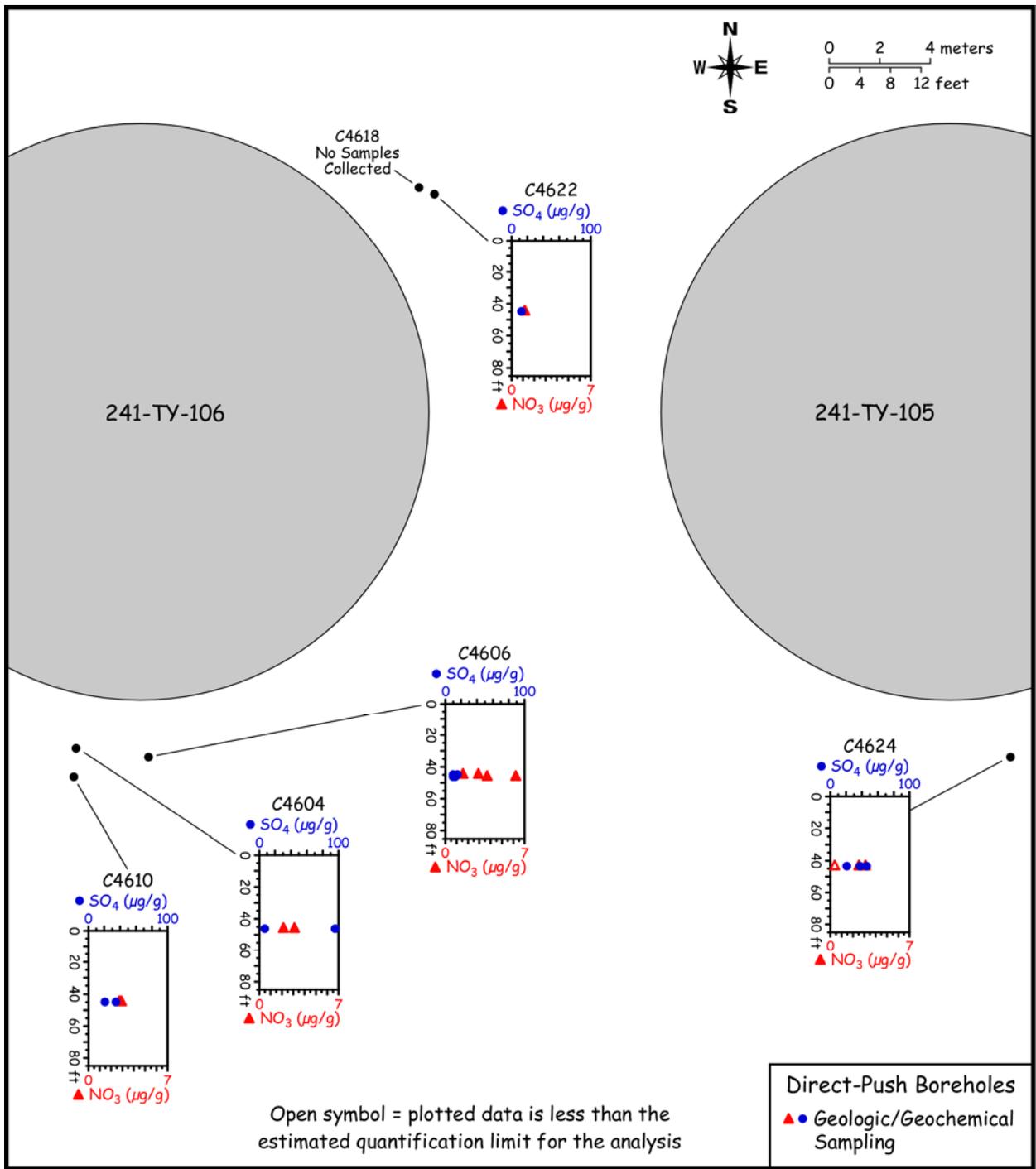
Sample ID	Probe Hole ID	Mid-Depth ft bgs	Fluoride $\mu\text{g/g}$	Chloride $\mu\text{g/g}$	Nitrate $\mu\text{g/g}$	Sulfate $\mu\text{g/g}$	Phosphate $\mu\text{g/g}$
S06001-1A	C4604	44.95	6.14E-01	<b>3.78E+00</b>	3.16E+00	<b>9.43E+01</b>	<b>6.80E-01</b>
S06001-1	C4604	Not Reported	2.89E-01	5.38E-01	2.15E+00	5.42E+00	<5.62E-01
S06001-2B	C4624	42.10	9.90E-01	1.36E+00	<4.33E-01	3.63E+01	<5.05E-01
S06001-2A	C4624	42.50	3.50E-01	<b>3.46E+00</b>	3.04E+00	4.49E+01	<5.05E-01
S06001-2	C4624	43.05	2.80E-01	6.85E-01	2.49E+00	1.98E+01	<5.05E-01
S06001-3A	C4610	43.80	<b>1.30E+00</b>	1.68E+00	2.96E+00	3.40E+01	<5.05E-01
S06001-3	C4610	44.21	6.10E-01	8.06E-01	2.76E+00	1.94E+01	<5.05E-01
S06001-4C	C4606	44.38	<b>1.09E+00</b>	1.18E+00	1.54E+00	1.50E+01	<5.05E-01
S06001-4B	C4606	44.67	3.93E-01	8.82E-01	2.98E+00	8.78E+00	<5.05E-01
S06001-4A	C4606	45.17	3.74E-01	7.23E-01	3.76E+00	1.11E+01	<5.05E-01
S06001-4A DUP	C4606	45.17	3.58E-01	6.48E-01	3.22E+00	6.93E+00	<5.05E-01
S06001-4	C4606	45.71	3.49E-01	1.09E+00	<b>6.15E+00</b>	8.72E+00	<5.05E-01
S06001-5	C4622	43.65	5.46E-01	1.12E+00	1.23E+00	1.25E+01	<5.05E-01

Bold values denote elevated concentrations.  
 Italicized values denote low concentrations.  
 Less than values indicate the instrument returned a negative value.  
 NR indicates the information was not reported on the chain of custody.  
 Shaded cells indicate grab samples.

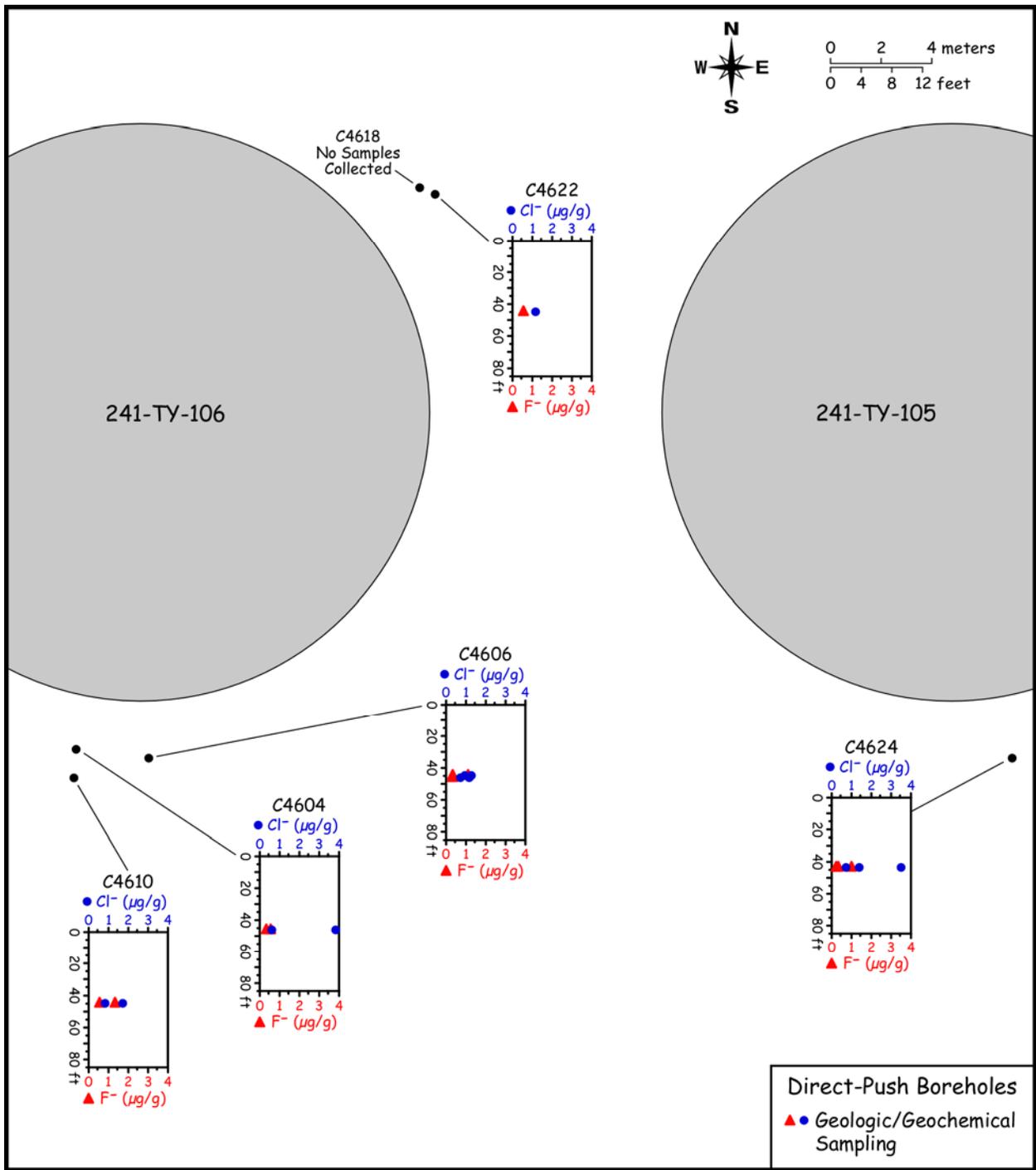
**Table 4.4.** Water-Extractable Major Cations in the TY Tank Farm Core and Grab Samples ( $\mu\text{g/g}$  dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Calcium $\mu\text{g/g}$	Potassium $\mu\text{g/g}$	Magnesium $\mu\text{g/g}$	Strontium $\mu\text{g/g}$	Sodium $\mu\text{g/g}$
S06001-1A	C4604	44.95	<b>8.22E+01</b>	<b>2.12E+01</b>	(1.35E-02)	<b>2.86E-01</b>	<b>7.87E+01</b>
S06001-1	C4604	NR	<i>3.46E+00</i>	(6.65E+00)	<i>6.20E-01</i>	(1.76E-02)	3.49E+01
S06001-2B	C4624	42.10	5.88E+00	(4.66E+00)	<i>6.49E-01</i>	(2.76E-02)	2.92E+01
S06001-2A	C4624	42.50	1.55E+01	(5.74E+00)	<b>2.42E+00</b>	7.55E-02	1.89E+01
S06001-2	C4624	43.05	1.01E+01	(5.53E+00)	1.68E+00	6.07E-02	1.43E+01
S06001-3A	C4610	43.80	7.49E+00	(5.72E+00)	1.53E+00	(4.08E-02)	3.31E+01
S06001-3	C4610	44.21	8.68E+00	(4.53E+00)	1.56E+00	(4.37E-02)	1.73E+01
S06001-4C	C4606	44.38	8.02E+00	(5.50E+00)	1.50E+00	(3.91E-02)	2.65E+01
S06001-4B	C4606	44.67	9.61E+00	(4.84E+00)	1.42E+00	5.24E-02	1.54E+01
S06001-4A	C4606	45.17	1.03E+01	(4.38E+00)	1.84E+00	5.68E-02	1.36E+01
S06001-4A DUP	C4606	45.17	8.37E+00	(4.14E+00)	1.41E+00	(4.48E-02)	1.32E+01
S06001-4	C4606	45.71	1.19E+01	(4.64E+00)	<b>2.23E+00</b>	6.18E-02	1.41E+01
S06001-5	C4622	43.65	7.11E+00	(5.87E+00)	1.18E+00	(3.35E-02)	2.47E+01

Bold values denote elevated concentrations.  
 Italicized values denote low concentrations.  
 Parentheses indicate reported value was less than the limit of quantification for the analysis.  
 NR indicates that the information was not reported on the chain of custody.  
 Shaded cells indicate grab samples.

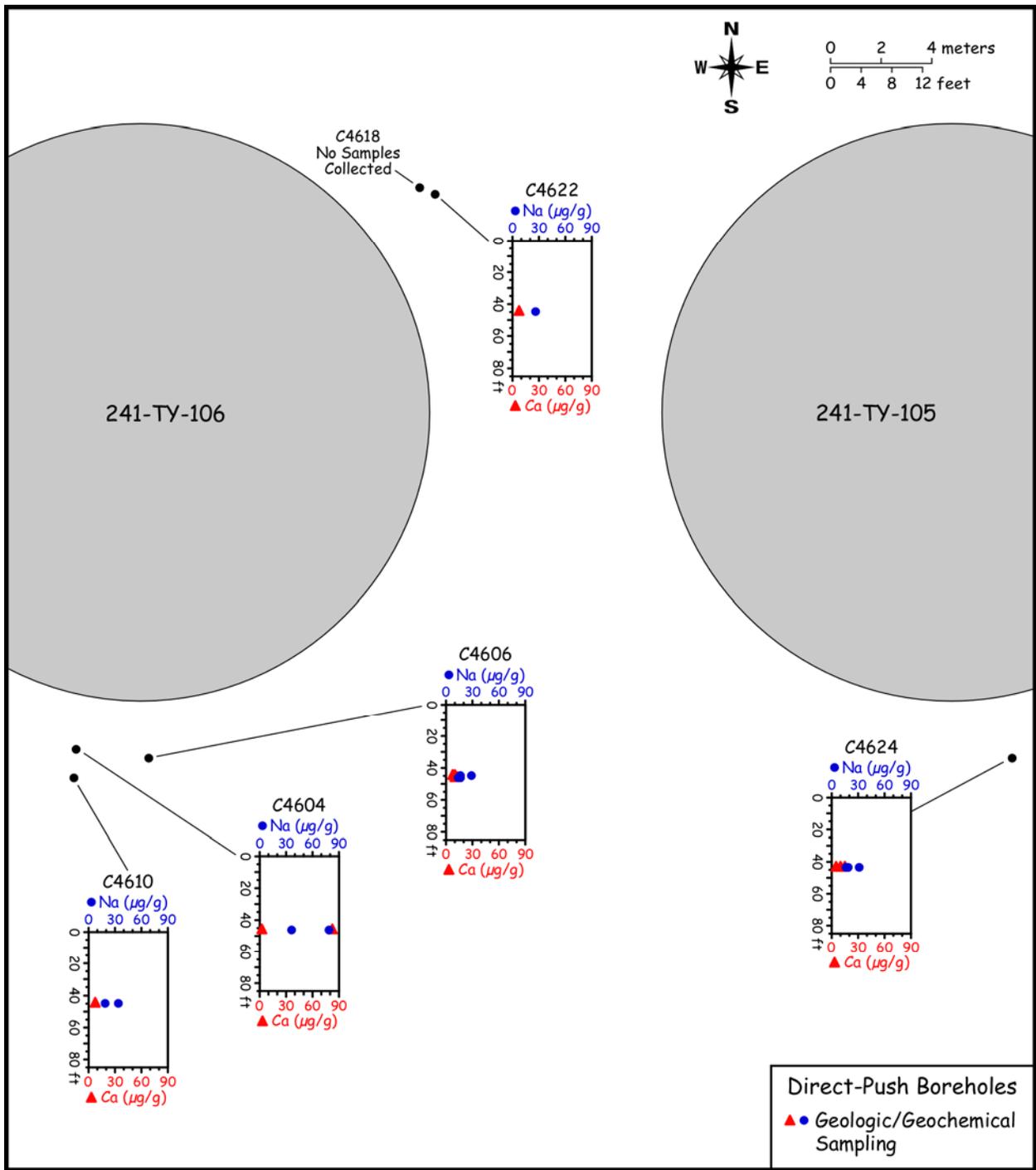


**Figure 4.3.** 1:1 Sediment:Water-Extractable Nitrate and Sulfate Data from the TY Tank Farm Direct Push Samples



2007/DCL/TY/006 (05/16)

**Figure 4.4.** 1:1 Sediment:Water-Extractable Chloride and Fluoride Data from the TY Tank Farm Direct Push Samples



2007/DCL/TY/004 (05/14)

**Figure 4.5.** 1:1 Sediment:Water-Extractable Sodium and Calcium Data from the TY Tank Farm Direct Push Samples

The water-extractable aluminum, iron, silicon, and sulfur in the TY direct push sediments are shown in Table 4.5. The sulfur data were converted to water-extractable sulfur as sulfate so that the results could be compared to the IC data presented in Table 4.3. The water-soluble aluminum was elevated (above the limit of detection) in samples from probe holes C4604 and C4610, which were both emplaced to the south of tank 241-TY-106. It appears that these elevated values of aluminum are a result of some chemical reactions (dissolution/precipitation) between alkaline tank fluids and native sediments that formed precipitates of amorphous aluminum phases that are more water soluble than crystalline aluminum-rich mineral phases in the native sediments. The A-sleeve material from borehole C4606 also contained elevated water-extractable sulfur (reported as sulfate in Table 4.5) and silicon. These results further support the hypothesis that the vadose zone sediments in the vicinity of this probe hole have been chemically altered due to interaction with tank-related waste. The agreement between directly measured sulfate in the water extracts using ion chromatography and indirectly by converting the ICP measurements for sulfur to sulfate was very good (Tables 4.3 and 4.5). Besides validating the ion chromatography data, we can state that the water-extractable sulfur was in fact sulfate.

The water extract data for potentially mobile metals, such as technetium-99, uranium-238, chromium, molybdenum, and ruthenium (Ru) are shown in Table 4.6. Additionally, the water-extractable uranium-238 is plotted as a function of depth in Figure 4.6. Not a single sample collected from the five probe holes (twelve samples total) contained water-leachable technetium-99. Elevated water-leachable uranium-238 was only found in a single sample (S06001-1) from probe hole C4604, which was emplaced just south of tank 241-TY-106. At only  $7.20\text{E-}03$   $\mu\text{g/g}$ , this sample was elevated by approximately a factor of 10 when compared to the average water-extractable uranium concentration found in sediment from borehole 299-W10-27 ( $9.97\text{E-}4$   $\mu\text{g/g}$ ). This sample did not have an elevated porewater alkalinity; however, sample S06001-1A, which was collected just shallower than sample S06001-1, had a porewater alkalinity of 113 meq/L, which was elevated by a factor of three above the average porewater alkalinity measured in all of the TY direct push samples, as well as the highest measured pH value (8.63). Therefore, it is possible that the slightly elevated uranium observed in sample S06001-1 could be an artifact of uranyl-carbonate complexation of naturally occurring labile uranium rather than soluble tank-waste-related contaminant uranium.

Elevated water-leachable chromium ( $2.64\text{E-}01$   $\mu\text{g/g}$ ) was only observed in sample S06001-1A collected from probe hole C4604. For comparative purposes, the average water-leachable chromium value for all of the remaining TY direct push samples was below the limit of quantification for the analysis (less than  $1.25\text{E-}2$   $\mu\text{g/g}$ ). Four samples appeared to have slightly elevated concentrations of water-leachable molybdenum ( $1.17\text{E-}01$  to  $1.66\text{E-}01$   $\mu\text{g/g}$ ) compared to the average water-leachable molybdenum concentration in samples from borehole 299-10-27 ( $5.72\text{E-}03$   $\mu\text{g/g}$ ). The samples containing elevated molybdenum came from probe holes C4604, C4610, and C4626, and could be a result of the dissolution of naturally present minerals via an alkaline tank waste solution. Once dissolved, the molybdenum would be quite mobile and could travel a significant distance from the point of discharge. None of the samples analyzed contained quantifiable concentrations of water-extractable ruthenium. However, this was not surprising given the lack of measurable technetium-99 in these samples.

**Table 4.5.** Water-Extractable Cations in the TY Tank Farm Core and Grab Samples ( $\mu\text{g/g}$  dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Aluminum $\mu\text{g/g}$	Iron $\mu\text{g/g}$	Sulfur as $\text{SO}_4^{2-}$ $\mu\text{g/g}$	Silicon $\mu\text{g/g}$
S06001-1A	C4604	44.95	<b>3.68E-01</b>	<i>(2.07E-03)</i>	<b>9.69E+01</b>	<b>3.80E+01</b>
S06001-1	C4604	NR	<i>(5.46E-02)</i>	6.34E-02	6.09E+00	1.71E+01
S06001-2B	C4624	42.10	<i>(5.85E-02)</i>	6.32E-02	3.69E+01	1.42E+01
S06001-2A	C4624	42.50	<i>(2.73E-02)</i>	<i>(2.06E-02)</i>	4.62E+01	2.21E+01
S06001-2	C4624	43.05	<i>(3.25E-02)</i>	3.91E-02	2.21E+01	1.40E+01
S06001-3A	C4610	43.80	<b>2.08E-01</b>	1.51E-01	3.66E+01	1.06E+01
S06001-3	C4610	44.21	<i>(8.88E-02)</i>	7.88E-02	2.07E+01	1.07E+01
S06001-4C	C4606	44.38	<i>(9.73E-02)</i>	1.03E-01	1.70E+01	1.18E+01
S06001-4B	C4606	44.67	<i>(5.94E-02)</i>	6.65E-02	9.90E+00	1.41E+01
S06001-4A	C4606	45.17	<i>(5.29E-02)</i>	5.58E-02	1.13E+01	1.36E+01
S06001-4A DUP	C4606	45.17	<i>(3.55E-02)</i>	4.35E-02	6.99E+00	1.33E+01
S06001-4	C4606	45.71	<i>(8.59E-02)</i>	1.25E-01	9.03E+00	1.28E+01
S06001-5	C4622	43.65	<i>(5.18E-02)</i>	5.58E-02	1.35E+01	1.67E+01

Bold values denote elevated concentrations.  
 Italicized values denote low concentrations.  
 Parentheses indicate reported value was less than the limit of quantification for the analysis.  
 NR indicates the information was not reported on the chain of custody.  
 Shaded cells indicate grab samples.

The mobile metal data do not indicate the presence of a significant amount of tank-related waste constituents in any of the TY direct push probe holes. Given the considerable amount of time that has elapsed since the 241-TY-105 and 241-TY-106 tanks were purported to have leaked, natural recharge could have pushed the mobile contaminants deep into the vadose, making their detection via shallow direct push sampling difficult.

#### 4.1.3 Vadose Zone Porewater Chemical Composition

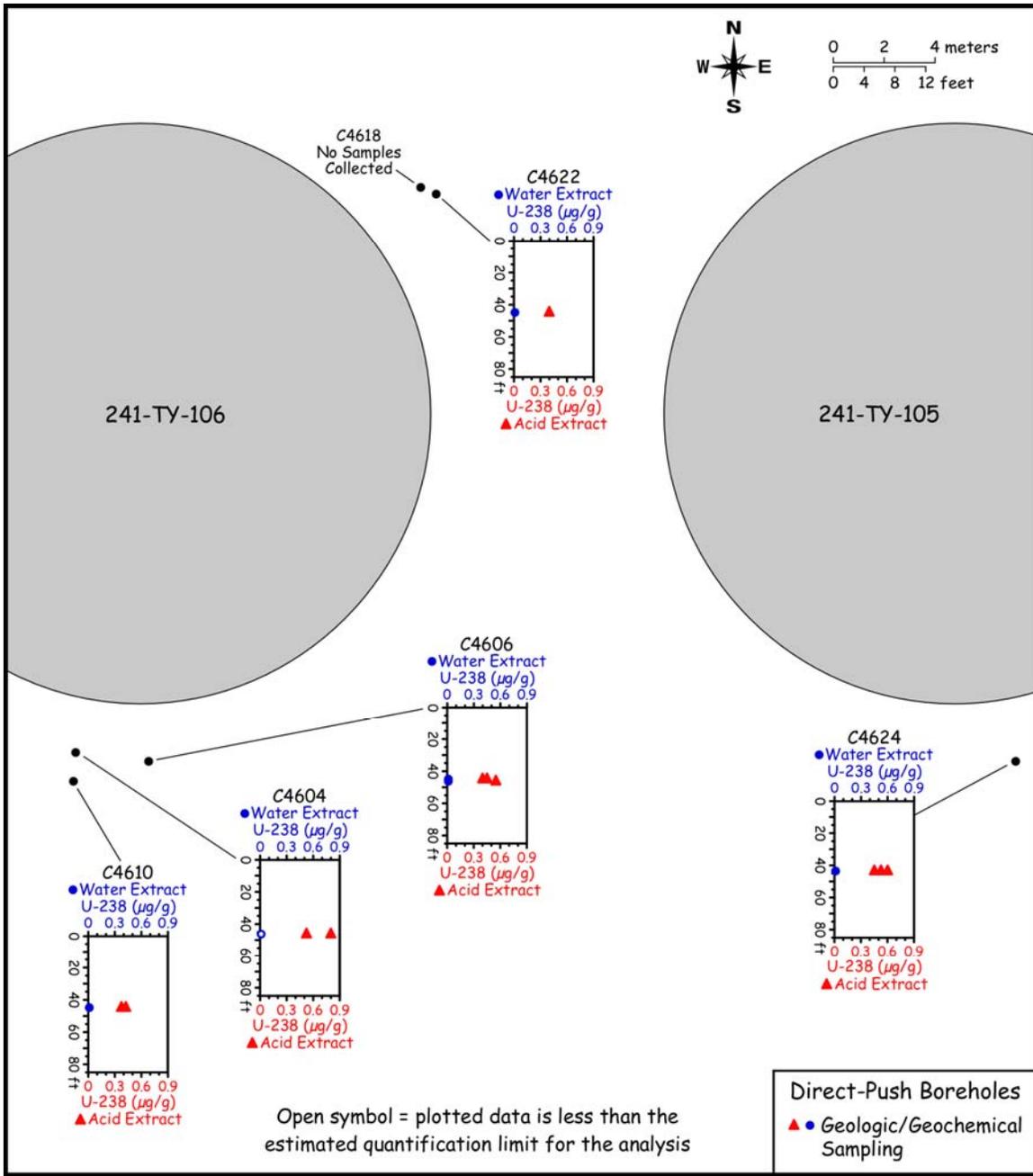
The 1:1 water extract data was processed to derive the pore water composition of the existing moisture in vadose zone sediments so that electrical balances (anions vs. cation) of the porewater could be evaluated. From knowledge of the moisture content of the sediment samples taken from the liners of each direct push sampler and the grab samples, the amount of de-ionized water that would be needed to make the water extract exactly one part water (total of native pore water and added de-ionized water) to one part by weight dry sediment was calculated. The ratio of the total volume of water in the extract to the native mass of pore water is the dilution factor. An assumption was made that the de-ionized water acted solely as a diluent of the existing pore water and that the de-ionized water did not dissolve any of the solids in the sediments. Thus by correcting for the dilution, an estimate of the actual chemical composition of the native pore-water in the vadose zone sediments could be derived.

The assumption that none of the solid is dissolved during the water extraction process is simplistic. In comparisons of actual vadose zone sediment pore water, which was obtained via ultracentrifugation of sediments, to the dilution-corrected calculated pore waters from both contaminated and uncontaminated sediments from the SX and B-BX Tank Farms (see Serne et al. 2002b, 2002c, 2002d, 2002e, 2002f), it was found that for highly contaminated sediments, the comparison is quite good. For slightly contaminated or uncontaminated sediments, the dilution-corrected water extract data is biased high by a factor of 2 to 7 for many constituents such that the true pore water is less saline. For the TY

**Table 4.6.** Water-Extractable Mobile Metals in the TY Tank Farm Core and Grab Samples ( $\mu\text{g/g}$  dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Technetium-99 pCi/g	Uranium-238 $\mu\text{g/g}$	Chromium $\mu\text{g/g}$	Molybdenum-95 $\mu\text{g/g}$	Ruthenium-101 $\mu\text{g/g}$	Ruthenium-102 $\mu\text{g/g}$
S06001-1A	C4604	44.95	<1.70E-01	(2.83E-06)	<b>2.64E-01</b>	<b>1.39E-01</b>	(6.69E-05)	<5.08E-03
S06001-1	C4604	NR	<1.89E-01	<b>7.20E-03</b>	(3.35E-03)	9.81E-03	(4.52E-05)	<6.52E-03
S06001-2B	C4624	42.10	<1.70E-01	3.26E-04	(1.25E-02)	<b>1.17E-01</b>	<1.25E-04	<5.20E-03
S06001-2A	C4624	42.50	<1.70E-01	1.01E-03	(1.04E-02)	2.78E-02	<1.25E-04	<5.70E-03
S06001-2	C4624	43.05	<1.70E-01	9.50E-04	(2.67E-03)	1.61E-02	(2.19E-06)	<5.31E-03
S06001-3A	C4610	43.80	<1.70E-01	6.66E-04	(3.21E-03)	<b>1.66E-01</b>	(9.17E-07)	<5.98E-03
S06001-3	C4610	44.21	<1.70E-01	7.82E-04	(2.70E-03)	<b>1.36E-01</b>	(9.07E-07)	<6.05E-03
S06001-4C	C4606	44.38	<1.70E-01	1.45E-03	(1.08E-03)	8.09E-02	(6.78E-07)	<6.61E-03
S06001-4B	C4606	44.67	<1.70E-01	1.29E-03	(1.59E-03)	1.64E-02	<1.25E-04	<5.72E-03
S06001-4A	C4606	45.17	<1.70E-01	2.01E-03	(4.60E-03)	1.60E-02	<1.25E-04	<5.44E-03
S06001-4A DUP	C4606	45.17	<1.70E-01	1.29E-03	(2.18E-03)	1.48E-02	(6.15E-07)	<5.92E-03
S06001-4	C4606	45.71	<1.70E-01	1.76E-03	(5.47E-03)	1.97E-02	(1.61E-06)	<6.57E-03
S06001-5	C4622	43.65	<1.70E-01	1.18E-03	(7.06E-03)	6.09E-02	<1.25E-04	<5.22E-03

Bold values denote elevated concentrations.  
 Parentheses indicate reported value was less than the limit of quantification for the analysis.  
 Less than values indicate the instrument returned a negative value.  
 NR indicates the information was not reported on the chain of custody.  
 Shaded cells indicate grab samples.



**Figure 4.6.** 1:1 Sediment:Water-Extractable and 8M Nitric Acid Extractable Uranium-238 Data from the TY Tank Farm Direct Push Samples

direct push data set, sufficient sample material was not available to enable the collection of actual porewater via ultracentrifugation. Therefore, it is assumed that the derived pore water concentrations for the TY direct push samples are slightly biased toward higher concentrations.

Tables 4.7 through 4.10 show the derived pore water composition of key constituents in meq/L and Figure 4.7 shows the porewater corrected alkalinity as CaCO<sub>3</sub> in units of mg/L. Sample S06001-1A was the only sediment sample tested that contained significantly more dissolved salts (approximately four

times more than the average for all of the samples measured) than the rest of the samples analyzed as part of this study. This sample, which was collected directly south of tank 241-TY-106, contained 155 meq/L anions vs. 158 meq/L cations. Sample S06001-1A consisted of 80.5 meq/L calcium, 67.2 meq/L sodium, 10.6 meq/L potassium, and trace amounts of magnesium (0.022 meq/L). The cation charge for this sample was compensated primarily by bicarbonate (113 meq/L) with lesser amounts of sulfate (38.6 meq/L), chloride (2.12 meq/L), nitrate (0.999 meq/L), fluoride (0.635 meq/L) and phosphate (0.422 meq/L). These concentrations are very dilute compared to the vadose zone pore waters found at the SX and BX tank farms, where the total dissolved salt loads were as high as 7,000 to 17,000 and 1,000 meq/L, respectively. The most concentrated pore waters below tank T-106 ranged from 200 to 250 meq/L each for cations and anions (total ~450 to 500 meq/L) and below tank TX-107, the most concentrated pore water had 850 total meq/L.

The remaining TY direct push sediments contained relatively low dissolved salt loads, which ranged from a low of 33.2 meq/L total (anions and cations) for sample S06001-4 to a high of 88.2 meq/L for sample S06001-4C. Both of these samples were collected south of tank 241-TY-106 and west of probe hole C4604. Probe hole C4606 was the only location where material was retrieved from the shoe and all three of the liners. Considering that the shoe was collected furthest below ground surface, while the S06001-4C was the shallowest sample collected, it appears that a depth-dependent dissolved salt profile could be present at this location. However, when the relatively dilute dissolved salt loads in these samples are compared with the average total dissolved salt load in the ostensibly uncontaminated 299-W10-27 (366 meq/L), it is difficult to claim that the observed depth-dependent total pore water salt profile is real and not an artifact of sampling depth (i.e., at the interface between the backfill and Hanford formation).

Overall, the calculated charge balance between cations and anions for all of the samples was quite good (less than 15% difference for most of the samples analyzed). However, samples S06001-2, S06001-4A, and S06001-4A Dup all contained approximately 20% less dissolved cations than anions. Based on comparison of this data, it appears that either the bicarbonate measurement for these samples is biased high, or analyses have not accounted for a dissolved metal that is present in sufficient quantity to properly balance the electrical charge of these samples.

Sodium was present as the dominant cation in all but two of the samples analyzed. Samples S06001-1A and S06001-1, both from probe hole C4606, contained calcium as the dominant cation. Bicarbonate (measured via titration) was the primary anionic species in all of the samples analyzed. The lack of samples containing calcium as the dominant cation indicates that the samples in this region have been impacted by a sodium-bearing waste fluid. The source(s) appears to be a moderately concentrated sodium-bearing waste solution that has displaced the natural divalent cations from the sediment cation exchange sites in the sediments. The total vertical extent of the ion exchange front is unknown due to the lack of sediment samples from deeper in the vadose zone.

As mentioned previously, none of the TY direct push sediment samples contained measurable concentrations of technetium-99. Three of the samples (S06001-1, S06001-4C, and S06001-4A) contained calculated uranium-238 porewater concentrations in excess of the drinking water standard. The maximum concentration of dissolved uranium was found in a sample from borehole C4604 at a concentration of 132 µg/L. The other two direct push samples (S06001-4A and S06001-4C), both collected from probe hole C4606, contained derived pore water uranium concentrations of 31.2 and 34.0 µg/L, respectively.

**Table 4.7.** Calculated Pore Water Anion Concentrations in the TY Tank Farm Core and Grab Samples

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Fluoride meq/L	Chloride meq/L	Nitrate meq/L	Sulfate meq/L	Phosphate meq/L	Alkalinity meq/L
S06001-1A	C4604	44.95	6.35E-01	<b>2.09E+00</b>	9.99E-01	3.85E+01	4.22E-01	1.13E+02
S06001-1	C4604	NR	2.79E-01	2.79E-01	6.35E-01	2.07E+00	<3.26E-01	3.69E+01
S06001-2B	C4624	42.10	9.23E-01	6.80E-01	<1.24E-01	1.34E+01	<2.83E-01	2.02E+01
S06001-2A	C4624	42.50	2.22E-01	<b>1.18E+00</b>	5.92E-01	1.13E+01	<1.92E-01	1.23E+01
S06001-2	C4624	43.05	2.81E-01	3.69E-01	7.65E-01	7.88E+00	<3.04E-01	2.42E+01
S06001-3A	C4610	43.80	<b>1.25E+00</b>	8.63E-01	8.67E-01	1.29E+01	<2.90E-01	2.58E+01
S06001-3	C4610	44.21	5.20E-01	3.68E-01	7.21E-01	6.53E+00	<2.58E-01	1.80E+01
S06001-4C	C4606	44.38	<b>1.34E+00</b>	7.84E-01	5.82E-01	7.33E+00	<3.74E-01	3.51E+01
S06001-4B	C4606	44.67	3.51E-01	4.22E-01	8.15E-01	3.10E+00	<2.71E-01	2.17E+01
S06001-4A	C4606	45.17	3.06E-01	3.17E-01	9.43E-01	3.60E+00	<2.48E-01	2.06E+01
S06001-4A DUP	C4606	45.17	2.87E-01	2.78E-01	7.90E-01	2.20E+00	<2.43E-01	1.95E+01
S06001-4	C4606	45.71	1.89E-01	3.15E-01	<b>1.02E+00</b>	1.87E+00	<1.64E-01	1.41E+01
S06001-5	C4622	43.65	6.34E-01	6.94E-01	4.37E-01	5.75E+00	<3.52E-01	3.27E+01

Bold values denote elevated concentrations.  
 Less than values indicate the instrument returned a negative value.  
 NR indicates the information was not reported on the chain of custody.  
 Shaded cells indicate grab samples.

**Table 4.8.** Calculated Pore Water Cation Concentrations in the TY Tank Farm Direct Push Core and Grab Samples

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Calcium meq/L	Potassium meq/L	Magnesium meq/L	Sodium meq/L
S06001-1A	C4604	44.95	<b>8.05E+01</b>	<b>1.06E+01</b>	(2.19E-02)	6.72E+01
S06001-1	C4604	NR	3.17E+00	(3.12E+00)	9.36E-01	2.79E+01
S06001-2B	C4624	42.10	5.20E+00	(2.11E+00)	9.46E-01	2.25E+01
S06001-2A	C4624	42.50	9.31E+00	(1.77E+00)	2.40E+00	<b>9.93E+00</b>
S06001-2	C4624	43.05	9.64E+00	(2.70E+00)	2.63E+00	1.19E+01
S06001-3A	C4610	43.80	6.79E+00	(2.66E+00)	2.29E+00	2.62E+01
S06001-3	C4610	44.21	7.01E+00	(1.88E+00)	2.08E+00	1.22E+01
S06001-4C	C4606	44.38	9.38E+00	(3.30E+00)	2.89E+00	2.71E+01
S06001-4B	C4606	44.67	8.13E+00	(2.10E+00)	1.98E+00	1.13E+01
S06001-4A	C4606	45.17	7.98E+00	(1.74E+00)	2.35E+00	<b>9.18E+00</b>
S06001-4A DUP	C4606	45.17	6.36E+00	(1.61E+00)	1.76E+00	<b>8.72E+00</b>
S06001-4	C4606	45.71	6.10E+00	(1.22E+00)	1.88E+00	6.30E+00
S06001-5	C4622	43.65	7.83E+00	(3.31E+00)	2.14E+00	2.37E+01

Bold values denote elevated concentrations.  
 Parentheses indicate reported value was less than the limit of quantification for the analysis.  
 NR indicates the information was not reported on the chain of custody.  
 Shaded cells indicate grab samples.

**Table 4.9.** Calculated Pore Water Metal Concentrations in the TY Tank Farm Direct Push Core and Grab Samples

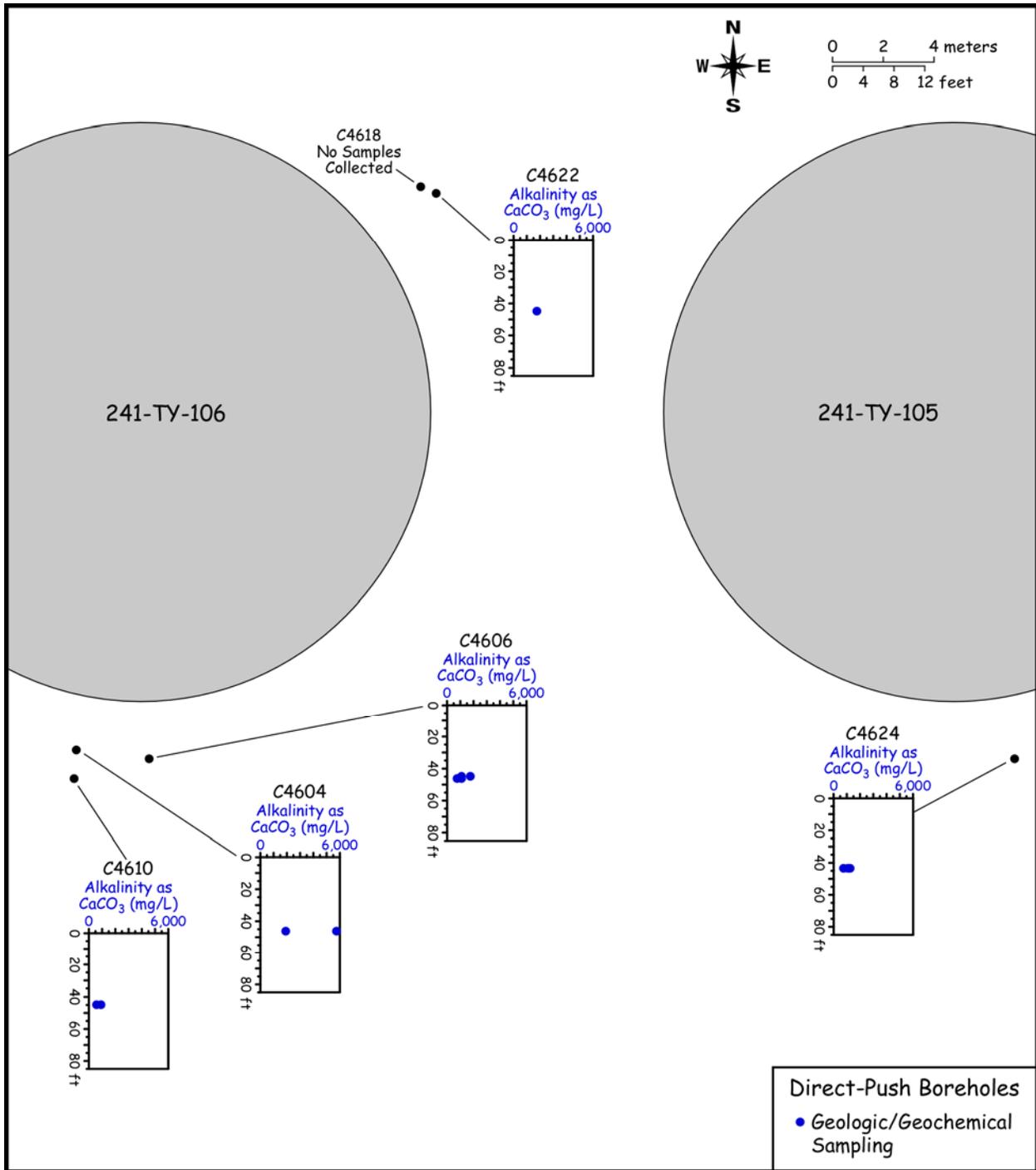
Sample ID	Probe Hole ID	Mid-Depth ft bgs	Aluminum meq/L	Iron meq/L	Sulfur meq/L	Silicon meq/L
S06001-1A	C4604	44.95	<b>8.02E-01</b>	(1.46E-03)	<b>1.19E+02</b>	<b>1.06E+02</b>
S06001-1	C4604	NR	(1.11E-01)	4.17E-02	6.98E+00	4.47E+01
S06001-2B	C4624	42.10	(1.15E-01)	4.01E-02	4.08E+01	3.59E+01
S06001-2A	C4624	42.50	(3.66E-02)	(8.88E-03)	3.47E+01	3.79E+01
S06001-2	C4624	43.05	(6.90E-02)	2.67E-02	2.63E+01	3.81E+01
S06001-3A	C4610	43.80	4.21E-01	<b>9.85E-02</b>	4.14E+01	2.74E+01
S06001-3	C4610	44.21	(1.60E-01)	4.56E-02	2.09E+01	2.47E+01
S06001-4C	C4606	44.38	(2.54E-01)	<b>8.61E-02</b>	2.48E+01	3.94E+01
S06001-4B	C4606	44.67	(1.12E-01)	4.04E-02	1.05E+01	3.41E+01
S06001-4A	C4606	45.17	(9.13E-02)	3.10E-02	1.10E+01	3.00E+01
S06001-4A DUP	C4606	45.17	(6.01E-02)	2.37E-02	6.65E+00	2.89E+01
S06001-4	C4606	45.71	(9.82E-02)	4.61E-02	5.80E+00	1.87E+01
S06001-5	C4622	43.65	(1.27E-01)	4.41E-02	1.86E+01	5.26E+01

Bold values denote elevated concentrations.  
 Parentheses indicate reported value was less than the limit of quantification for the analysis.  
 NR indicates the information was not reported on the chain of custody.  
 Shaded cells indicate grab samples.

**Table 4.10.** Calculated Pore Water Mobile Metal Concentrations of Key Contaminants of Concern in the TY Tank Farm Direct Push Core and Grab Samples

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Techneium-99 pCi/L	Uranium-238 µg/L	Chromium µg/L	Molybdenum-95 µg/L
S06001-1A	C4604	44.95	<3.33E+03	(5.56E-02)	<b>5.18E+03</b>	2.73E+03
S06001-1	C4604	NR	<3.46E+03	<b>1.32E+02</b>	(6.16E+01)	1.80E+02
S06001-2B	C4624	42.10	<3.00E+03	5.78E+00	(2.22E+02)	2.07E+03
S06001-2A	C4624	42.50	<2.05E+03	1.22E+01	(1.26E+02)	3.36E+02
S06001-2	C4624	43.05	<3.24E+03	1.81E+01	(5.09E+01)	3.07E+02
S06001-3A	C4610	43.80	<3.08E+03	1.21E+01	(5.83E+01)	3.03E+03
S06001-3	C4610	44.21	<2.74E+03	1.27E+01	(4.38E+01)	2.21E+03
S06001-4C	C4606	44.38	<3.98E+03	3.40E+01	(2.54E+01)	1.90E+03
S06001-4B	C4606	44.67	<2.88E+03	2.19E+01	(2.70E+01)	2.79E+02
S06001-4A	C4606	45.17	<2.63E+03	3.12E+01	(7.15E+01)	2.48E+02
S06001-4A DUP	C4606	45.17	<2.58E+03	1.97E+01	(3.33E+01)	2.25E+02
S06001-4	C4606	45.71	<1.74E+03	1.81E+01	(5.62E+01)	2.03E+02
S06001-5	C4622	43.65	<3.74E+03	2.61E+01	(1.56E+02)	1.34E+03

Bold values denote elevated concentrations.  
 Parentheses indicate reported value was less than the limit of quantification for the analysis.  
 Less than symbols indicate the instrument returned a negative value.  
 NR indicates the information was not contained on the chain of custody.  
 Shaded cells indicate grab samples.



2007/DCL/TY/003 (05/14)

**Figure 4.7.** 1:1 Sediment:Water-Extractable Alkalinity Data from the TY Tank Farm Direct Push Samples

#### 4.1.4 8 M Nitric Acid-Extractable Amounts of Selected Elements in the TY Tank Farm Direct Push Sediments

The same cores and grab samples that were characterized for water-leachable constituents were also characterized to see how much of the various constituents could be extracted with hot 8 M nitric acid. A comparison between the quantities that were acid extractable with those that are water-extractable often indicates the relative mobility of a given constituent and can sometimes differentiate man-disposed from naturally occurring constituents. The acid extractable concentrations are shown in Tables 4.11 through 4.13. For a majority of the constituents, there were no significantly elevated acid-extractable values in the TY Tank Farm direct push sediments, with the exception of chromium, molybdenum, and ruthenium.

Elevated acid-extractable chromium was found in the shoe material from direct push hole C4624. The chromium concentration in this sample was more than three times greater than that of the other direct push sediment samples. The same sample from the C4624 probe hole contained elevated molybdenum, which could be another indication of residual waste material in the sample. An alternate explanation is that the elevated chromium and molybdenum are from shavings lost from the sampler, which was composed of stainless steel, as it was being driven into the ground. Ruthenium was elevated in one of the direct push samples from probe hole C4606 and one sample from probe hole C4624.

**Table 4.11.** Acid-Extractable Cations in the TY Tank Farm Direct Push Core and Grab Samples (µg/g dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Calcium µg/g	Potassium µg/g	Magnesium µg/g
S06001-1A	C4604	44.95	<b>1.67E+04</b>	1.06E+03	3.98E+03
S06001-1	C4604	NR	7.70E+03	1.30E+03	4.12E+03
S06001-2B	C4624	42.10	7.95E+03	1.01E+03	4.01E+03
S06001-2A	C4624	42.50	<b>1.40E+04</b>	8.76E+02	4.34E+03
S06001-2	C4624	43.05	9.39E+03	8.52E+02	4.47E+03
S06001-3A	C4610	43.80	6.53E+03	8.48E+02	3.30E+03
S06001-3	C4610	44.21	6.11E+03	9.46E+02	3.32E+03
S06001-4C	C4606	44.38	6.73E+03	(8.25E+02)	3.32E+03
S06001-4B	C4606	44.67	6.35E+03	7.70E+02	2.95E+03
S06001-4A	C4606	45.17	6.48E+03	9.91E+02	3.76E+03
S06001-4A DUP	C4606	45.17	7.58E+03	1.09E+03	4.00E+03
S06001-4	C4606	45.71	8.21E+03	1.38E+03	4.98E+03
S06001-5	C4622	43.65	8.99E+03	(5.57E+02)	2.40E+03

Bold values denote elevated concentrations.  
 Parentheses indicate the reported value is below the limit of quantification for the analysis.  
 NR indicates the information was not contained on the chain of custody.  
 Shaded cells indicate grab samples.

**Table 4.12.** Acid-Leachable Cations in the TY Tank Farm Core and Grab Samples ( $\mu\text{g/g}$  dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Aluminum $\mu\text{g/g}$	Iron $\mu\text{g/g}$	Phosphorus $\mu\text{g/g}$	Sulfur $\mu\text{g/g}$
S06001-1A	C4604	44.95	8.03E+03	2.49E+04	1.00E+03	<b>4.18E+02</b>
S06001-1	C4604	NR	7.25E+03	2.31E+04	1.11E+03	(4.30E+01)
S06001-2B	C4624	42.10	6.94E+03	2.45E+04	1.08E+03	(6.67E+01)
S06001-2A	C4624	42.50	7.76E+03	2.51E+04	1.06E+03	2.21E+02
S06001-2	C4624	43.05	8.73E+03	4.31E+04	9.57E+02	2.14E+02
S06001-3A	C4610	43.80	4.68E+03	1.50E+04	8.99E+02	(4.36E+01)
S06001-3	C4610	44.21	4.45E+03	1.72E+04	7.32E+02	(3.54E+01)
S06001-4C	C4606	44.38	6.13E+03	2.08E+04	8.86E+02	(4.07E+01)
S06001-4B	C4606	44.67	3.90E+03	1.49E+04	1.01E+03	(3.99E+01)
S06001-4A	C4606	45.17	6.11E+03	1.94E+04	9.14E+02	(3.72E+01)
S06001-4A DUP	C4606	45.17	6.80E+03	2.16E+04	1.03E+03	(3.97E+01)
S06001-4	C4606	45.71	8.27E+03	1.90E+04	6.08E+02	(3.30E+01)
S06001-5	C4622	43.65	3.24E+03	1.20E+04	8.80E+02	(9.02E+01)

Bold values denote elevated concentrations.  
 Parentheses indicated the reported value is below the limit of quantification for the analysis.  
 NR indicates the information was not contained on the chain of custody.  
 Shaded cells indicate grab samples.

**Table 4.13.** Acid-Extractable Mobile Metals in the TY Tank Farm Direct Push Core and Grab Samples ( $\mu\text{g/g}$  dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Technetium-99 pCi/g	Uranium-238 $\mu\text{g/g}$	Molybdenum-95 $\mu\text{g/g}$	Ruthenium-101 $\mu\text{g/g}$	Ruthenium-102 $\mu\text{g/g}$
S06001-1A	C4604	44.95	<4.31E+01	5.29E-01	4.16E+00	(2.50E-03)	<5.08E-03
S06001-1	C4604	NR	<5.53E+01	8.04E-01	5.57E-01	<b>2.55E-02</b>	<6.52E-03
S06001-2B	C4624	42.10	<4.41E+01	5.25E-01	1.55E+00	<5.20E-03	<5.20E-03
S06001-2A	C4624	42.50	(1.01E-01)	6.00E-01	2.39E+00	<5.70E-03	<5.70E-03
S06001-2	C4624	43.05	(1.50E+00)	4.45E-01	<b>2.57E+01</b>	<b>8.21E-05</b>	<5.31E-03
S06001-3A	C4610	43.80	<5.07E+01	4.34E-01	1.86E+00	<5.98E-03	<5.98E-03
S06001-3	C4610	44.21	<5.13E+01	3.81E-01	6.83E+00	<6.05E-03	<6.05E-03
S06001-4C	C4606	44.38	<5.60E+01	4.47E-01	1.32E+00	<6.61E-03	<6.61E-03
S06001-4B	C4606	44.67	<4.85E+01	4.10E-01	4.28E-01	<5.72E-03	<5.72E-03
S06001-4A	C4606	45.17	<4.61E+01	5.45E-01	3.84E-01	<5.44E-03	<5.44E-03
S06001-4A DUP	C4606	45.17	<5.02E+01	5.75E-01	3.72E-01	<5.92E-03	<5.92E-03
S06001-4	C4606	45.71	<5.57E+01	5.43E-01	2.92E-01	<6.57E-03	<6.57E-03
S06001-5	C4622	43.65	<4.42E+01	4.15E-01	1.37E+00	<5.22E-03	<5.22E-03

Bold values denote elevated concentrations.  
 Parentheses indicate reported value is less than the limit of quantification for the analysis.  
 Less than symbol indicates the instrument returned a negative value.  
 NR indicates the information was not contained on the chain of custody.  
 Less than symbols indicate the instrument returned a negative value.  
 Shaded cells indicate grab samples.

Comparison of the water to acid-extractable quantities of each constituent was performed by taking the data in Tables 4.3 through 4.6 and dividing them by the data in Tables 4.11 through 4.13. The data are not presented herein, but show that less than 0.1% of the acid-extractable quantities of the following elements were water leachable: aluminum, barium, iron, lead, magnesium, manganese, phosphorous as phosphate, titanium, and zirconium. Less than 0.5% of the acid-extractable quantities of the following elements were water leachable: calcium, chromium, copper, nickel, and zinc. Less than 5% of the acid-extractable potassium, strontium, and uranium were water-extractable. Finally, less than 30% of the acid-extractable sulfur, as sulfate, was water-extractable.

#### 4.1.5 Radionuclide Content in Vadose Zone Sediment from the TY Tank Farm Direct Push Holes

Data from the gamma energy analysis of the samples are shown in Table 4.14 and Figure 4.8. The direct measurement of sediment for gamma-emitting radionuclides showed that the sediments contained natural potassium-40 in all of the direct push probe holes except C4622, which is located northeast of tank 241-TY-106. The fission product isotope cesium-137 was found in both of the samples retrieved from probe hole C4604. The shoe material from probe hole C4604 contained 1.5 pCi/g cesium-137 while the A-sleeve sample contained 0.6 pCi/g cesium-137. The A-sleeve sediment from probe hole C4604 was the only sample with an elevated soil pH. Based on this, it seems likely that the slightly elevated pH in this sample coupled with the cesium-137 contamination is a result of contamination from a tank-related waste source. The most probable source of the contamination is the proposed leak from tank 241-TY-106.

**Table 4.14.** Gamma Emitting Radionuclides in the TY Tank Farm Direct Push Sediments

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Potassium-40 pCi/g	Cesium-137 pCi/g
S06001-1A	C4604	44.95	1.13E+01	<b>5.90E-01</b>
S06001-1	C4604	NR	9.72E+00	<b>1.53E+00</b>
S06001-2B	C4624	42.10	<7.35E+00	<4.22E-01
S06001-2A	C4624	42.50	2.07E+00	<4.11E-01
S06001-2	C4624	43.05	1.34E+01	<2.45E-01
S06001-3A	C4610	43.80	<7.64E+00	<3.87E-01
S06001-3	C4610	44.21	1.69E+01	<4.43E-01
S06001-4C	C4606	44.38	8.85E+00	<2.24E-01
S06001-4B	C4606	44.67	<8.68E+00	<2.16E-01
S06001-4A	C4606	45.17	1.40E+01	<4.05E-01
S06001-4A DUP	C4606	45.17	1.33E+01	<3.34E-01
S06001-4	C4606	45.71	<6.85E+00	<2.23E-01
S06001-5	C4622	43.65	1.13E+01	<b>5.90E-01</b>

Bold values denote elevated concentrations.  
 ND indicates the analyte was not detected in the sample.  
 NR indicates the information was not contained on the chain of custody.  
 Shaded cells indicate grab samples.

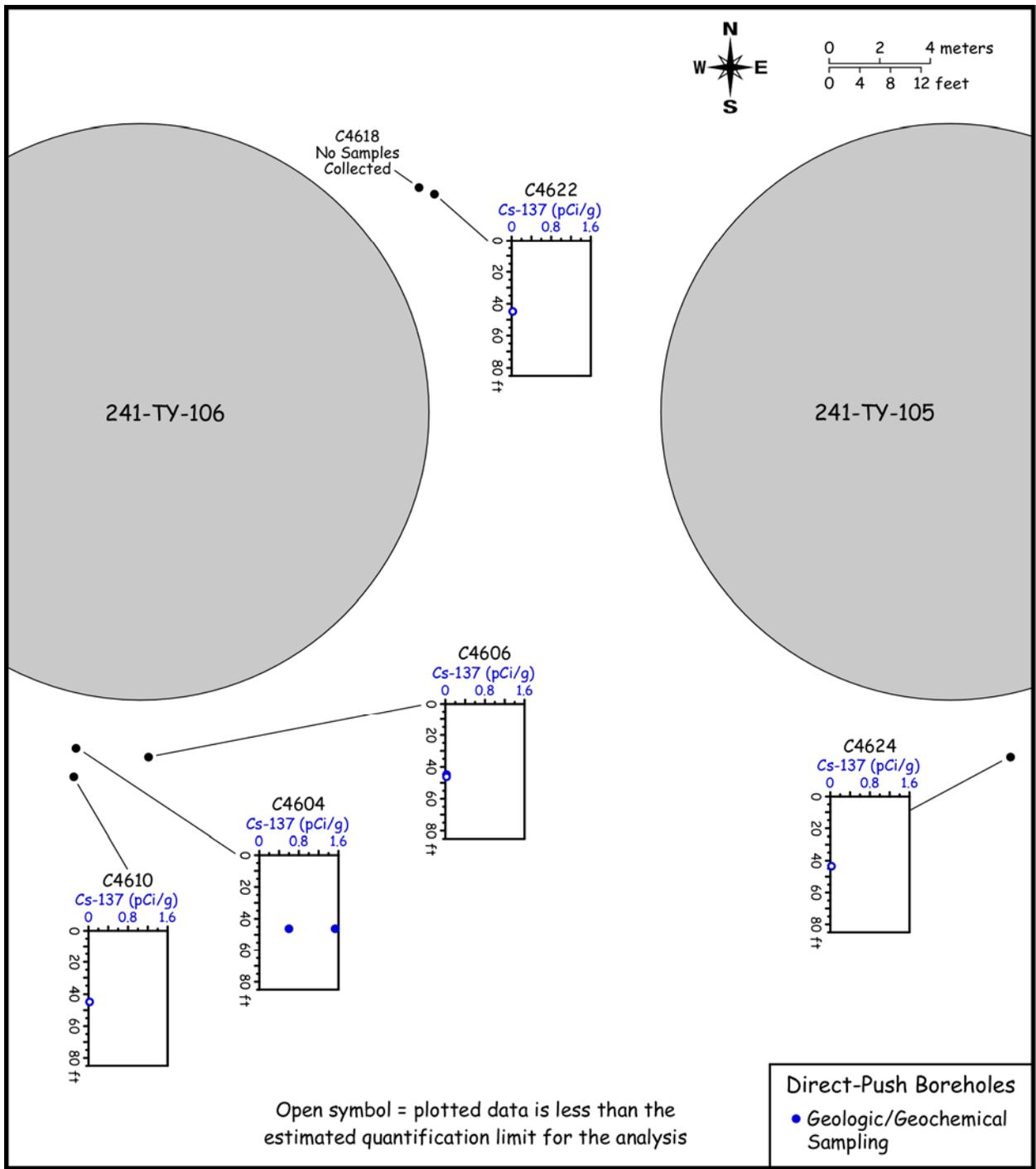


Figure 4.8. Gamma Energy Analysis Data (Cesium-137) from the TY Tank Farm Direct Push Samples

#### **4.1.6 Total Carbon, Calcium Carbonate, and Organic Carbon Content of Vadose Zone Sediment from the TY Tank Farm Direct Push Holes**

Data from the total carbon, inorganic carbon, and organic carbon (calculated by difference) contents of the TY Tank Farm direct push sediments are shown in Table 4.15. The inorganic carbon was converted to the equivalent calcium carbonate content. In general, the sediments were low in organic carbon (<0.15% by weight) which is typical of Hanford Site sediments. As a comparison, the average amount of organic carbon in sediments collected from the background borehole (299-W10-27) was 0.05% by weight, while the average for all of the TY Tank Farm direct push samples was 0.07% by weight. Inorganic carbon, as CaCO<sub>3</sub>, was also present at concentrations that are typical for Hanford formation sediments (0.5 to 3.7 wt% as CaCO<sub>3</sub>) and compare well with other Hanford formation samples from uncontaminated locations (Serne et al. 2004a,b).

### **4.2 Vadose Zone Sediment from the T Tank Farm Direct Push Samples**

#### **4.2.1 Moisture Content**

The moisture contents of the 23 core liners and 5 grab samples collected from the T direct push holes are presented as a function of depth in Table 4.16 and Figure 4.9. Several of the samples contained high soil moisture contents: the C-liner collected in probe hole C5378 at approximately 45 ft bgs (11.7%), all three liners collected from probe hole C5374 at depths ranging from approximately 80 to 81.5 ft bgs (14.9-18.2%), and the A- and B-liners collected from probe hole C5382 from a depth of approximately 79 ft bgs (22.7% and 14.9%). The B and C liners from probe hole C5378 (collected at approximately 45 ft bgs) contained sediment with appreciably different moisture contents (approximately a 50% difference), indicating that the contact for the zone of increased moisture was encountered within the interval comprising the two liners (1 ft). Photographs of the sediment removed from each liner, which are contained in Appendix C of this report, confirm the presence of finer-grained particles in the sediment contained within the C liner. The B and C liners from probe hole C5382 (collected at approximately 78 ft bgs) also appeared to capture the contact between the Hanford formation and Cold Creek Unit. Photographs of the material taken from these two cores confirm the transition from a silt-dominated material to coarse-grained sand over the 12-inch span captured by the two liners.

The average gravimetric moisture content of all of the samples measured in this study was 7.9 wt%, which was slightly higher than the average moisture content in core samples collected within the Hanford formation H2 unit (3.9%) at the nearby TX Tank Farm characterization site (background borehole 299-W10-27 just east of the TY Tank Farm). However, the Cold Creek Unit was intercepted by several of the T direct samples, which caused the average moisture content for all of the samples to be biased high when compared to the coarse-grained materials comprising the Hanford formation H2 unit.

#### **4.2.2 1:1 Sediment:Water Extracts**

The samples from the T Tank Farm direct push were characterized by performing 1:1 sediment:water extracts. The following tables present the mass of a given constituent leached per gram of sediment as measured in the water extracts. Other tables show dilution-corrected values that represent concentrations in vadose zone pore water. As discussed in several other Vadose Zone Characterization Project reports, the dilution-corrected 1:1 sediment:water extracts are a reasonable estimate of the actual vadose zone pore water (see Serne et al. 2002a, 2002b, 2002c, 2002e, 2002f).

**Table 4.15.** Carbon Content of the TY Tank Farm Vadose Zone Samples

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Total Carbon (%)	Inorganic Carbon (%)	Inorganic Carbon as CaCO3 (%)	Organic Carbon (%)
S06001-1A	C4604	44.95	3.54E-01	2.47E-01	2.06E+00	1.08E-01
S06001-1	C4604	NR	1.63E-01	1.12E-01	9.33E-01	5.10E-02
S06001-2B	C4624	42.10	2.04E-01	1.14E-01	9.53E-01	8.96E-02
S06001-2A	C4624	42.50	5.75E-01	4.38E-01	3.65E+00	1.37E-01
S06001-2	C4624	43.05	1.78E-01	1.05E-01	8.73E-01	7.36E-02
S06001-3A	C4610	43.80	1.76E-01	9.38E-02	7.82E-01	8.18E-02
S06001-3	C4610	44.21	2.08E-01	1.58E-01	1.32E+00	5.05E-02
S06001-4C	C4606	44.38	1.20E-01	5.52E-02	4.60E-01	6.52E-02
S06001-4B	C4606	44.67	1.93E-01	1.42E-01	1.19E+00	5.07E-02
S06001-4A	C4606	45.17	2.24E-01	1.71E-01	1.43E+00	5.30E-02
S06001-4A DUP	C4606	45.17	2.40E-01	1.80E-01	1.50E+00	5.99E-02
S06001-4	C4606	45.71	2.78E-01	1.92E-01	1.60E+00	8.62E-02
S06001-5	C4622	43.65	3.44E-01	2.92E-01	2.44E+00	5.13E-02

NR indicates the information was not contained on the chain of custody.  
Shaded cells indicate grab samples.

**Table 4.16.** Gravimetric Moisture Content of Samples Obtained from the T Tank Farm Direct Push Probe Holes

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Moisture (%)
B1KC35A	C4598	43.8	3.97%
B1KC35B	C4598	43.3	4.30%
B1KC36	C4596	48.9	3.50%
B1KC36A	C4596	48.3	6.37%
B1KC36B	C4596	47.8	4.21%
B1KC36C	C4596	47.3	4.57%
B1KC37A	C5378	46.3	2.58%
B1KC37B	C5378	45.8	5.87%
B1KC37C	C5378	45.3	11.7%
B1KC38	C5378	63.8	4.40%
B1KC38A	C5378	63.3	5.18%
B1KC38B	C5378	62.8	5.48%
B1KC38C	C5378	62.3	6.51%
B1KC39	C5384	45.8	4.66%
B1KC39A	C5384	45.3	3.56%
B1KC39B	C5384	44.8	4.54%
B1KC39C	C5384	44.3	6.10%
B1KC40	C5374	81.8	8.35%
B1KC40A	C5374	81.3	16.6%
B1KC40B	C5374	80.8	18.2%
B1KC40C	C5374	80.3	14.9%
B1LB07A	C5382	79.3	22.7%
B1LB07B	C5382	78.8	14.9%
B1LB07C	C5382	78.3	5.98%
B1LB08	C5380	51.8	5.65%
B1LB08A	C5380	51.3	8.33%
B1LB08B	C5380	50.8	9.14%
B1LB08C	C5380	50.3	8.27%

Shaded cells indicate grab samples.

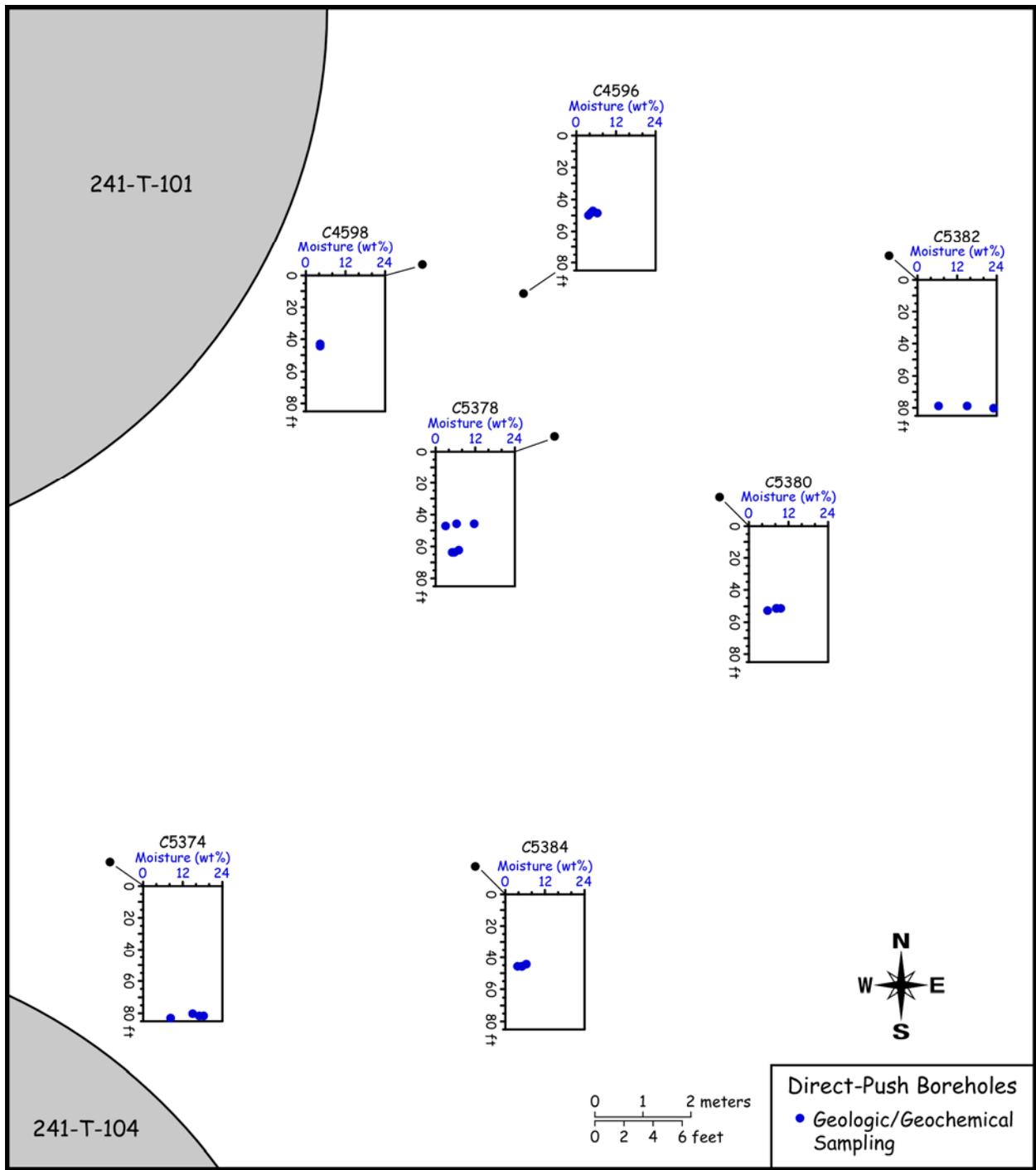
#### 4.2.2.1 pH and Electrical Conductivity

The 1:1 sediment:water extract pH and EC data for the T Tank Farm core and grab samples are shown in Table 4.17 and Figure 4.10. The pH is tabulated as measured in the 1:1 sediment:water extracts but the EC is corrected for dilution and tabulated as if it was actual pore water. Several of the 1:1 sediment:water extracts were elevated in pH (greater than 8.5). The sediments characterized as having an elevated pH (>8.5) were collected from probe holes C4598, C4596, and C5378 at depths ranging from approximately 43 to 63 ft bgs. Previous borehole reports have shown that regions of elevated soil pH are considered to be good indicators of the location of the original leak event or very near-field close to the initial tank waste entry zone (see Serne et al. 2002a, 2002b, 2002c, 2002e, 2002f). Therefore, we can conclude that the elevated pH data indicates the presence of caustic tank-related waste from tank 241-T-101.

The pore water-corrected EC data for many of the samples were low, with a range of 1.26 to 6.58 mS/cm. However, all of the samples that exhibited elevated sediment pH's also had elevated porewater conductivities because of more abundant water-dissolvable salts remaining on the sediment after tank-waste contact. For example, the core samples taken from probe hole C4598 had the highest porewater-corrected conductivities (at 19.2 and 21.1 mS/cm) measured as part of the T Tank Farm direct push study. Not surprisingly, probe hole C4598 was the closest sampling hole in proximity to tank

**Table 4.17.** pH for 1:1 Sediment:Water Extracts and Dilution-Corrected EC Values from T Tank Farm Core and Grab Samples

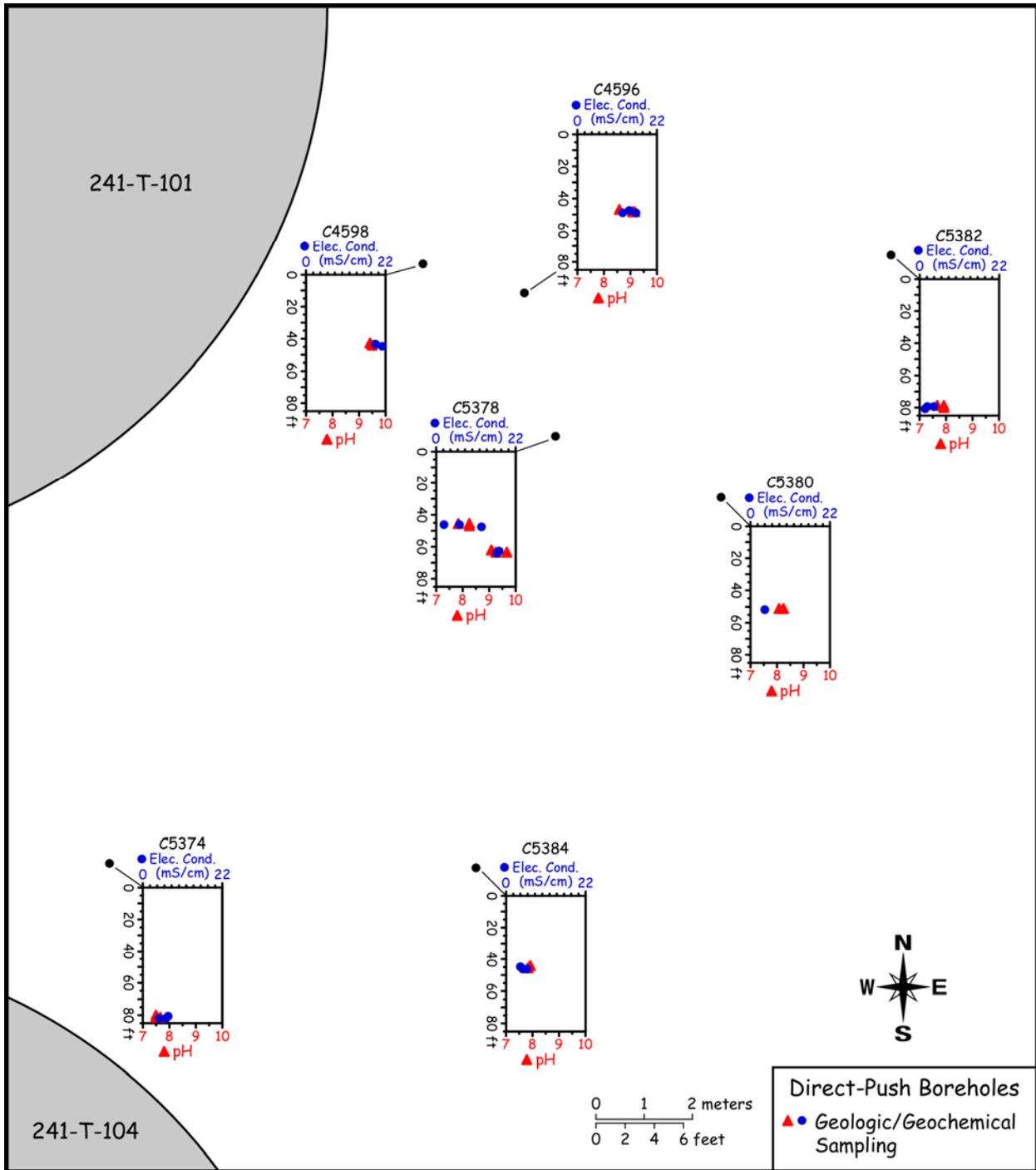
Sample ID	Probe Hole ID	Mid-Depth ft bgs	pH	Conductivity (mS/cm)
B1KC35A	C4598	43.8	<b>9.51</b>	<b>21.1</b>
B1KC35B	C4598	43.3	<b>9.46</b>	<b>19.2</b>
B1KC36A	C4596	48.3	<b>9.07</b>	<b>12.2</b>
B1KC36B	C4596	47.8	<b>9.16</b>	<b>16.1</b>
B1KC36C	C4596	47.3	<b>8.77</b>	<b>13.9</b>
B1KC37A	C5378	46.3	8.23	<b>12.4</b>
B1KC37B	C5378	45.8	8.28	6.22
B1KC37C	C5378	45.3	7.83	2.09
B1KC38A	C5378	63.3	<b>9.64</b>	<b>16.8</b>
B1KC38B	C5378	62.8	<b>9.29</b>	<b>16.3</b>
B1KC38C	C5378	62.3	<b>9.13</b>	<b>16.9</b>
B1KC39A	C5384	45.3	7.82	5.45
B1KC39B	C5384	44.8	7.82	4.63
B1KC39C	C5384	44.3	7.94	3.93
B1KC40A	C5374	81.3	7.65	6.01
B1KC40B	C5374	80.8	7.55	4.22
B1KC40C	C5374	80.3	7.49	6.58
B1LB07A	C5382	79.3	7.95	1.26
B1LB07B	C5382	78.8	7.92	1.71
B1LB07C	C5382	78.3	7.64	3.70
B1LB08A	C5380	51.3	8.10	3.76
B1LB08B	C5380	50.8	8.09	3.53
B1LB08C	C5380	50.3	8.26	3.69
Bold values denote elevated concentrations.				
EC values are dilution corrected and represent pore water concentrations not 1:1 extract values.				



2007/DCL/T/006 (05/14)

**Figure 4.9.** Moisture Content Data for the T Tank Farm Direct Push Samples

241-T-101. The next highest conductivity was found in samples from probe hole C5378, which was located approximately 5 m to the southeast of tank 241-T-101. These samples were collected at a depth of approximately 63 ft bgs, which was 20 ft deeper than the depth of the C4598 samples. These results indicate that the initial impact zone from waste released from tank 241-T-101 migrated to the southeast of the tank to at least the location and depth intercepted by probe hole C5378.



2007/DCL/T/010 (05/14)

**Figure 4.10.** pH for 1:1 Sediment:Water Extracts and Dilution-Corrected EC Values from T Tank Farm

#### 4.2.2.2 Composition of the 1:1 Sediment:Water Extracts from the T Tank Farm Core and Grab Samples

The water extract values for the major anions, cations, and several trace constituents are discussed in this section. The anion data are tabulated in Table 4.18 and Figures 4.11 and 4.12 in units of mass per gram of dry sediment. Several of the 1:1 sediment:water extracts contained slightly elevated concentrations of fluoride (greater than 1  $\mu\text{g/g}$ ). Unfortunately, there was an unidentified chromatographic interference that precluded the quantification of fluoride in most of the direct push samples. The average 1:1 sediment:water extract fluoride value for the T Tank Farm probe holes that could be resolved (1.34  $\mu\text{g/g}$ ) was approximately a factor of two higher than the average fluoride concentration (0.60  $\mu\text{g/g}$ ) measured in the background borehole 299-W10-27. Elevated water-extractable chloride was found in one core sample from probe hole C5382. Probe hole C5382 was emplaced the furthest eastward with respect to tank 241-T-101. Additionally, the sample was collected at approximately 78 ft bgs. The combination of its location relative to the tank and its depth in the vadose zone can potentially provide insight on the migration pathway of mobile contaminants. Water-extractable nitrate was significantly elevated (in excess of 250  $\mu\text{g/g}$ ) in the string of cores collected from probe hole C5374 from approximately 80 ft bgs within the fine-grained Upper Cold Creek Unit. Probe hole C5374 was emplaced to the south of tank 241-T-101 and adjacent to tank 241-T-104. It is obvious that tank waste has impacted the vadose zone at this location; however, this single set of data does not permit the source of the contamination to be identified. The same samples that contained significantly elevated water-extractable nitrate also contained elevated sulfate (93.9 to 117  $\mu\text{g/g}$ ). It is possible that the elevated sulfate in these samples is natural sulfate present in the sediments that has been displaced by the nitrate plume in the area. The majority of the samples did not contain quantifiable amounts of water-extractable phosphate; however, a few of the samples collected shallower in the vadose zone contained water-extractable phosphate in excess of 1  $\mu\text{g/g}$ . Interestingly, none of the waste streams purported to have been part of the composition of the leak from tank T-101 contained phosphate (Serne et al. 2007)

The water-extractable major cations in the T Tank Farm probe hole sediments are tabulated in Table 4.19 and Figure 4.13 in units of mass per gram of sediment on a dry weight basis. All three cores from probe hole C5374 contained elevated concentrations of calcium, potassium, magnesium, strontium, and sodium. Although the sediments from this probe hole contained elevated concentrations of water-extractable sodium, they were the only samples analyzed that had calcium as the dominant water-extractable cation. It was surprising to find elevated calcium, magnesium, and sodium together in the same sample, since the sodium would typically drive the divalent cations off the exchange sites; this phenomenon could indicate that the samples were collected near the leading edge of the ion exchange front. However, it is impossible to confirm this hypothesis given the lack of sample coverage (particularly with respect to depth) in the area. All of the remaining core samples analyzed contained sodium as the dominant water-extractable cation, including those collected from probe hole C5382. Probe hole C5382 was emplaced to the same approximate depth as probe hole C5374, but was located much further to the northeast. If the tank waste residuals found in these two probe holes are a result of the same leak event, it appears that the ion exchange front resides deeper in the vadose zone to the east of tank 241-T-101 than it does to the southeast. However, given the overall lack of sample coverage, it is not possible to determine if the two probe holes have intercepted the same leak event. Either way, based on the water-extractable concentrations of sodium, calcium, and magnesium, there are signs of cation exchange in all of the probe holes emplaced around tanks 241-T-101 and 241-T-104.

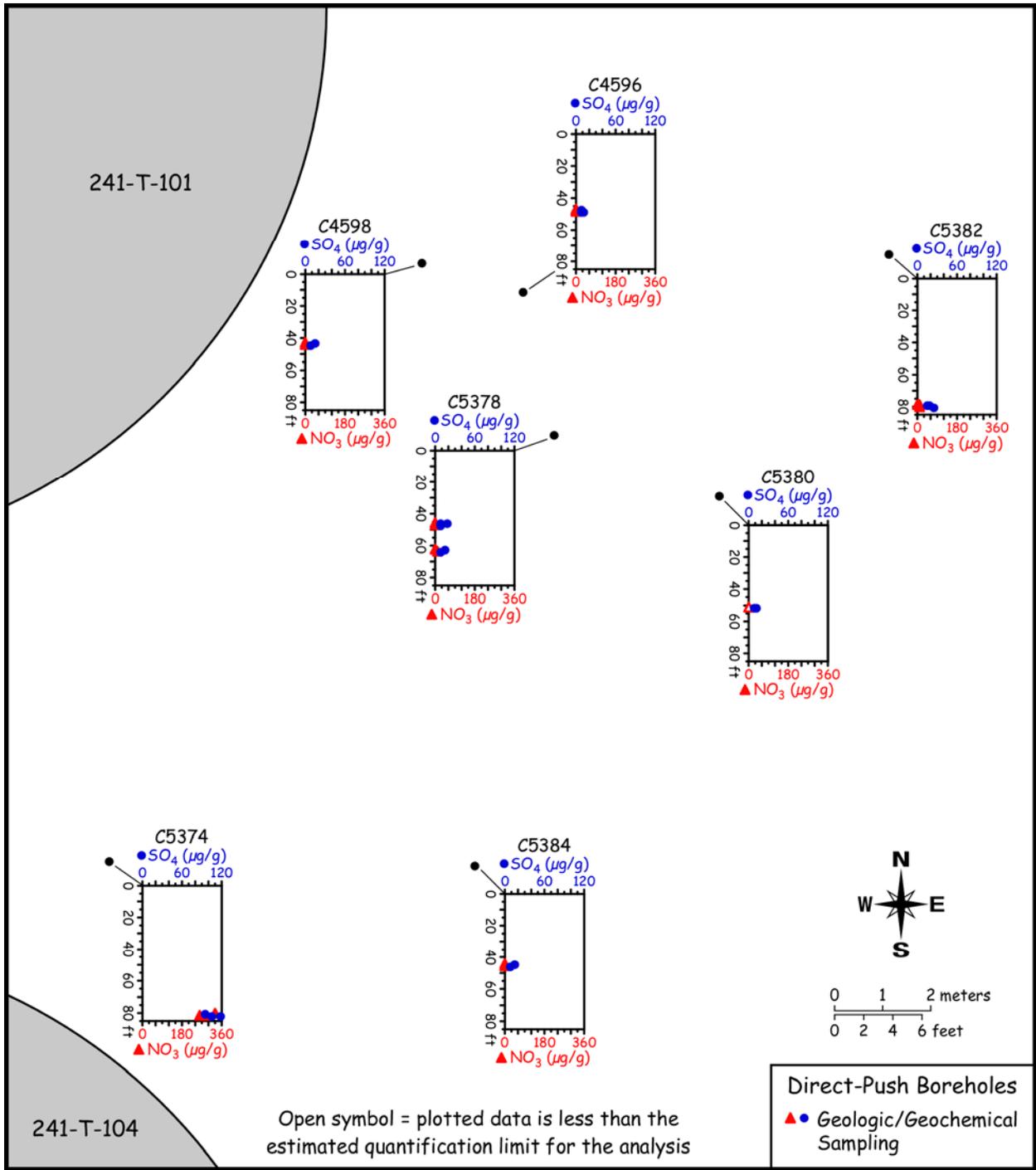
**Table 4.18.** Water-Extractable Anions in the T Tank Farm Core and Grab Samples ( $\mu\text{g/g}$  dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Fluoride $\mu\text{g/g}$	Chloride $\mu\text{g/g}$	Nitrate $\mu\text{g/g}$	Sulfate $\mu\text{g/g}$	Phosphate $\mu\text{g/g}$
B1KC35A	C4598	43.8	ND	<5.02E-01	4.49E+00	5.81E+00	<b>2.08E+00</b>
B1KC35B	C4598	43.3	ND	2.30E+00	5.90E+00	1.24E+01	ND
B1KC36A	C4596	48.3	ND	<5.05E-01	4.52E+00	1.11E+01	<b>2.64E+00</b>
B1KC36B	C4596	47.8	ND	<5.18E-01	2.11E+00	8.05E+00	<1.56E+00
B1KC36C	C4596	47.3	ND	<5.33E-01	2.06E+00	8.10E+00	<b>1.64E+00</b>
B1KC37A	C5378	46.3	ND	<5.19E-01	1.21E+00	7.00E+00	<1.56E+00
B1KC37B	C5378	45.8	<b>1.41E+00</b>	<5.00E-01	2.02E+00	8.12E+00	<1.50E+00
B1KC37C	C5378	45.3	<b>1.34E+00</b>	1.54E+00	3.59E+00	1.59E+01	ND
B1KC38A	C5378	63.3	ND	<5.16E-01	<b>8.33E+00</b>	5.78E+00	<1.55E+00
B1KC38B	C5378	62.8	ND	<5.06E-01	<b>6.47E+00</b>	6.93E+00	<b>1.50E+00</b>
B1KC38C	C5378	62.3	<b>3.31E+00</b>	<5.14E-01	4.45E+00	1.30E+01	<b>1.94E+00</b>
B1KC39A	C5384	45.3	4.94E-01	<5.05E-01	2.06E+00	8.02E+00	<b>2.58E+00</b>
B1KC39B	C5384	44.8	6.47E-01	<5.10E-01	2.74E+00	7.73E+00	<1.52E+00
B1KC39C	C5384	44.3	<b>1.10E+00</b>	9.24E-01	1.83E+00	1.46E+01	<1.53E+00
B1KC40A	C5374	81.3	ND	1.69E+01	<b>2.94E+02</b>	<b>1.17E+02</b>	ND
B1KC40B	C5374	80.8	ND	1.52E+01	<b>2.65E+02</b>	<b>1.04E+02</b>	<1.52E+00
B1KC40C	C5374	80.3	ND	1.79E+01	<b>3.31E+02</b>	<b>9.39E+01</b>	<1.52E+00
B1LB07A	C5382	79.3	ND	2.12E+00	<b>1.12E+01</b>	2.50E+01	<1.51E+00
B1LB07B	C5382	78.8	ND	2.54E+00	<b>6.70E+00</b>	1.64E+01	<1.51E+00
B1LB07C	C5382	78.3	ND	<b>5.60E+00</b>	1.65E+00	1.21E+01	<1.51E+00
B1LB08A	C5380	51.3	ND	6.48E-01	<1.03E+00	9.50E+00	ND
B1LB08B	C5380	50.8	ND	7.94E-01	1.66E+00	6.49E+00	ND
B1LB08C	C5380	50.3	<b>1.08E+00</b>	9.60E-01	<1.02E+00	5.58E+00	<1.51E+00

Bold values denote elevated concentrations.  
Less than values indicate the instrument returned a negative value or the reported value is less than the limit of quantification.  
ND indicates the analyte was not determined due to chromatographic interference.

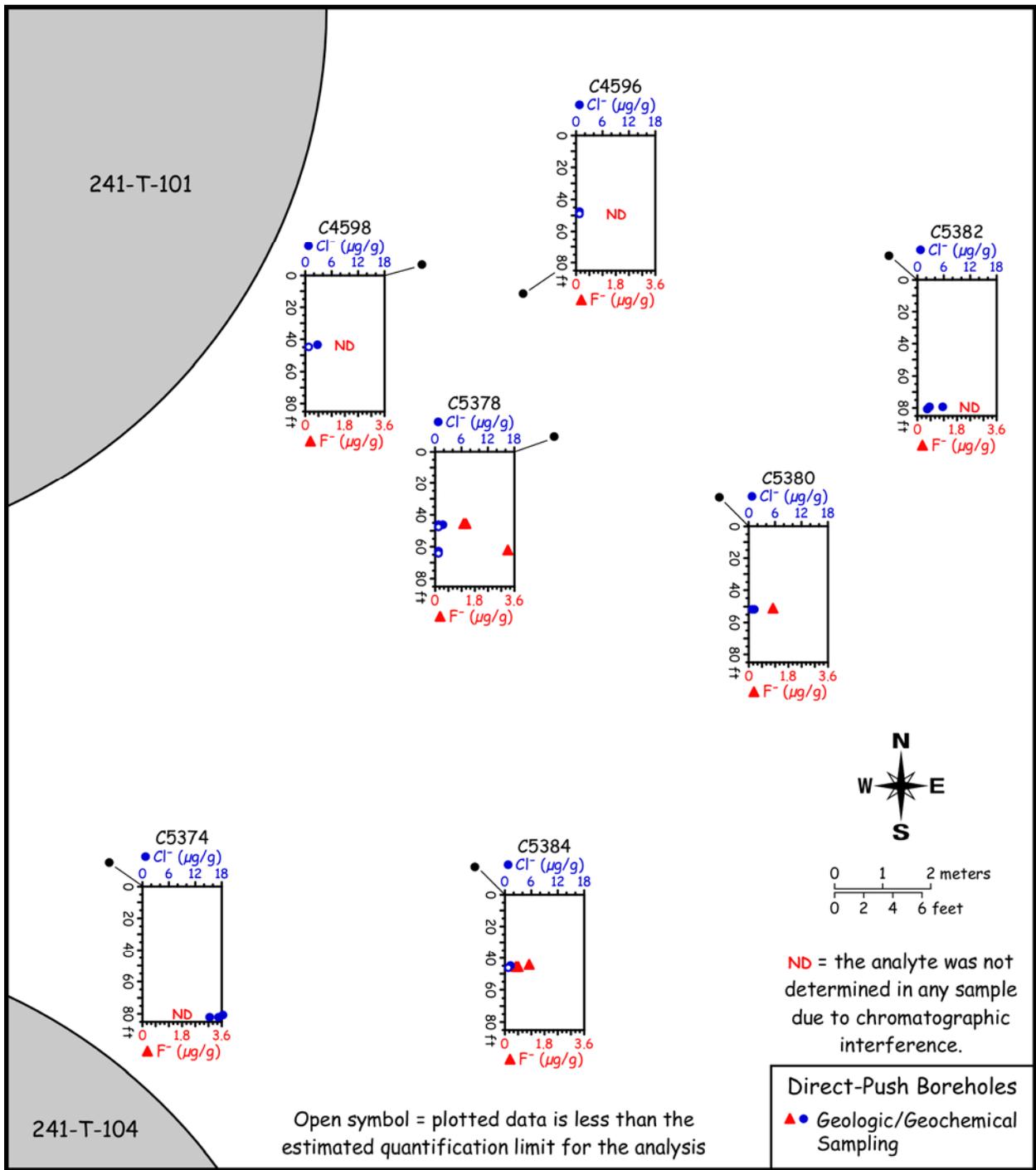
The water-extractable aluminum, iron, silicon, and sulfur in the T Tank Farm direct push sediments are shown in Table 4.20. The sulfur data were converted to water-extractable sulfur as sulfate so that the results could be compared to the IC data presented in Table 4.18. The agreement between measuring the water extracts for sulfate directly with the ion chromatograph and indirectly by converting the ICP measurements for sulfur to sulfate was very good. Besides validating the ion chromatography data, we can state that the water-extractable sulfur was in fact sulfate. Water-soluble aluminum was elevated (above the limit of detection) in sediment from all of the probe holes except that from probe hole C5374. It appears that these elevated values are a result of some chemical reaction, such as dissolution or precipitation, between alkaline tank fluids and native sediments that formed precipitates of amorphous aluminum phases that are more water soluble than aluminum-rich crystalline mineral phases in the native sediments.

The water extract data for potentially mobile metals, such as technetium-99, uranium-238, chromium, molybdenum and ruthenium are shown in Table 4.21. Additionally, the water-extractable technetium-99 and uranium-238 are plotted as a function of depth in Figures 4.14 and 4.15. Water-extractable



2007/DCL/T/013 (05/16)

**Figure 4.11.** 1:1 Sediment:Water-Extractable Nitrate and Sulfate data from the T Tank Farm Direct Push Samples



**Figure 4.12.** 1:1 Sediment:Water-Extractable Chloride and Fluoride Data from the T Tank Farm Direct Push Samples

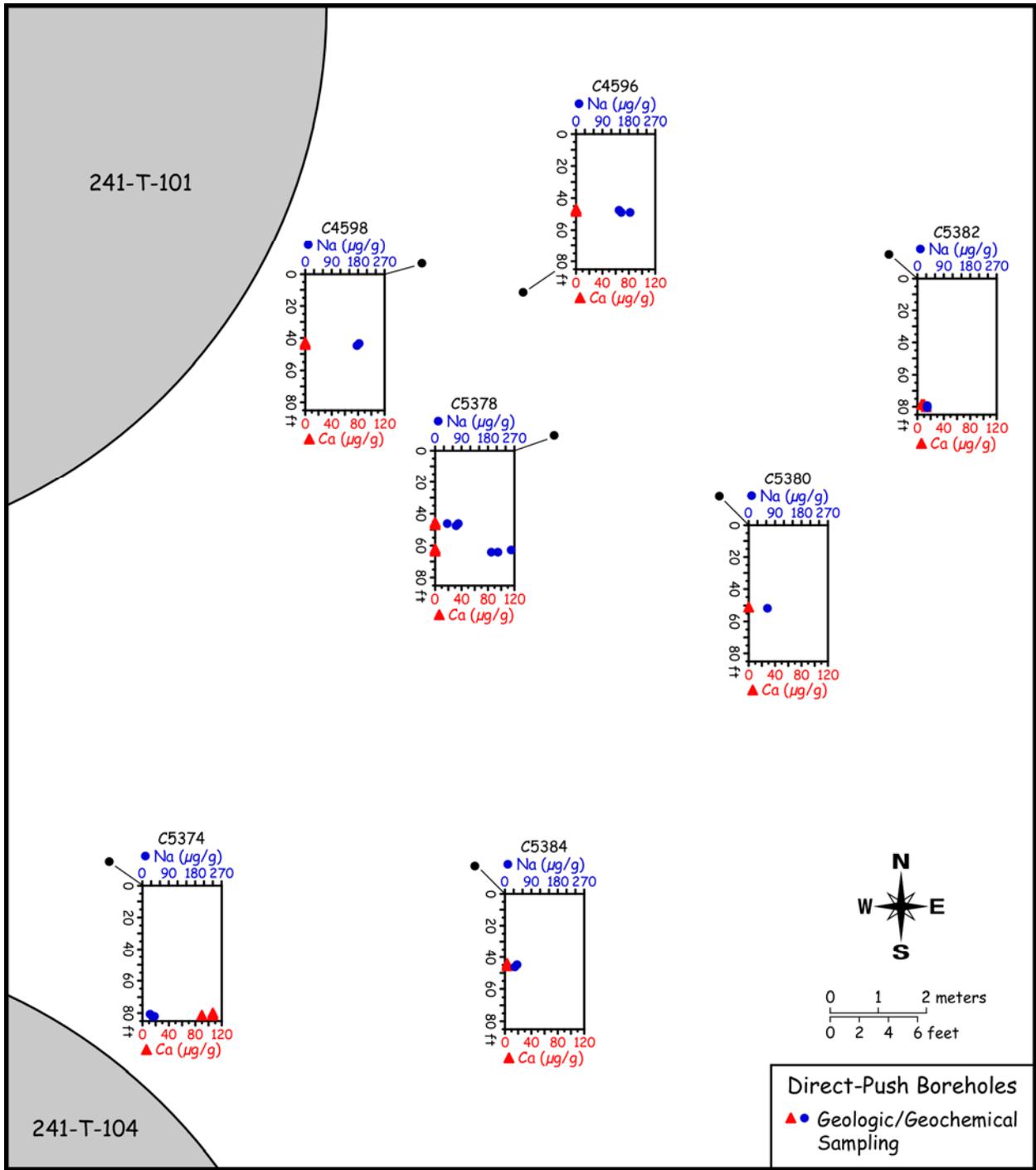
**Table 4.19.** Water-Extractable Major Cations in the T Tank Farm Core and Grab Samples ( $\mu\text{g/g}$  dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Calcium $\mu\text{g/g}$	Potassium $\mu\text{g/g}$	Magnesium $\mu\text{g/g}$	Strontium $\mu\text{g/g}$	Sodium $\mu\text{g/g}$
B1KC35A	C4598	43.8	<i>4.59E-01</i>	(2.48E+00)	(8.05E-02)	(3.04E-03)	<b>1.76E+02</b>
B1KC35B	C4598	43.3	<i>5.49E-01</i>	(3.49E+00)	(1.02E-01)	(3.25E-03)	<b>1.82E+02</b>
B1KC36A	C4596	48.3	<i>8.54E-01</i>	(2.01E+00)	(1.94E-01)	(5.15E-03)	<b>1.79E+02</b>
B1KC36B	C4596	47.8	<i>9.48E-01</i>	(1.65E+00)	(9.04E-02)	(5.01E-03)	<b>1.48E+02</b>
B1KC36C	C4596	47.3	<i>5.23E-01</i>	(1.66E+00)	(7.72E-02)	(3.30E-03)	<b>1.43E+02</b>
B1KC37A	C5378	46.3	<i>7.25E-01</i>	(1.73E+00)	(1.95E-01)	(5.29E-03)	<b>6.52E+01</b>
B1KC37B	C5378	45.8	<i>7.01E-01</i>	(1.84E+00)	(1.58E-01)	(4.30E-03)	<b>7.40E+01</b>
B1KC37C	C5378	45.3	<i>1.79E+00</i>	(3.14E+00)	<i>5.58E-01</i>	(8.07E-03)	<b>4.06E+01</b>
B1KC38A	C5378	63.3	<i>6.52E-01</i>	(1.84E+00)	(6.51E-02)	(3.72E-03)	<b>1.91E+02</b>
B1KC38B	C5378	62.8	<i>6.01E-01</i>	(1.66E+00)	(6.25E-02)	(3.10E-03)	<b>2.11E+02</b>
B1KC38C	C5378	62.3	<i>1.08E+00</i>	(2.25E+00)	(1.03E-01)	(5.41E-03)	<b>2.55E+02</b>
B1KC39A	C5384	45.3	<i>2.02E+00</i>	(2.82E+00)	<i>5.02E-01</i>	(1.16E-02)	<b>3.18E+01</b>
B1KC39B	C5384	44.8	<i>2.25E+00</i>	(2.90E+00)	<i>5.63E-01</i>	(1.29E-02)	<b>3.30E+01</b>
B1KC39C	C5384	44.3	<i>3.71E+00</i>	(4.58E+00)	<i>9.71E-01</i>	(1.99E-02)	<b>4.09E+01</b>
B1KC40A	C5374	81.3	<b>1.05E+02</b>	<b>8.77E+00</b>	<b>2.30E+01</b>	<b>4.80E-01</b>	<b>3.91E+01</b>
B1KC40B	C5374	80.8	<b>9.19E+01</b>	<b>8.14E+00</b>	<b>2.03E+01</b>	<b>4.26E-01</b>	<b>3.22E+01</b>
B1KC40C	C5374	80.3	<b>1.06E+02</b>	<b>1.08E+01</b>	<b>2.52E+01</b>	<b>5.17E-01</b>	<b>2.66E+01</b>
B1LB07A	C5382	79.3	<i>1.51E+01</i>	(4.92E+00)	<i>3.35E+00</i>	<i>8.00E-02</i>	<b>3.00E+01</b>
B1LB07B	C5382	78.8	<i>1.10E+01</i>	(4.28E+00)	<i>2.35E+00</i>	<i>5.34E-02</i>	<b>2.94E+01</b>
B1LB07C	C5382	78.3	<i>7.56E+00</i>	(3.82E+00)	<i>1.68E+00</i>	<i>4.11E-02</i>	<b>2.70E+01</b>
B1LB08A	C5380	51.3	<i>9.82E-01</i>	(3.91E+00)	(1.73E-01)	(4.84E-03)	<b>6.10E+01</b>
B1LB08B	C5380	50.8	<i>9.23E-01</i>	(4.62E+00)	(1.63E-01)	(4.52E-03)	<b>6.17E+01</b>
B1LB08C	C5380	50.3	<i>1.08E+00</i>	(4.31E+00)	(2.49E-01)	(5.32E-03)	<b>6.36E+01</b>

Bold values denote elevated concentrations.  
 Italicized values denote low concentrations.  
 Parentheses indicate reported value was less than the limit of quantification for the analysis.

The water extract data for potentially mobile metals, such as technetium-99, uranium-238, chromium, molybdenum, and ruthenium, are shown in Table 4.21. Additionally, the water-extractable technetium-99 and uranium-238 are plotted as a function of depth in Figures 4.14 and 4.15. Water-extractable technetium-99 was found in most of the direct push core samples analyzed; however, it was only significantly elevated (79.5 pCi/g) in the sediments collected from probe hole C5374. Not surprisingly, these were some of the deepest direct push samples collected as part of the T Tank Farm sampling campaign. Technetium-99 is generally considered quite mobile in the subsurface, and as such, peak concentrations in the vadose zone are often found well below 115 ft bgs in regions that have been contaminated by tank loss events (Serne et al. 2004b, Brown et al. 2006). Water-leachable uranium-238 was all less than 0.2  $\mu\text{g/g}$ , indicating that there is not a significant amount of contaminant uranium in the vadose zone at these sampling locations. However, uranium was not estimated to be a significant component of the waste that was allegedly lost during the tank 241-T-101 leak event (Wood et al. 2001).

Elevated water-leachable chromium (nearly 4  $\mu\text{g/g}$ ) was also found in sediments from probe hole C5374. For comparative purposes, the average water-leachable chromium values for all of the remaining T Tank Farm direct push samples were less than 0.1  $\mu\text{g/g}$ . The three core samples from probe hole C5374 also had elevated water-extractable ruthenium. Furthermore, differences between the measured ruthenium-101 and ruthenium-102 concentrations indicate that the ruthenium is present as a fission product produced during the fuel burn-up cycle. These three samples are excellent candidates for performing ruthenium isotopic analysis for source identification.



**Figure 4.13.** 1:1 Sediment:Water-Extractable Sodium and Calcium data from the T Tank Farm Direct Push Samples

**Table 4.20.** Water-Extractable Cations in the T Tank Farm Core and Grab Samples ( $\mu\text{g/g}$  dry sediment)

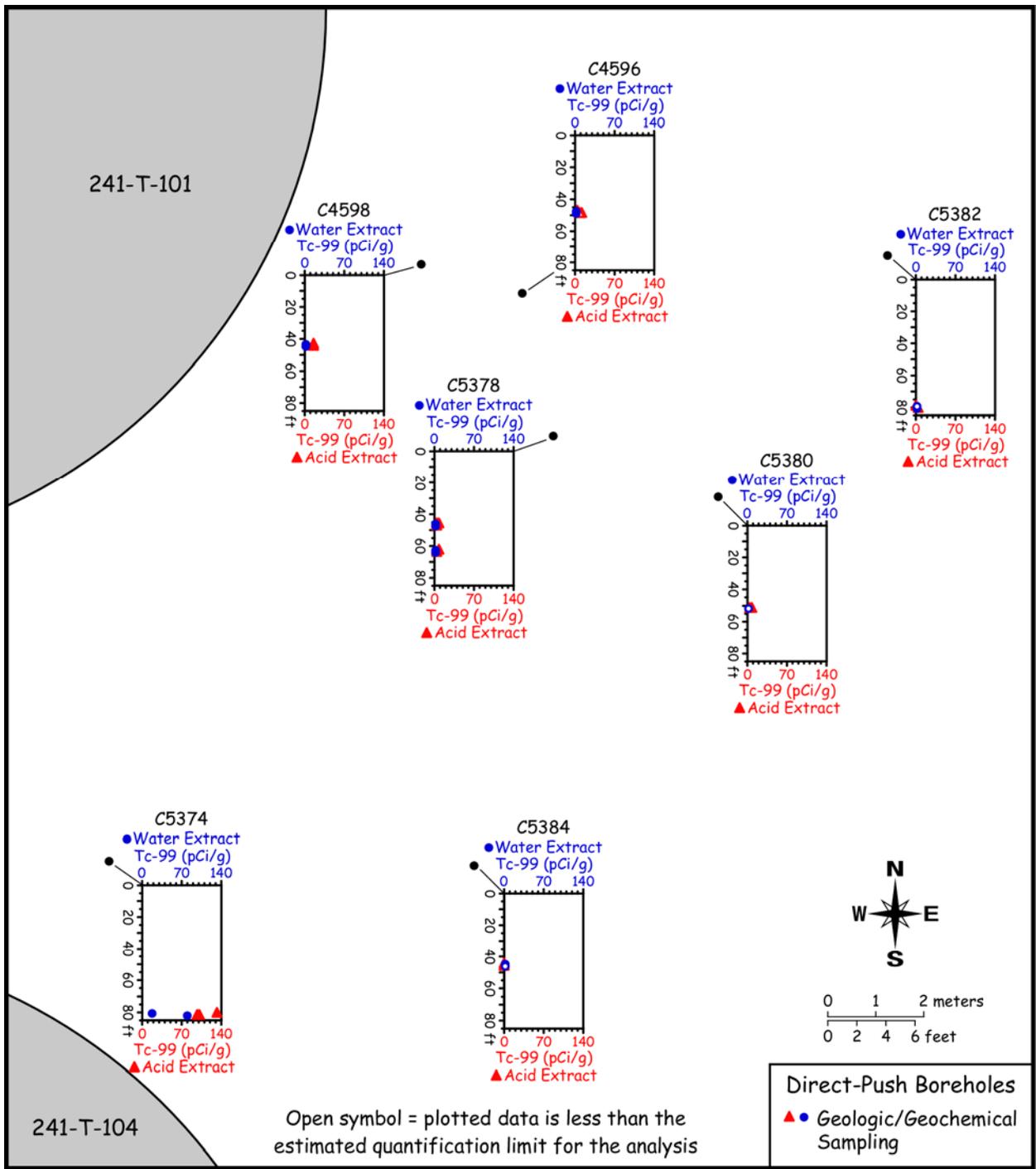
Sample ID	Probe Hole ID	Mid-Depth ft bgs	Aluminum $\mu\text{g/g}$	Iron $\mu\text{g/g}$	Sulfur as $\text{SO}_4^{2-}$ $\mu\text{g/g}$	Silicon $\mu\text{g/g}$
B1KC35A	C4598	43.8	2.71E-01	3.34E-01	(8.04E+00)	2.19E+01
B1KC35B	C4598	43.3	2.76E-01	3.08E-01	1.96E+01	1.51E+01
B1KC36A	C4596	48.3	3.30E-01	2.11E-01	(1.28E+01)	1.25E+01
B1KC36B	C4596	47.8	2.25E-01	2.41E-01	(1.08E+01)	1.82E+01
B1KC36C	C4596	47.3	2.45E-01	2.85E-01	(8.71E+00)	2.17E+01
B1KC37A	C5378	46.3	3.92E-01	4.62E-01	(8.54E+00)	1.61E+01
B1KC37B	C5378	45.8	1.82E-01	1.65E-01	(9.49E+00)	1.51E+01
B1KC37C	C5378	45.3	1.53E-01	1.92E-01	1.75E+01	1.55E+01
B1KC38A	C5378	63.3	1.98E-01	2.33E-01	(7.79E+00)	1.82E+01
B1KC38B	C5378	62.8	1.68E-01	2.20E-01	(1.00E+01)	2.05E+01
B1KC38C	C5378	62.3	1.62E-01	2.62E-01	1.64E+01	1.85E+01
B1KC39A	C5384	45.3	1.38E-01	1.29E-01	(8.84E+00)	9.82E+00
B1KC39B	C5384	44.8	1.29E-01	1.36E-01	(9.02E+00)	1.08E+01
B1KC39C	C5384	44.3	9.67E-02	9.27E-02	1.66E+01	8.41E+00
B1KC40A	C5374	81.3	<i>&lt;2.54E-02</i>	<i>(2.24E-03)</i>	<b>1.12E+02</b>	1.08E+01
B1KC40B	C5374	80.8	<i>&lt;2.54E-02</i>	<i>(4.24E-03)</i>	<b>1.00E+02</b>	1.05E+01
B1KC40C	C5374	80.3	<i>&lt;2.52E-02</i>	<i>(3.10E-03)</i>	<b>9.09E+01</b>	9.59E+00
B1LB07A	C5382	79.3	(1.78E-02)	3.41E-02	2.62E+01	1.34E+01
B1LB07B	C5382	78.8	7.43E-02	6.81E-02	1.78E+01	1.34E+01
B1LB07C	C5382	78.3	3.86E-02	3.82E-02	(1.33E+01)	1.14E+01
B1LB08A	C5380	51.3	1.35E-01	1.52E-01	(1.20E+01)	1.33E+01
B1LB08B	C5380	50.8	2.15E-01	2.78E-01	(8.56E+00)	1.24E+01
B1LB08C	C5380	50.3	2.40E-01	2.87E-01	(7.47E+00)	1.12E+01

Bold values denote elevated concentrations.  
 Italicized values denote low concentrations.  
 Parentheses indicate reported value was less than the limit of quantification for the analysis.

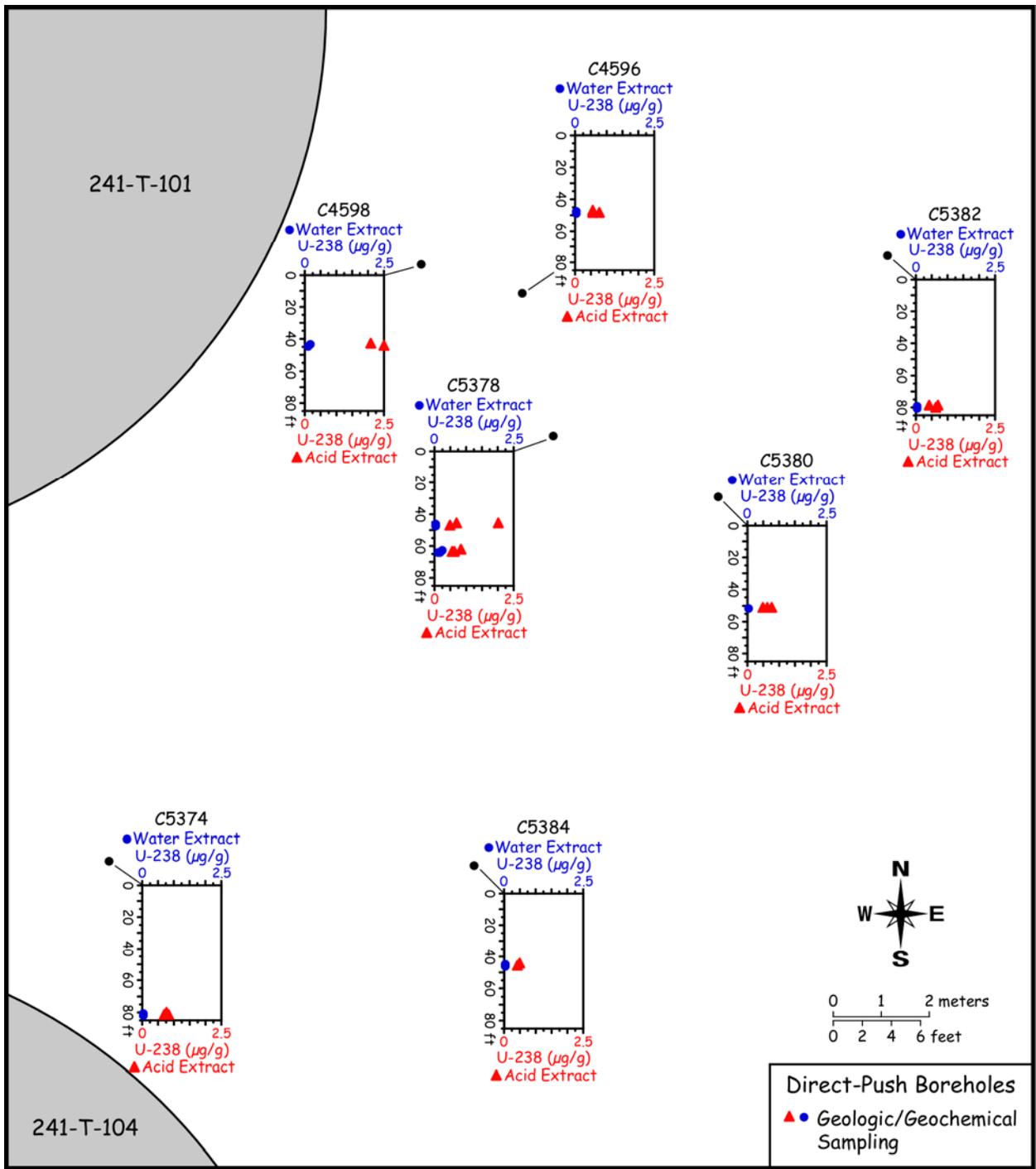
**Table 4.21.** Water-Extractable Mobile Metals in the T Tank Farm Core and Grab Samples ( $\mu\text{g/g}$  dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Technetium-99 pCi/g	Uranium-238 $\mu\text{g/g}$	Chromium-52 $\mu\text{g/g}$	Molybdenum-95 $\mu\text{g/g}$	Ruthenium-101 $\mu\text{g/g}$	Ruthenium-102 $\mu\text{g/g}$
B1KC35A	C4598	43.8	<b>1.28E+00</b>	1.10E-01	1.16E-02	3.06E-02	(1.25E-04)	(2.71E-05)
B1KC35B	C4598	43.3	<b>1.75E+00</b>	1.40E-01	6.48E-03	2.21E-01	(1.07E-04)	(4.03E-06)
B1KC36A	C4596	48.3	<b>4.87E-01</b>	3.04E-02	3.64E-02	6.81E-02	(3.66E-04)	(1.54E-04)
B1KC36B	C4596	47.8	<b>2.95E-01</b>	1.63E-02	3.46E-02	3.44E-02	(3.56E-04)	(1.26E-04)
B1KC36C	C4596	47.3	<b>5.93E-01</b>	1.66E-02	8.22E-03	3.12E-02	(7.04E-05)	(9.60E-06)
B1KC37A	C5378	46.3	<b>9.86E-02</b>	1.81E-02	7.87E-03	2.50E-02	(6.23E-05)	<1.04E-03
B1KC37B	C5378	45.8	<b>1.19E-01</b>	1.93E-02	1.45E-02	2.83E-02	(1.75E-04)	(7.20E-05)
B1KC37C	C5378	45.3	<b>5.48E-02</b>	2.73E-03	2.06E-02	7.69E-02	(2.42E-05)	<1.01E-03
B1KC38A	C5378	63.3	<b>2.26E+00</b>	1.07E-01	6.15E-02	1.99E-02	(5.95E-04)	(2.56E-04)
B1KC38B	C5378	62.8	<b>1.48E+00</b>	1.23E-01	7.90E-02	3.21E-02	(4.26E-04)	(1.45E-04)
B1KC38C	C5378	62.3	<b>1.41E+00</b>	1.84E-01	8.28E-02	9.43E-02	(7.61E-04)	(3.04E-04)
B1KC39A	C5384	45.3	<3.43E-02	2.07E-03	(1.56E-03)	2.17E-02	<1.01E-03	<1.01E-03
B1KC39B	C5384	44.8	<3.46E-02	2.47E-03	(1.25E-03)	2.43E-02	(1.43E-05)	<1.02E-03
B1KC39C	C5384	44.3	(2.04E-02)	2.11E-03	(1.41E-03)	1.67E-01	<1.00E-03	<1.00E-03
B1KC40A	C5374	81.3	<b>7.91E+01</b>	2.08E-03	<b>3.88E+00</b>	1.79E-02	<b>3.35E-03</b>	<b>1.72E-03</b>
B1KC40B	C5374	80.8	<b>7.95E+01</b>	1.86E-03	<b>3.94E+00</b>	1.52E-02	<b>4.02E-03</b>	<b>2.06E-03</b>
B1KC40C	C5374	80.3	<b>1.74E+01</b>	1.65E-03	9.60E-02	6.93E-02	<b>3.87E-03</b>	<b>2.11E-03</b>
B1LB07A	C5382	79.3	<b>1.12E-01</b>	3.70E-03	(4.02E-03)	7.30E-02	<1.00E-03	<1.00E-03
B1LB07B	C5382	78.8	<b>2.82E-02</b>	3.47E-03	(3.09E-03)	8.62E-02	<1.04E-03	<1.04E-03
B1LB07C	C5382	78.3	<3.41E-02	2.35E-03	(6.57E-04)	6.56E-02	<1.00E-03	<1.00E-03
B1LB08A	C5380	51.3	(1.75E-02)	1.25E-02	(1.71E-03)	7.31E-02	(4.23E-05)	<1.03E-03
B1LB08B	C5380	50.8	<b>2.84E-02</b>	1.68E-02	(2.55E-03)	8.10E-02	(5.03E-05)	<1.05E-03
B1LB08C	C5380	50.3	<b>6.57E-02</b>	1.33E-02	(2.22E-03)	1.08E-01	(7.14E-05)	<1.02E-03

Bold values denote elevated concentrations.  
 Parentheses indicate reported value was less than the limit of quantification for the analysis.  
 Less than values indicate the instrument returned a negative value.



**Figure 4.14.** 1:1 Sediment:Water-Extractable and 8M Nitric Acid Extractable Technetium-99 data from the T Tank Farm Direct Push Samples



2007/DCL/T/015 (05/16)

**Figure 4.15.** 1:1 Sediment:Water-Extractable and 8M Nitric Acid Extractable Uranium-238 data from the T Tank Farm Direct Push Samples

### 4.2.3 Vadose Zone Porewater Chemical Composition

The 1:1 water extract data was manipulated to derive the pore water composition of the vadose zone sediments so that electrical balances (anions vs. cations) of the samples could be evaluated. From knowledge of the moisture content of the sediment samples taken from the liners of each direct push sample and the grab samples, the amount of de-ionized water that would be needed to make the water extract exactly one part water (total of native pore water and added de-ionized water) to one part by weight dry sediment was calculated. The ratio of the total volume of water in the extract to the native mass of pore water is the dilution factor. An assumption was made that the de-ionized water acted solely as a diluent of the existing pore water and that the de-ionized water did not dissolve any of the solids in the sediments. Thus by correcting for the dilution, an estimate of the actual chemical composition of the native pore-water in the vadose zone sediments could be derived.

Tables 4.22 and 4.23 show the derived pore water composition of key constituents in meq/L and Figure 4.16 shows the porewater corrected alkalinity (as CaCO<sub>3</sub>) in units of mg/L. The highest dissolved salt loads were found in the sediment collected within probe hole C4598, which was one of the closest locations to the side of T-101 sampled. The sediment was collected from approximately 43 ft bgs and had some of the highest pH values measured in the T Tank Farm direct push samples. As a result of the high pH, carbon dioxide was absorbed by the porewater present in the sediment and resulted in the majority of the anionic charge being attributed to alkalinity (192 meq/L). The remainder of the dissolved anionic species were sulfate (3.05 meq/L), nitrate (1.82 meq/L), and phosphate (1.65 meq/L), for a total anionic charge of 199 meq/L. The anions in this samples were primarily balanced by sodium (193 meq/L), with trace amounts of calcium (0.576 meq/L). These concentrations are very dilute compared to the vadose zone pore waters found at the SX and BX tank farms, where the total dissolved salt loads were as high as 7,000 to 17,000 and 1,000 meq/L, respectively. The most concentrated pore waters below tank T-106 ranged from 200 to 250 meq/L each for cations and anions (total ~450 to 500 meq/L) and below tank TX-107, the most concentrated pore water had 850 total meq/L.

The samples that had the highest concentrations of mobile tank waste constituents (namely technetium-99 and nitrate) were found in probe hole C5374. The sample with the peak dissolved salt load in the three liners from probe hole C5374 contained 62 meq/L anions and 59 meq/L cations. The dissolved anions included nitrate (35.9 meq/L), sulfate (13.2 meq/L), alkalinity (9.27 meq/L), and chloride (3.10 meq/L). The dissolved anions were balanced by calcium (35.4 meq/L), magnesium (19.2 meq/L), sodium (7.79 meq/L), and potassium 1.92 meq/L). Again, these samples were quite dilute when compared to contaminated sediments collected during other characterization campaigns; including the T-106 boreholes C4104 and C4105 (see Serne et al. (2004b).

Overall, the calculated charge balance between cations and anions for all of the samples was quite good (less than 10% difference for most of the samples analyzed). However, samples from probe holes C5378, C5380, C5382, and C5384 contained in general 10-20% less dissolved cations than anions. Based on comparison of this data, it appears that either the bicarbonate measurement for these samples is biased high, or analyses have not accounted for a dissolved metal that is present in sufficient quantity to properly balance the electrical charge of these samples.

As mentioned previously, sodium was present as the dominant cation in all of the samples except those from probe hole C5374, which contained calcium as the dominant cation. Bicarbonate (measured as alkalinity via titration) was the primary anionic species in all of the samples except those from probe

hole C5374, which contained nitrate as the dominant anion. The lack of samples containing calcium as the dominant cation indicates that the samples in this region have been impacted by a sodium-bearing waste fluid. The source(s) appears to be a moderately concentrated sodium-bearing waste solution that has displaced the natural divalent cations from the sediment cation exchange sites in the sediments. The total vertical extent of the ion exchange front is unknown due to the lack of sediment samples from deeper in the vadose zone.

The porewater-corrected concentrations of mobile metals are presented in Table 4.24 in units of pCi/L (for technetium-99) or µg/L (for all other constituents). A porewater-corrected technetium-99 activity in excess of 45,000 pCi/L was measured in one sample from probe hole C5374. Although an activity of 45,000 pCi/L is 50 times the maximum contaminant level (MCL) for technetium-99, it is important to note that this value represents a porewater concentration and would be diluted significantly should the solution make it to the water table. The other thing to note is that while there was a relatively small amount of water-extractable uranium-238 present in these samples, the porewater-corrected uranium-238 concentrations exceeded the MCL of 30 µg/L in nearly all of the samples analyzed. Again, these porewater-corrected concentrations would be significantly diluted should these solutions ever reach the water table.

**Table 4.22.** Calculated Pore Water Anion Concentrations in the T Tank Farm Core and Grab Samples

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Fluoride meq/L	Chloride meq/L	Nitrate meq/L	Sulfate meq/L	Phosphate meq/L	Alkalinity meq/L
B1KC35A	C4598	43.8	ND	<3.56E-01	1.82E+00	3.05E+00	1.65E+00	1.92E+02
B1KC35B	C4598	43.3	ND	1.51E+00	2.21E+00	6.03E+00	ND	1.71E+02
B1KC36A	C4596	48.3	ND	<2.23E-01	1.14E+00	3.63E+00	1.31E+00	1.25E+02
B1KC36B	C4596	47.8	ND	<3.48E-01	8.10E-01	3.99E+00	<1.17E+00	1.62E+02
B1KC36C	C4596	47.3	ND	<3.29E-01	7.28E-01	3.69E+00	1.13E+00	1.44E+02
B1KC37A	C5378	46.3	ND	<5.67E-01	7.59E-01	5.65E+00	<1.90E+00	1.22E+02
B1KC37B	C5378	45.8	1.27E+00	<2.40E-01	5.55E-01	2.88E+00	<8.07E-01	6.37E+01
B1KC37C	C5378	45.3	6.05E-01	3.73E-01	4.96E-01	2.84E+00	ND	1.79E+01
B1KC38A	C5378	63.3	ND	<2.81E-01	2.60E+00	2.32E+00	<9.44E-01	1.66E+02
B1KC38B	C5378	62.8	ND	<2.60E-01	1.91E+00	2.64E+00	1.12E+00	1.69E+02
B1KC38C	C5378	62.3	2.67E+00	<2.23E-01	1.10E+00	4.16E+00	1.25E+00	1.68E+02
B1KC39A	C5384	45.3	7.29E-01	<4.00E-01	9.31E-01	4.69E+00	<1.34E+00	4.91E+01
B1KC39B	C5384	44.8	7.51E-01	<3.17E-01	9.74E-01	3.55E+00	<1.07E+00	4.58E+01
B1KC39C	C5384	44.3	9.49E-01	4.27E-01	4.83E-01	4.98E+00	ND	3.60E+01
B1KC40A	C5374	81.3	ND	2.88E+00	2.86E+01	1.47E+01	<2.90E-01	1.12E+01
B1KC40B	C5374	80.8	ND	2.36E+00	2.35E+01	1.19E+01	<2.64E-01	7.63E+00
B1KC40C	C5374	80.3	ND	3.40E+00	3.59E+01	1.32E+01	<3.21E-01	9.27E+00
B1LB07A	C5382	79.3	ND	2.64E-01	7.98E-01	2.29E+00	<2.10E-01	9.15E+00
B1LB07B	C5382	78.8	ND	4.82E-01	7.26E-01	2.29E+00	ND	1.42E+01
B1LB07C	C5382	78.3	ND	2.64E+00	4.45E-01	4.22E+00	<7.96E-01	3.17E+01
B1LB08A	C5380	51.3	ND	2.19E-01	<2.00E-01	2.38E+00	ND	3.72E+01
B1LB08B	C5380	50.8	ND	2.45E-01	2.92E-01	1.48E+00	ND	3.38E+01
B1LB08C	C5380	50.3	6.88E-01	3.28E-01	<1.99E-01	1.41E+00	ND	4.50E+01

Less than values indicate the instrument returned a negative value.  
 ND indicates the analyte was not determined due to chromatographic interference.

**Table 4.23.** Calculated Pore Water Cation Concentrations in the T Tank Farm Direct Push Core and Grab Samples

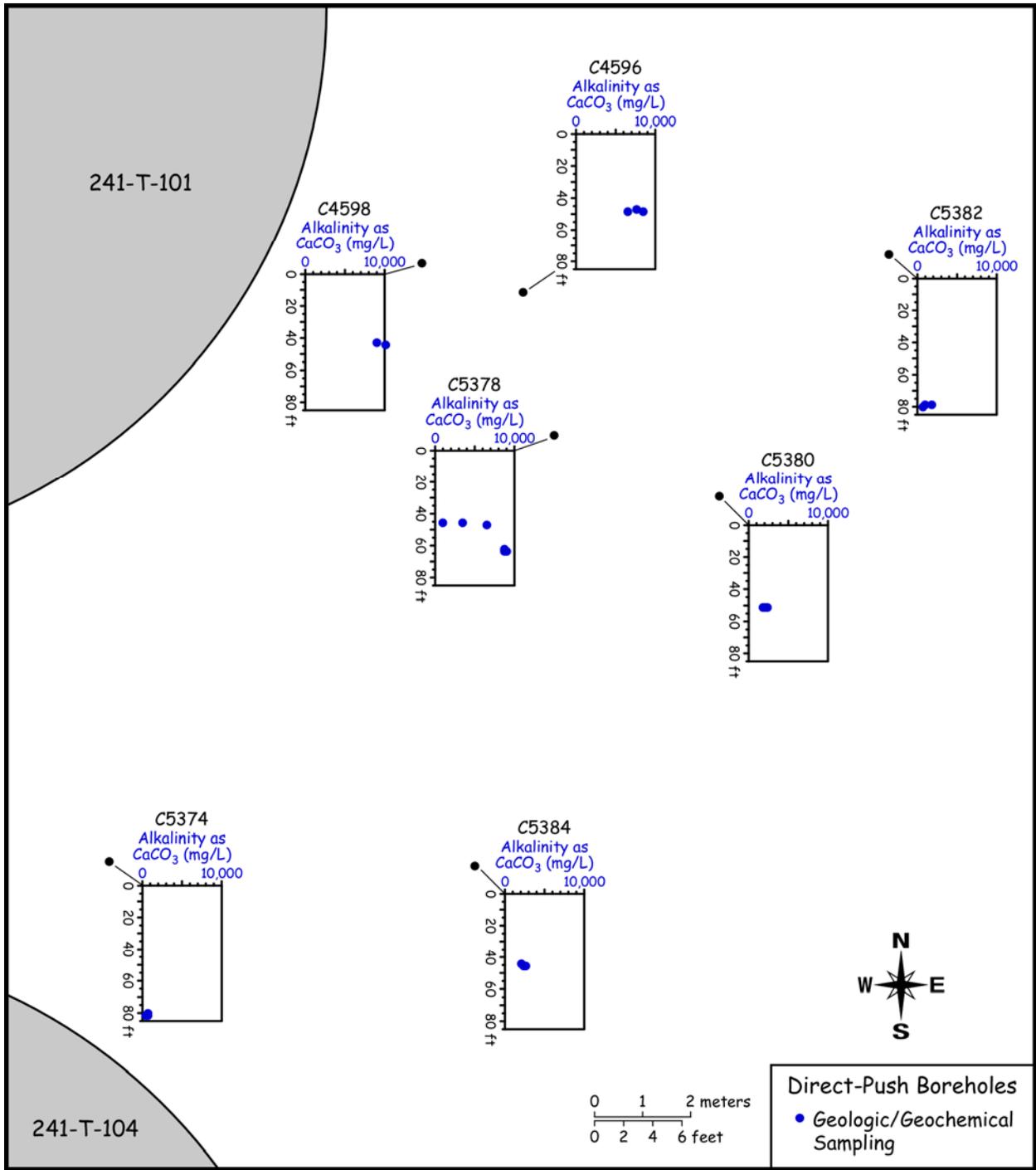
Sample ID	Probe Hole ID	Mid-Depth ft bgs	Calcium meq/L	Potassium meq/L	Magnesium meq/L	Sodium meq/L
B1KC35A	C4598	43.8	5.76E-01	(1.64E+00)	(1.67E-01)	1.93E+02
B1KC35B	C4598	43.3	6.38E-01	(2.14E+00)	(1.95E-01)	1.84E+02
B1KC36A	C4596	48.3	6.69E-01	(8.31E-01)	(2.51E-01)	1.22E+02
B1KC36B	C4596	47.8	1.12E+00	(1.03E+00)	(1.77E-01)	1.53E+02
B1KC36C	C4596	47.3	5.71E-01	(9.54E-01)	(1.39E-01)	1.36E+02
B1KC37A	C5378	46.3	1.40E+00	(1.76E+00)	(6.20E-01)	1.10E+02
B1KC37B	C5378	45.8	5.96E-01	(8.25E-01)	(2.22E-01)	5.48E+01
B1KC37C	C5378	45.3	7.64E-01	(7.07E-01)	3.93E-01	1.51E+01
B1KC38A	C5378	63.3	6.28E-01	(9.32E-01)	(1.03E-01)	1.60E+02
B1KC38B	C5378	62.8	5.48E-01	(7.96E-01)	(9.40E-02)	1.67E+02
B1KC38C	C5378	62.3	8.32E-01	(9.10E-01)	(1.30E-01)	1.70E+02
B1KC39A	C5384	45.3	2.83E+00	(2.08E+00)	1.16E+00	3.88E+01
B1KC39B	C5384	44.8	2.48E+00	(1.66E+00)	1.02E+00	3.16E+01
B1KC39C	C5384	44.3	3.03E+00	(1.97E+00)	1.31E+00	2.91E+01
B1KC40A	C5374	81.3	3.17E+01	1.39E+00	1.14E+01	1.02E+01
B1KC40B	C5374	80.8	2.52E+01	1.18E+00	9.19E+00	7.68E+00
B1KC40C	C5374	80.3	3.54E+01	1.92E+00	1.40E+01	7.79E+00
B1LB07A	C5382	79.3	3.32E+00	(5.71E-01)	1.21E+00	5.74E+00
B1LB07B	C5382	78.8	3.68E+00	(7.56E-01)	1.30E+00	8.58E+00
B1LB07C	C5382	78.3	6.31E+00	(1.68E+00)	2.31E+00	1.97E+01
B1LB08A	C5380	51.3	5.88E-01	(1.24E+00)	(1.71E-01)	3.18E+01
B1LB08B	C5380	50.8	5.04E-01	(1.33E+00)	(1.47E-01)	2.93E+01
B1LB08C	C5380	50.3	6.49E-01	(1.37E+00)	(2.48E-01)	3.34E+01

Parentheses indicate reported value was less than the limit of quantification for the analysis.

**Table 4.24.** Calculated Pore Water Mobile Metal Concentrations of Key Contaminants of Concern in the T Tank Farm Direct Push Core and Grab Samples

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Technetium-99 pCi/L	Uranium-238 µg/L	Chromium-52 µg/L	Molybdenum-95 µg/L
B1KC35A	C4598	43.8	<b>3.22E+04</b>	2.77E+03	2.93E+02	7.69E+02
B1KC35B	C4598	43.3	<b>4.08E+04</b>	3.26E+03	1.51E+02	5.15E+03
B1KC36A	C4596	48.3	<b>7.64E+03</b>	4.76E+02	5.72E+02	1.07E+03
B1KC36B	C4596	47.8	<b>7.02E+03</b>	3.87E+02	8.24E+02	8.18E+02
B1KC36C	C4596	47.3	<b>1.30E+04</b>	3.64E+02	1.80E+02	6.83E+02
B1KC37A	C5378	46.3	<b>3.82E+03</b>	6.99E+02	3.05E+02	9.69E+02
B1KC37B	C5378	45.8	<b>2.02E+03</b>	3.28E+02	2.47E+02	4.82E+02
B1KC37C	C5378	45.3	4.69E+02	2.33E+01	1.76E+02	6.58E+02
B1KC38A	C5378	63.3	<b>4.36E+04</b>	2.06E+03	1.19E+03	3.84E+02
B1KC38B	C5378	62.8	<b>2.69E+04</b>	2.24E+03	1.44E+03	5.85E+02
B1KC38C	C5378	62.3	<b>2.17E+04</b>	2.82E+03	1.27E+03	1.45E+03
B1KC39A	C5384	45.3	<9.62E+02	5.81E+01	(4.37E+01)	6.08E+02
B1KC39B	C5384	44.8	<7.63E+02	5.44E+01	(2.77E+01)	5.36E+02
B1KC39C	C5384	44.3	(3.34E+02)	3.47E+01	(2.31E+01)	2.74E+03
B1KC40A	C5374	81.3	<b>4.77E+05</b>	1.26E+01	2.34E+04	1.08E+02
B1KC40B	C5374	80.8	<b>4.36E+05</b>	1.02E+01	2.16E+04	8.35E+01
B1KC40C	C5374	80.3	<b>1.17E+05</b>	1.11E+01	6.45E+02	4.66E+02
B1LB07A	C5382	79.3	4.96E+02	1.63E+01	(1.77E+01)	3.22E+02
B1LB07B	C5382	78.8	1.89E+02	2.33E+01	(2.07E+01)	5.79E+02
B1LB07C	C5382	78.3	<5.70E+02	3.92E+01	(1.10E+01)	1.10E+03
B1LB08A	C5380	51.3	(2.10E+02)	1.50E+02	(2.05E+01)	8.77E+02
B1LB08B	C5380	50.8	3.11E+02	1.84E+02	(2.79E+01)	8.86E+02
B1LB08C	C5380	50.3	7.95E+02	1.61E+02	(2.68E+01)	1.31E+03

Bold values denote elevated concentrations.  
 Parentheses indicate reported value was less than the limit of quantification for the analysis.  
 Less than symbols indicate the instrument returned a negative value.



2007/DCL/T/012 (05/10)

**Figure 4.16.** 1:1 Sediment:Water-Extractable Alkalinity Data from the T Tank Farm Direct Push Samples

#### 4.2.4 8 M Nitric Acid-Extractable Amounts of Selected Elements in the T Tank Farm Direct Push Sediments

The same cores and grab samples that were characterized for water-leachable constituents were also characterized to see how much of the various constituents could be extracted with hot 8 M nitric acid. A comparison between the quantities that were acid extractable with those that are water-extractable often indicates the relative mobility of a given constituent and can sometimes differentiate man-disposed from naturally occurring constituents. The acid extractable concentrations are shown in Tables 4.25 through Table 4.27. For a majority of the constituents, there were no significantly elevated acid-extractable values from the T Tank Farm direct push sediments with the exception of technetium-99 and possibly small amounts of uranium-238 in a few of the samples. Quantifiable concentrations of acid extractable technetium-99 were detected in probe holes C4598, C4596, C5378, and C5374. Furthermore, when these concentrations were compared to the water-extractable technetium-99 concentrations, it was found that in most cases the amount of technetium-99 that was acid extractable was significantly higher. The difference in measured technetium-99 values between the acid leaches and water extracts ranged from a low of 124% for sample B1KC40A (probe hole C5374) to a high of 2,700% for sample B1KC36A (probe hole C4596). In previous borehole reports, the acid-leachable technetium-99 has been considered to be less valid than the water-extractable technetium-99 data, and as such, has been reported as qualitative. However, this trend, in which acid-leachable concentrations of technetium-99 are significantly higher than water-extractable technetium-99 concentrations from separate aliquots from the same homogenized sample, has occurred in many of the contaminated boreholes measured as part of the Single Shell Tank Vadose Zone Project, as well as in many of the residual tank sludge samples analyzed as part of the Geochemical Testing and Residual Tank Waste Model Development Project. A current hypothesis is that some of the technetium-99 is being sequestered with iron oxides that result from the interaction of caustic tank waste with the vadose zone sediment or tank sludge. From a long-term risk standpoint, it is imperative to quantify the total concentration of technetium-99 present in these samples; therefore, additional analyses were performed (presented in Section 4.3) in order to determine if these elevated values of technetium-99 were real, or just artifacts of analysis.

Three of the acid extracts contained approximately 2 µg/g uranium-238. The three sediments were collected from probe holes C4598 and C5378, respectively. Although Hanford sediment contains 3-5 µg/g natural uranium, it is doubtful the uranium-238 measured in these three samples was solely natural uranium. Natural uranium minerals present in Hanford sediments are very recalcitrant to leaching; generally less than 5% of the uranium present in the minerals can be leached using 8M nitric acid. Therefore, it appears that trace amounts of process uranium are present in a few of the direct push sediment samples collected near tank 241-T-101.

**Table 4.25.** Acid-Extractable Cations in the T Tank Farm Direct Push Core and Grab Samples  
( $\mu\text{g/g}$  dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Calcium $\mu\text{g/g}$	Potassium $\mu\text{g/g}$	Magnesium $\mu\text{g/g}$	Strontium $\mu\text{g/g}$
B1KC35A	C4598	43.8	8.56E+03	1.10E+03	5.42E+03	3.62E+01
B1KC35B	C4598	43.3	9.08E+03	1.21E+03	5.38E+03	4.14E+01
B1KC36A	C4596	48.3	9.10E+03	1.23E+03	6.14E+03	4.10E+01
B1KC36B	C4596	47.8	8.16E+03	1.01E+03	5.55E+03	3.45E+01
B1KC36C	C4596	47.3	7.66E+03	9.79E+02	5.41E+03	3.56E+01
B1KC37A	C5378	46.3	8.32E+03	8.23E+02	4.91E+03	3.38E+01
B1KC37B	C5378	45.8	7.62E+03	9.14E+02	5.19E+03	3.43E+01
B1KC37C	C5378	45.3	1.07E+04	1.81E+03	6.79E+03	4.34E+01
B1KC38A	C5378	63.3	9.62E+03	7.04E+02	4.85E+03	3.44E+01
B1KC38B	C5378	62.8	1.04E+04	6.67E+02	4.71E+03	3.50E+01
B1KC38C	C5378	62.3	1.06E+04	6.47E+02	4.40E+03	4.21E+01
B1KC39A	C5384	45.3	8.55E+03	9.50E+02	5.45E+03	3.68E+01
B1KC39B	C5384	44.8	8.58E+03	9.83E+02	5.18E+03	3.47E+01
B1KC39C	C5384	44.3	9.10E+03	9.62E+02	5.71E+03	4.00E+01
B1KC40A	C5374	81.3	1.41E+04	2.03E+03	8.91E+03	5.07E+01
B1KC40B	C5374	80.8	1.29E+04	1.62E+03	7.84E+03	4.66E+01
B1KC40C	C5374	80.3	1.33E+04	1.56E+03	7.51E+03	4.89E+01
B1LB07A	C5382	79.3	1.48E+04	1.70E+03	7.75E+03	4.65E+01
B1LB07B	C5382	78.8	2.23E+04	1.59E+03	7.90E+03	6.12E+01
B1LB07C	C5382	78.3	1.37E+04	7.51E+02	5.31E+03	4.37E+01
B1LB08A	C5380	51.3	9.58E+03	1.04E+03	5.51E+03	3.57E+01
B1LB08B	C5380	50.8	8.64E+03	1.03E+03	5.50E+03	3.41E+01
B1LB08C	C5380	50.3	8.15E+03	1.08E+03	5.25E+03	3.01E+01

**Table 4.26.** Acid-Leachable Cations in the T Tank Farm Core Samples ( $\mu\text{g/g}$  dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Aluminum $\mu\text{g/g}$	Iron $\mu\text{g/g}$	Phosphorus $\mu\text{g/g}$	Chromium $\mu\text{g/g}$
B1KC35A	C4598	43.8	9.56E+03	2.03E+04	6.53E+02	2.23E+01
B1KC35B	C4598	43.3	9.46E+03	2.57E+04	7.73E+02	7.68E+01
B1KC36A	C4596	48.3	9.54E+03	1.85E+04	6.38E+02	2.14E+01
B1KC36B	C4596	47.8	7.97E+03	1.72E+04	5.33E+02	2.29E+01
B1KC36C	C4596	47.3	8.18E+03	1.84E+04	5.91E+02	2.58E+01
B1KC37A	C5378	46.3	7.08E+03	1.69E+04	5.96E+02	1.20E+01
B1KC37B	C5378	45.8	7.72E+03	1.88E+04	6.73E+02	1.41E+01
B1KC37C	C5378	45.3	1.10E+04	2.09E+04	5.71E+02	2.97E+01
B1KC38A	C5378	63.3	7.87E+03	2.14E+04	8.31E+02	1.85E+01
B1KC38B	C5378	62.8	7.38E+03	2.24E+04	9.59E+02	1.70E+01
B1KC38C	C5378	62.3	7.37E+03	1.98E+04	8.89E+02	2.00E+01
B1KC39A	C5384	45.3	7.58E+03	1.72E+04	6.02E+02	1.68E+01
B1KC39B	C5384	44.8	7.39E+03	1.71E+04	5.81E+02	1.54E+01
B1KC39C	C5384	44.3	8.97E+03	2.05E+04	6.89E+02	2.34E+01
B1KC40A	C5374	81.3	1.87E+04	2.41E+04	6.64E+02	3.02E+01
B1KC40B	C5374	80.8	1.24E+04	1.93E+04	7.78E+02	3.27E+01
B1KC40C	C5374	80.3	1.16E+04	1.85E+04	8.45E+02	4.33E+01
B1LB07A	C5382	79.3	1.18E+04	1.91E+04	6.90E+02	2.04E+01
B1LB07B	C5382	78.8	1.23E+04	2.06E+04	6.97E+02	2.59E+01
B1LB07C	C5382	78.3	7.38E+03	1.96E+04	7.31E+02	1.58E+01
B1LB08A	C5380	51.3	8.70E+03	2.21E+04	8.56E+02	2.92E+01
B1LB08B	C5380	50.8	7.88E+03	1.80E+04	6.05E+02	2.90E+01
B1LB08C	C5380	50.3	7.10E+03	1.60E+04	5.78E+02	3.05E+01
Indicates the information was not determined for the sample.						

**Table 4.27.** Acid-Extractable Mobile Metals in the T Tank Farm Direct Push Core and Grab Samples (µg/g dry sediment)

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Technetium-99 pCi/g	Uranium-238 µg/g	Molybdenum-95 µg/g	Ruthenium-101 µg/g	Ruthenium-102 µg/g
B1KC35A	C4598	43.8	<b>1.56E+01</b>	2.52E+00	7.85E-01	(1.03E-02)	(3.25E-02)
B1KC35B	C4598	43.3	<b>1.47E+01</b>	2.07E+00	8.94E+00	(1.29E-02)	(3.59E-02)
B1KC36A	C4596	48.3	<b>1.32E+01</b>	7.67E-01	3.59E-01	(2.45E-02)	(4.15E-02)
B1KC36B	C4596	47.8	(6.93E+00)	5.38E-01	4.12E-01	(7.19E-03)	(3.29E-02)
B1KC36C	C4596	47.3	(5.38E+00)	5.58E-01	4.80E-01	(1.61E-02)	(3.46E-02)
B1KC37A	C5378	46.3	(2.64E+00)	5.22E-01	3.36E-01	(5.47E-03)	(3.28E-02)
B1KC37B	C5378	45.8	(3.15E+00)	6.71E-01	3.77E-01	(1.26E-02)	(3.47E-02)
B1KC37C	C5378	45.3	(6.59E+00)	2.06E+00	9.06E-01	(3.48E-02)	(5.21E-02)
B1KC38A	C5378	63.3	(5.80E+00)	5.85E-01	3.94E-01	(6.77E-03)	(3.40E-02)
B1KC38B	C5378	62.8	(4.45E+00)	6.22E-01	3.66E-01	(7.88E-03)	(3.14E-02)
B1KC38C	C5378	62.3	<b>8.30E+00</b>	8.53E-01	5.57E-01	(2.15E-02)	(4.35E-02)
B1KC39A	C5384	45.3	(8.66E-01)	4.61E-01	2.91E-01	<5.06E-02	(2.99E-02)
B1KC39B	C5384	44.8	<1.04E+01	4.42E-01	(2.98E-01)	(9.82E-04)	(2.88E-02)
B1KC39C	C5384	44.3	(5.31E-01)	4.63E-01	7.55E-01	<4.97E-02	(2.90E-02)
B1KC40A	C5374	81.3	<b>9.77E+01</b>	8.80E-01	3.07E-01	(1.48E-02)	(5.07E-02)
B1KC40B	C5374	80.8	<b>1.00E+02</b>	6.97E-01	3.59E-01	(1.61E-02)	(4.32E-02)
B1KC40C	C5374	80.3	<b>1.34E+02</b>	7.89E-01	6.83E-01	(2.77E-02)	(5.38E-02)
B1LB07A	C5382	79.3	(2.70E+00)	6.43E-01	3.56E-01	(9.71E-04)	(4.28E-02)
B1LB07B	C5382	78.8	(8.63E-01)	6.90E-01	5.08E-01	(5.19E-05)	(5.29E-02)
B1LB07C	C5382	78.3	(8.00E-01)	4.45E-01	7.56E-01	<5.49E-02	(3.27E-02)
B1LB08A	C5380	51.3	(4.01E+00)	6.02E-01	5.35E-01	(2.22E-02)	(3.43E-02)
B1LB08B	C5380	50.8	(5.93E+00)	7.65E-01	5.31E-01	(1.39E-02)	(2.96E-02)
B1LB08C	C5380	50.3	(8.83E+00)	5.21E-01	7.83E-01	(1.75E-02)	(3.05E-02)

Bold values denote elevated concentrations.  
 Parentheses indicate reported value is less than the limit of quantification for the analysis.  
 Less than symbol indicates the instrument returned a negative value.

Comparison of the water to acid-extractable quantities of each constituent was performed by taking the data in Tables 4.19 through 4.21 and dividing them by the data in Tables 4.25 through 4.27. The data are not presented herein, but show that less than 0.1% of the acid-extractable quantities of the following elements were water leachable: aluminum, barium, cobalt, iron, manganese, titanium, and zirconium. Less than 1% of the acid-extractable quantities of the following elements were water leachable: calcium, copper, magnesium, nickel, phosphorous as phosphate, potassium, and zinc. Less than 5% of the acid-extractable molybdenum, silver, and strontium were water-extractable. Less than 10% of the acid-extractable chromium was water-extractable. Finally, less than 30% of the acid-extractable uranium was water-extractable. These results imply that some of the sediments collected as part of the T Tank Farm direct push campaign contain chromium and uranium contamination resulting from Hanford waste processes. These results imply that some of the sediments collected as part of the T farm direct push campaign contain chromium and uranium contamination resulting from Hanford waste processes.

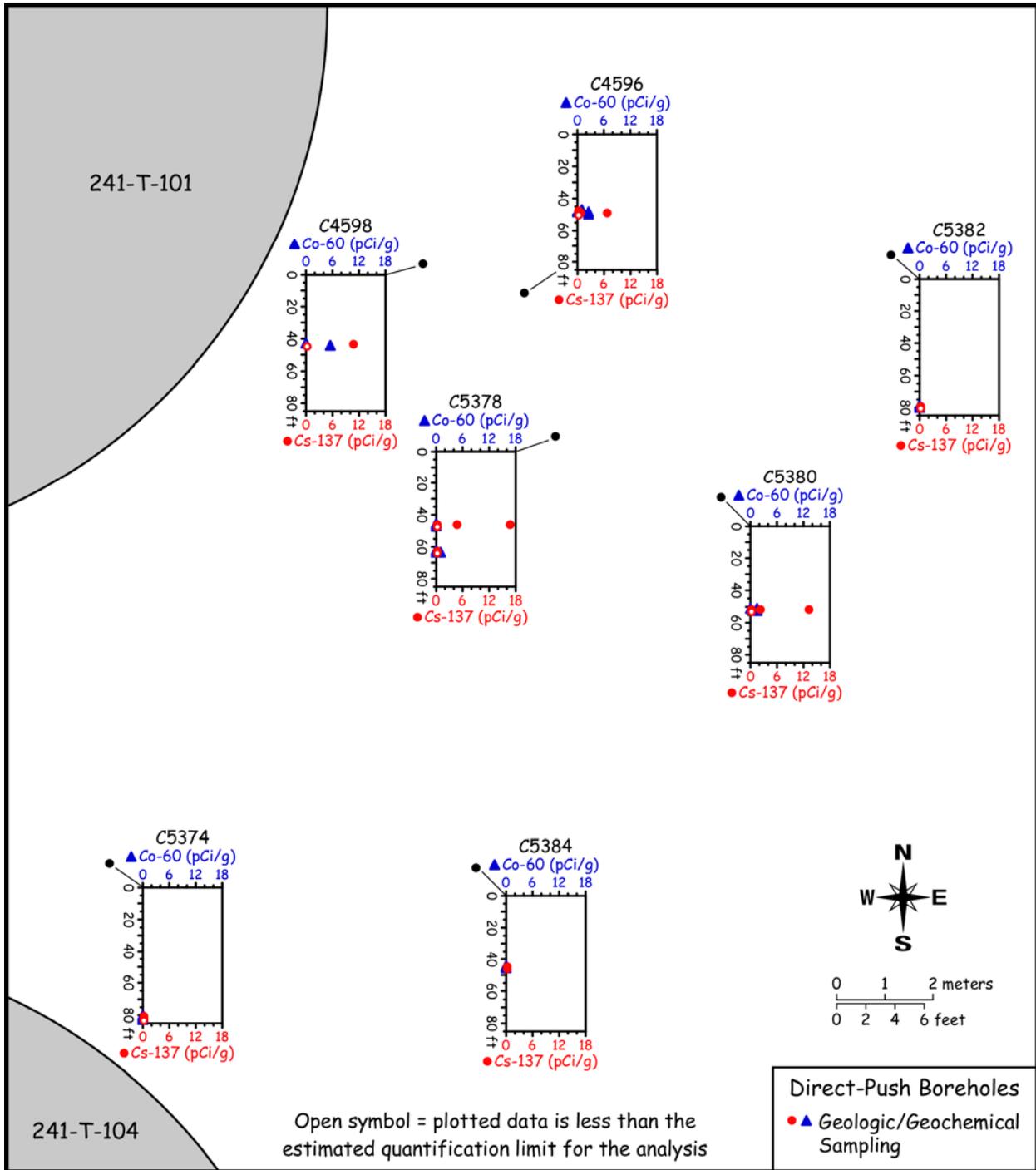
#### 4.2.5 Radionuclide Content in Vadose Zone Sediment from the TY Tank Farm Direct Push Holes

Data from the gamma energy analysis of the samples are shown in Table 4.28 and Figures 4.17 and 4.18. The direct measurement of sediments for gamma-emitting radionuclides showed that they contained natural potassium-40, the activation product cobalt-60, and the fission product isotopes cesium-137, europium-152, europium-154, and europium-155. The samples that contained the man-made gamma-emitting radionuclides were from the four probe holes emplaced closest to tank 241-T-101. For comparison purposes, the highest europium-154 activity measured in these samples was 139 pCi/g vs. 2000 pCi/g at the 241-T-106 borehole (C4104) (Serne et al. 2004b). As much as 40 pCi/g cesium-137 was measured in borehole C4104 (Serne et al. 2004b), while the peak activity measured as part of this study was 16.8 pCi/g. Given the mixed-depth sampling frequency that was performed during the direct push campaign, it is difficult to say anything about the relative mobility of the radionuclides; however, it appears that they may have migrated southeast from tank 241-T-101.

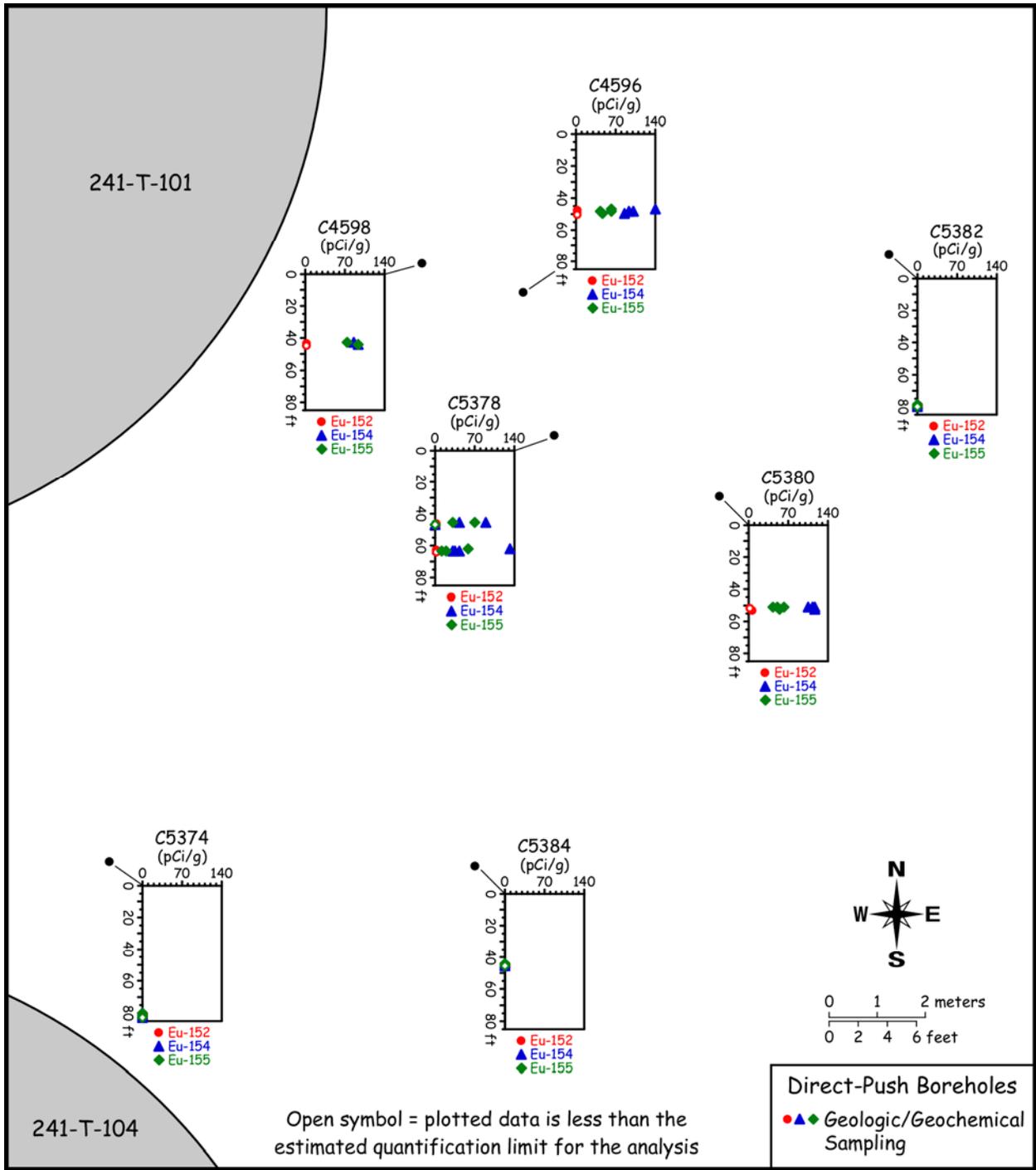
**Table 4.28.** Gamma-Emitting Radionuclides in the T Tank Farm Direct Push Sediments

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Potassium -40 pCi/g	Cobalt -60 pCi/g	Cesium -137 pCi/g	Europium-152 pCi/g	Europium-154 pCi/g	Europium-155 pCi/g
B1KC35A	C4598	43.8	1.55E+01	5.49E+00	<3.20E+00	<2.97E+00	9.41E+01	9.21E+01
B1KC35B	C4598	43.3	<1.08E+01	<1.56E+00	1.08E+01	<4.59E+00	8.41E+01	7.32E+01
B1KC36	C4596	48.9	1.79E+01	2.52E+00	<1.45E+00	<2.66E+00	8.70E+01	4.71E+01
B1KC36A	C4596	48.3	1.68E+01	2.71E+00	6.37E+00	<2.93E+00	1.02E+02	6.42E+01
B1KC36B	C4596	47.8	<5.79E+00	<5.65E-01	7.93E-01	<2.27E+00	9.28E+01	4.19E+01
B1KC36C	C4596	47.3	1.57E+01	1.26E+00	<1.53E+00	2.33E+00	1.39E+02	6.39E+01
B1KC37A	C5378	46.3	1.93E+01	<4.91E-01	<4.45E-01	<1.56E+00	<9.25E-01	<1.39E+00
B1KC37B	C5378	45.8	<5.37E+00	<5.03E-01	4.47E+00	<1.84E+00	4.27E+01	3.24E+01
B1KC37C	C5378	45.3	<6.27E+00	<7.40E-01	1.68E+01	<2.56E+00	9.11E+01	6.88E+01
B1KC38	C5378	63.8	<6.86E+00	<5.31E-01	<7.09E-01	<1.87E+00	3.27E+01	1.34E+01
B1KC38A	C5378	63.3	<4.76E+00	<4.28E-01	<5.32E-01	<1.54E+00	3.38E+01	1.36E+01
B1KC38B	C5378	62.8	1.27E+01	8.66E-01	<7.96E-01	<1.86E+00	4.15E+01	2.12E+01
B1KC38C	C5378	62.3	<4.96E+00	<7.70E-01	<9.88E-01	<2.49E+00	1.33E+02	5.80E+01
B1KC39	C5384	45.8	1.62E+01	<2.16E-01	<2.94E-01	<1.08E+00	<6.08E-01	<1.03E+00
B1KC39A	C5384	45.3	<4.95E+00	<1.74E-01	<2.24E-01	<7.54E-01	<4.58E-01	<7.09E-01
B1KC39B	C5384	44.8	1.78E+01	<2.30E-01	<2.68E-01	<1.04E+00	<5.87E-01	<1.01E+00
B1KC39C	C5384	44.3	<4.75E+00	<1.69E-01	<1.85E-01	<6.55E-01	<4.14E-01	<6.51E-01
B1KC40	C5374	81.8	1.80E+01	<3.13E-01	<3.64E-01	<1.42E+00	<7.96E-01	<1.34E+00
B1KC40A	C5374	81.3	<5.90E+00	<2.61E-01	<2.73E-01	<9.11E-01	<5.44E-01	<9.19E-01
B1KC40B	C5374	80.8	1.55E+01	<2.78E-01	<3.16E-01	<1.30E+00	<7.32E-01	<1.29E+00
B1KC40C	C5374	80.3	<5.68E+00	<2.48E-01	<2.65E-01	<9.74E-01	<5.69E-01	<9.52E-01
B1LB07A	C5382	79.3	1.96E+01	<2.50E-01	<3.23E-01	<1.29E+00	<7.21E-01	<1.25E+00
B1LB07B	C5382	78.8	<5.74E+00	<2.01E-01	<2.66E-01	<9.09E-01	<5.64E-01	<8.59E-01
B1LB07C	C5382	78.3	1.36E+01	<2.04E-01	<2.60E-01	<9.63E-01	<5.43E-01	<9.12E-01
B1LB08	C5380	51.8	1.37E+01	1.33E+00	<1.30E+00	2.95E+00	1.16E+02	5.61E+01
B1LB08A	C5380	51.3	<5.25E+00	<5.74E-01	1.30E+01	<2.28E+00	1.05E+02	4.32E+01
B1LB08B	C5380	50.8	<5.94E+00	<6.11E-01	1.98E+00	<2.63E+00	1.16E+02	5.07E+01
B1LB08C	C5380	50.3	1.73E+01	1.44E+00	<1.66E+00	<2.87E+00	1.15E+02	6.19E+01

Shaded cells indicate grab samples.  
 < indicates the analyte was not detected in the sample, the MDA has been reported.



**Figure 4.17.** Gamma Energy Analysis Data (Cobalt-60 and Cesium-137) from the T Tank Farm Direct Push Samples



**Figure 4.18.** Gamma Energy Analysis Data (Europium Isotopes) from the T Tank Farm Direct Push Samples

#### 4.2.6 Total Carbon, Calcium Carbonate, and Organic Carbon Content of Vadose Zone Sediment from the TY Tank Farm Direct Push Holes

Data from the total carbon, inorganic carbon, and organic carbon (calculated by difference) contents of the T Tank Farm direct push sediments are shown in Table 4.29. The inorganic carbon was converted to the equivalent calcium carbonate content. In general, the sediments were low in organic carbon (<0.15% by weight), which is typical of Hanford Site sediments. Inorganic carbon, as CaCO<sub>3</sub>, was also present at concentrations that are typical for Hanford formation sediments (0.5 to 3.34 wt% as CaCO<sub>3</sub>) and compare well with other samples from uncontaminated locations (Serne et al. 2004a,b).

**Table 4.29.** Carbon Content of the T Tank Farm Vadose Zone Samples

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Total Carbon (%)	Inorganic Carbon (%)	Inorganic Carbon as CaCO <sub>3</sub> (%)	Organic Carbon (%)
B1KC35A	C4598	43.8	2.70E-01	1.78E-01	1.49E+00	8.62E-02
B1KC35B	C4598	43.3	2.58E-01	1.44E-01	1.20E+00	1.14E-01
B1KC36A	C4596	48.3	2.81E-01	1.66E-01	1.39E+00	1.14E-01
B1KC36B	C4596	47.8	2.42E-01	1.51E-01	1.26E+00	9.17E-02
B1KC36C	C4596	47.3	2.25E-01	1.30E-01	1.09E+00	9.41E-02
B1KC37A	C5378	46.3	2.70E-01	1.97E-01	1.65E+00	7.24E-02
B1KC37B	C5378	45.8	2.30E-01	1.51E-01	1.26E+00	7.91E-02
B1KC37C	C5378	45.3	3.06E-01	2.40E-01	2.00E+00	6.63E-02
B1KC38A	C5378	63.3	1.82E-01	8.07E-02	6.73E-01	1.01E-01
B1KC38B	C5378	62.8	2.49E-01	1.71E-01	1.43E+00	7.78E-02
B1KC38C	C5378	62.3	2.46E-01	1.83E-01	1.52E+00	6.31E-02
B1KC39A	C5384	45.3	3.15E-01	2.42E-01	2.01E+00	7.30E-02
B1KC39B	C5384	44.8	2.46E-01	1.78E-01	1.49E+00	6.77E-02
B1KC39C	C5384	44.3	2.69E-01	1.88E-01	1.56E+00	8.13E-02
B1KC40A	C5374	81.3	3.95E-01	3.66E-01	3.05E+00	2.88E-02
B1KC40B	C5374	80.8	3.86E-01	3.40E-01	2.83E+00	4.65E-02
B1KC40C	C5374	80.3	3.97E-01	3.60E-01	3.00E+00	3.78E-02
B1LB07A	C5382	79.3	4.47E-01	4.01E-01	3.34E+00	4.63E-02
B1LB07B	C5382	78.8	4.25E-01	3.77E-01	3.14E+00	4.79E-02
B1LB07C	C5382	78.3	2.51E-01	2.15E-01	1.79E+00	3.66E-02
B1LB08A	C5380	51.3	1.91E-01	1.31E-01	1.09E+00	6.05E-02
B1LB08B	C5380	50.8	2.08E-01	1.43E-01	1.19E+00	6.55E-02
B1LB08C	C5380	50.3	2.70E-01	1.88E-01	1.57E+00	8.18E-02

#### 4.3 Tier II Sample Investigations

Upon completion of the Tier I testing, a subset of samples from the T Tank Farm direct push sampling campaign were subjected to Tier II analyses or interpretations. These additional efforts were performed to 1) further investigate the discrepancy between water-extractable and acid-leachable technetium-99 in the T direct push samples, 2) see if ruthenium isotopic analyses could be used to identify contaminant source terms, and 3) see if chloride data generated during the 1:1 sediment:water extraction process could be used to investigate the effect of the tank drip line on recharge. Results from Tier II tests and analyses are presented in the following sections.

### 4.3.1 Technetium-99 Extraction and Analysis

The 1:1 sediment:water-extractable Tier II technetium-99 data pre- and post-resin treatment are presented in Tables 4.30 and 4.31 in units of  $\mu\text{g/g}$ . The data for the triplicate samples have been averaged, and the percent relative standard deviation (%RSD), based on one standard deviation, for the triplicate samples has been calculated. Also contained in the tables are the total technetium-99 recoveries for a blank spike and two matrix spikes that were prepared with each sample set. The %RSDs for the 1:1 sediment:water extract samples that were not resin-treated (Table 4.30) were excellent. For the four sample sets that contained technetium-99 in excess of the limit of quantification for analysis, the %RSDs ranged from 0.759 to 2.30%. As expected, the background sediment collected from the Integrated Low Activity Waste (ILAW) borehole (C3177) did not contain a quantifiable amount of technetium-99. Spike recoveries performed as quality control for this data set had mixed results. Generally, recoveries in excess of 85% are considered acceptable, and two of the samples met this criterion: the blank spike and the background sediment matrix spike. However, the direct push sample matrix spike had a total recovery of only 62.8%. The low recovery associated with this sample is surprising given the overall success of the two other spiked samples. The samples underwent minimal processing after being spiked; therefore, the most likely cause of the low technetium-99 recovery in the direct push matrix spike was due to improper addition of the spike. Although the data are reported in different units herein (mass instead of activity), comparison of the results in Table 4.30 to those generated during the Tier I sediment:water extracts also yielded mixed results. For two of the three samples where comparative data was available, the agreement was excellent; the relative percent difference between data sets was 1.96% for sample B1KC40A and 9.97% for sample B1KC40B. However, agreement for sample B1KC40C was poor, with a relative difference of 44%. Given the internal agreement between triplicate sediment:water extracts performed on sediment from B1KC40C during Tier II testing, it appears that the 44% difference in technetium-99 concentrations between the two data sets was a result of heterogeneity of the sample (the sample was mixed well prior to Tier II testing).

**Table 4.30.** Water-Extractable Technetium-99 Concentrations in the T Tank Farm Vadose Zone Samples

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Technetium-99 $\mu\text{g/g}$	Relative Standard Deviation (%)	Technetium-99 Recovery (%)
B1KC40	C5374	81.8	1.10E-03	2.30	NA
B1KC40A	C5374	81.3	4.57E-03	1.89	NA
B1KC40B	C5374	80.8	5.16E-03	1.42	NA
B1KC40C	C5374	80.3	2.31E-03	0.759	NA
B1KC40-MS	C5382	79.3	NA	NA	62.8
C3177	C5382	NA	(4.92E-05)	79.5	NA
C3177-MS	C5382	NA	NA	NA	90.1
Blank Spike	NA	NA	NA	NA	86.6

Shaded cells indicate grab sample.  
 Parentheses indicate the reported value is below the limit of quantification for the analysis.  
 NA indicates not applicable.

**Table 4.31.** Water-Extractable Technetium-99 Concentrations in the T Tank Farm Vadose Zone Samples After TEVA Resin Treatment

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Technetium-99 $\mu\text{g/g}$	Relative Standard Deviation (%)	Technetium-99 Recovery (%)
B1KC40	C5374	81.8	9.92E-04	2.57	NA
B1KC40A	C5374	81.3	4.64E-03	4.08	NA
B1KC40B	C5374	80.8	5.04E-03	2.60	NA
B1KC40C	C5374	80.3	2.15E-03	1.09	NA
B1KC40-MS	C5382	79.3	NA	NA	62.2
C3177	C5382	NA	<1.42E-06	NA	NA
C3177-MS	C5382	NA	NA	NA	90.0
Blank Spike	NA	NA	NA	NA	84.9

Shaded cells indicate grab sample.  
MS indicates matrix spike.  
Less than values indicate the instrument returned a negative value.  
NA indicates not applicable.

The %RSDs for the 1:1 sediment:water extract samples that were treated with TEVA® resin (Table 4.31) were also excellent. For the four sample sets that contained technetium-99 in excess of the limit of quantification for analysis, the %RSDs ranged from 1.09 to 4.08%. Consistent with the non-resin-treated samples, the background sediment (C3177) did not contain a quantifiable amount of technetium-99. Spike recoveries for the aliquots of sample that were treated with the resin had the same mixed results as the non-treated aliquots. Once again, the blank spike and the background sediment matrix spike both had recoveries of 85% or greater. However, the direct push sample matrix spike had a total recovery of only 62.2% (which was identical to the matrix spike recovery of 62.8% for the non-treated samples). The fact that this sample had low recovery through two analytical processes lends support to the hypothesis that an inappropriate amount of technetium-99 was initially spiked into the sample prior to processing via the 1:1 sediment:water extraction technique (i.e. the laboratory technician spiked the sample with less technetium-99 than was recorded on their bench sheets). was initially spiked into the sample prior to processing via the 1:1 sediment:water extraction technique. Comparison of the data in Table 4.31 to the non-resin-treated data in Table 4.30 showed excellent agreement between the analyses. Relative differences between the two data sets for average concentrations of the samples from probe hole C5374 (as measured via the three replicate samples) ranged from 1.42% to 9.97%. These results indicate that technetium-99 reported in the 1:1 sediment:water extracts is indeed technetium-99 (i.e., a matrix interference is not present in these samples). These results show that the additional step of treating the samples with TEVA® resin is not necessary when quantifying technetium-99 in water extract samples.

The 8M nitric acid extractable Tier II technetium-99 data pre- and post-resin treatment are presented in Tables 4.32 and 4.33 in units of  $\mu\text{g/g}$ . Once again, the data for the triplicate samples has been averaged, and the percent relative standard deviation (%RSD) based on one standard deviation for the triplicate samples has been calculated. Also contained in the tables are the total technetium-99 recoveries for the blank spike and two matrix spikes that were prepared with each sample set. The %RSDs for the 8M nitric acid extract samples that were not resin-treated (Table 4.32) were acceptable, although they weren't as good as those for the water extract samples. For the three sample sets that contained technetium-99 in excess of the limit of quantification for analysis, the %RSDs ranged from 6.39% to 12.5%. As expected, the background sediment collected from the Integrated Low Activity Waste (ILAW)

**Table 4.32.** Acid Extractable Technetium-99 Concentrations in the T Tank Farm Vadose Zone

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Technetium-99 $\mu\text{g/g}$	Relative Standard Deviation (%)	Technetium-99 Recovery (%)
B1KC40	C5374	81.8	(1.71E-03)	4.27	NA
B1KC40A	C5374	81.3	5.50E-03	6.73	NA
B1KC40B	C5374	80.8	5.93E-03	6.39	NA
B1KC40C	C5374	80.3	5.93E-03	12.5	NA
B1KC40-MS	C5382	79.3	NA	NA	88.7
C3177	C5382	NA	(1.15E-04)	40.5	NA
C3177-MS	C5382	NA	NA	NA	89.5
Blank Spike	NA	NA	NA	NA	87.5

Shaded cells indicate grab sample.  
MS indicates matrix spike.  
Parentheses indicate the reported value is below the limit of quantification for the analysis.  
NA indicates not applicable.

**Table 4.33.** Acid Extractable Technetium-99 Concentrations in the T Tank Farm Vadose Zone After Resin Treatment

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Technetium-99 $\mu\text{g/g}$	Relative Standard Deviation (%)	Technetium-99 Recovery (%)
B1KC40	C5374	81.8	(1.38E-03)	8.92	NA
B1KC40A	C5374	81.3	4.81E-03	3.44	NA
B1KC40B	C5374	80.8	5.35E-03	6.15	NA
B1KC40C	C5374	80.3	5.34E-03	12.9	NA
B1KC40-MS	C5382	79.3	NA	NA	46.7
C3177	C5382	NA	(1.45E-05)	52.2	NA
C3177-MS	C5382	NA	NA	NA	72.8
Blank Spike	NA	NA	NA	NA	80.5

Shaded cells indicate grab sample.  
MS indicates matrix spike.  
Parentheses indicate the reported value is below the limit of quantification for the analysis.  
NA indicates not applicable.

borehole (C3177) did not contain a quantifiable amount of acid-extractable technetium-99. Spike recoveries performed as quality control for this data set worked quite well. All three spikes, the blank spike, the background sediment matrix spike, and the direct push sample matrix spike all had recoveries in excess of 85%. These results indicate that technetium-99 is stable throughout the 8M nitric acid extraction process. Although the data are reported in different units herein, comparison of the results in Table 4.32 to those generated during the Tier I 8M nitric acid extracts also yielded mixed results. For two of the three samples where comparative data was available, the agreement was excellent; the relative percent difference between data sets was 4.62% for sample B1KC40A and 0.338% for sample B1KC40B. However, agreement for sample B1KC40C was poor, with a relative difference of 28.6%. The fact that discrepancies arose between the water extract Tier I and Tier II data sets for this sample, combined with the differences measured here, implies that sample heterogeneity was the lead cause of the discrepancies.

The %RSDs for the 8M nitric acid extract samples that were treated with TEVA® resin (Table 4.33) were slightly better than those for the non-treated samples. For the three sample sets that contained technetium-99 in excess of the limit of quantification for analysis, the %RSDs ranged from 3.44% to 12.9%. Consistent with the non-resin-treated samples, the background sediment (C3177) did not contain

a quantifiable amount of technetium-99. Spike recoveries for the aliquots of sample that were treated with the resin were inadequate. None of the TEVA® resin-treated spikes had recoveries of 85% or greater. Additionally, the direct push matrix spike sample (B1KC40C-MS) only had a recovery of 46.7%. The best spike recovery for the resin-treated nitric acid extracts occurred in the blank spike, which had a total technetium-99 recovery of 80.5%. These results clearly indicate that technetium-99 was lost between the 8M nitric acid extraction step (which generated the data in Table 4.32) and analysis of the resin-treated samples. In other words, something that occurred during processing of the samples in preparation for the resin treatment step, or the resin treatment step itself, caused the poor recoveries measured with this data set. The two most probable steps that could have led to a deficiency in technetium-99 recoveries were heating of the samples to dryness once the 8M nitric acid extracts were complete (this step was performed to change the sample matrix prior to its addition to the TEVA columns), or fouling of the resin columns by the high concentrations of dissolved solids in the acid extract samples. Both of these potential issues could be corrected for through the addition of a tracer (such as technetium-95 m) to the extracts prior to processing them for resin treatment. Using this approach, recoveries for each sample could be measured, and the reported technetium-99 concentrations could be appropriately corrected for each sample.

Although there were issues with the total recovery of technetium-99 through the resin treatment process, the results of this test do allow for some conclusions to be drawn for the Tier II acid extract data (and subsequently to the Tier I acid extract data). Comparison of the acid extract data in Table 4.33 to the non-resin-treated data in Table 4.32 shows good agreement between the analyses. Relative differences between the two data sets for average concentrations of the samples from probe hole C5374 (as measured via the three replicate samples) ranged from 10.3% to 13.3% (the technetium-99 concentrations in the resin-treated acid extract samples were consistently lower than those in the untreated samples). There was exceptionally good agreement between the data sets given the low total recoveries measured after resin treatment of the samples. Additionally, it appears that a matrix effect is not the cause of the elevated technetium-99 in the acid extracts vs. the water extracts. These results imply that some credence should be given to the 8M acid extract technetium-99 data. However, before quantitative results are provided, the 8M nitric acid extracts should be taken through the resin treatment process again after the addition of a tracer to monitor recoveries through the treatment steps.

The microwave-digested Tier II technetium-99 results pre- and post-resin treatment are presented in Tables 4.34 and 4.35 in units of  $\mu\text{g/g}$ . Once again, the data for the triplicate samples has been averaged, and the percent relative standard deviation (%RSD), based on one standard deviation, for the triplicate samples has been calculated. Also contained in the tables are the total technetium-99 recoveries for the blank spike and two matrix spikes that were prepared with each sample set. The %RSDs for the microwave digests that were not resin-treated (Table 4.34) were not valid, given that technetium-99 was not measured above the limit of quantification for the analysis. Microwave digestion generates greater sample dilution due to a higher solution to solid ratio (100:1 vs. approximately 6:1 for the nitric acid extracts and 1:1 for the sediment:water extracts). On a positive note, spike recoveries performed as quality control for this data set worked quite well. All three spikes—the blank spike, the background sediment matrix spike, and the direct push sample matrix spike—had recoveries in excess of 85%. These results indicate that technetium-99 is stable throughout the microwave digestion process, but higher sample concentrations are necessary to alleviate detection limit issues associated with the technique. Given the lack of quantitative data, results in Table 4.34 cannot be compared with total technetium-99 concentrations measured via the other two extraction techniques.

**Table 4.34.** Microwave Digestible Technetium-99 Concentrations in the T Tank Farm Vadose Zone

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Technetium-99 µg/g	Relative Standard Deviation (%)	Technetium-99 Recovery (%)
B1KC40	C5374	81.8	(1.31E-03)	15.5	NA
B1KC40A	C5374	81.3	(3.63E-03)	46.0	NA
B1KC40B	C5374	80.8	(3.10E-03)	18.2	NA
B1KC40C	C5374	80.3	(5.27E-03)	63.2	NA
B1KC40-MS	C5382	79.3	NA	NA	91.7
C3177	C5382	NA	<2.18E-02	NA	NA
C3177-MS	C5382	NA	NA	NA	85.6
Blank Spike	NA	NA	NA	NA	86.5

Shaded cells indicate grab sample.  
MS indicates matrix spike.  
Parentheses indicate the reported value is below the limit of quantification for the analysis.  
Less than values indicate the instrument returned a negative value.  
NA indicates not applicable.

**Table 4.35.** Microwave Digestible Technetium-99 Concentrations in the T Tank Farm Vadose Zone After Resin Treatment

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Technetium-99 µg/g	Relative Standard Deviation (%)	Technetium-99 Recovery (%)
B1KC40	C5374	81.8	1.50E-03	12.1	NA
B1KC40A	C5374	81.3	4.15E-03	3.82	NA
B1KC40B	C5374	80.8	4.73E-03	28.5	NA
B1KC40C	C5374	80.3	6.76E-03	42.0	NA
B1KC40-MS	C5382	79.3	NA	NA	73.1
C3177	C5382	NA	<8.71E-05	NA	NA
C3177-MS	C5382	NA	NA	NA	86.5
Blank Spike	NA	NA	NA	NA	39.1

Less than values indicate the instrument returned a negative value.  
Shaded cells indicate grab sample.  
MS indicates matrix spike.  
NA indicates not applicable.

Treatment of the microwave-digested samples with TEVA® resin (Table 4.35) resulted in quantitative technetium-99 data for all of the direct push samples from probe hole C5374. However, the %RSDs for the microwave digested samples varied considerably. The %RSDs for the four direct push sample sets ranged from 15.5% to 63.2%. Consistent with the non-resin-treated samples, the background sediment (C3177) did not contain a quantifiable amount of technetium-99. Spike recoveries for the aliquots of sample that were treated with the resin were sporadic. One of the TEVA® resin-treated spikes (the background matrix spike) had a recovery of greater than 85%. The T Tank Farm direct push sample matrix spike had a recovery of 73.1 and ironically, the blank spike had the poorest recovery at just 39.1%. As with the acid extract data, these results clearly indicate that technetium-99 was lost between the microwave digestion step (which generated the data in Table 4.34) and analysis of the resin-treated samples. The same two steps that could have led to a deficiency in technetium-99 recoveries in the 8M nitric acid extracts are suspected as being the primary culprits with these poor recoveries on these samples as well. Again, both of these potential issues, heating of the samples to dryness or fouling of the resin

columns, could be accounted for through the addition of a tracer to the extracts prior to processing them for resin treatment. Using this approach, recoveries for each sample could be measured, and the reported technetium-99 concentrations could be appropriately corrected for each sample.

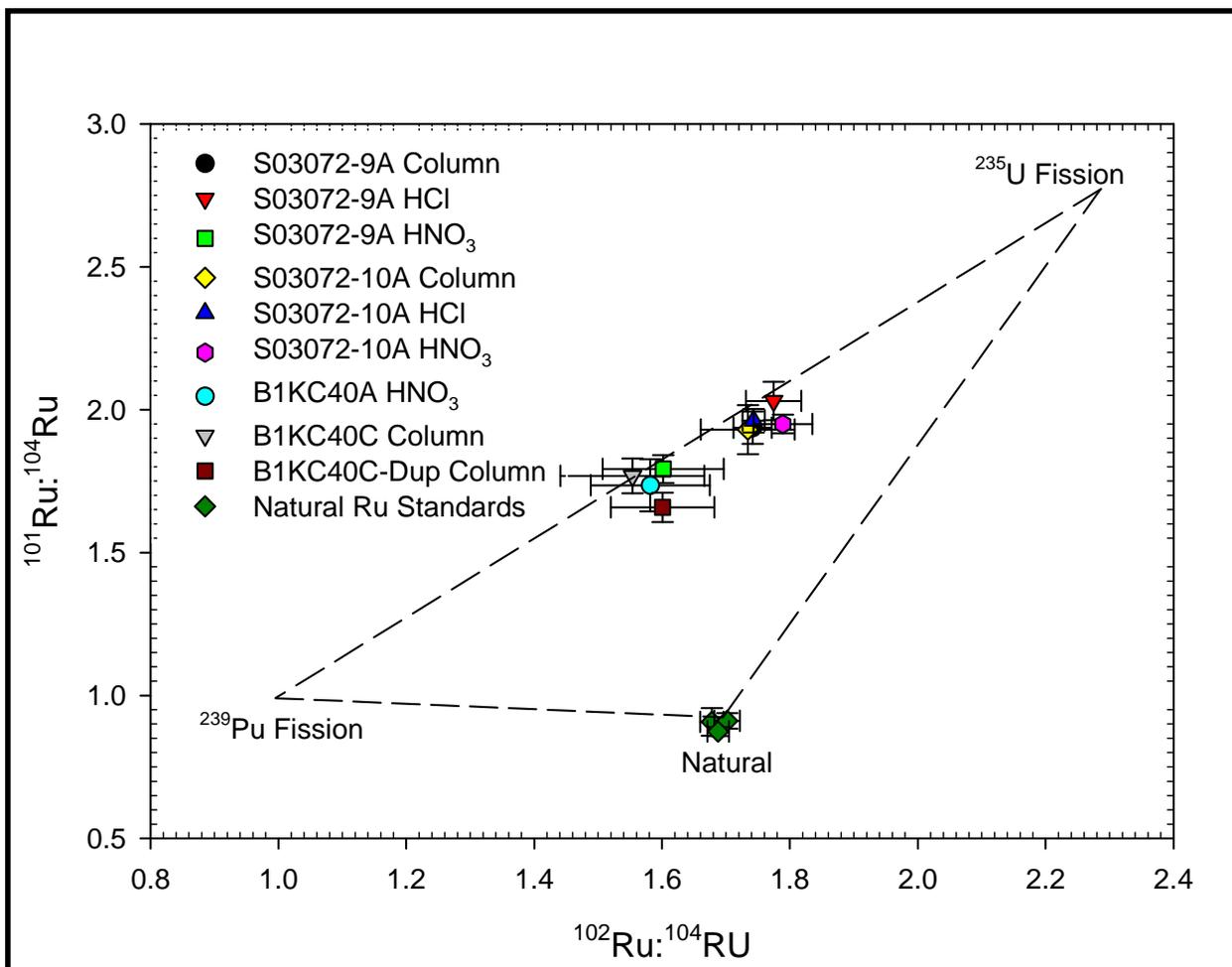
Even though there were issues with the total recovery of technetium-99 with this data set, these results can be used to qualitatively assess the thoroughness of the Tier I water and acid extraction techniques. Comparison of the data in Table 4.35 to water and acid extract results contained in Tables 4.30 through 4.33 shows that significantly more technetium-99 can be extracted via nitric acid or with the aid of microwave digestion than was released using water as the leachant. For example, the two Tier II water extraction tests leached an average of  $2.23\text{E-}03$   $\mu\text{g/g}$  technetium-99 from samples B1KC40C. These results were approximately a factor of two higher than the amount leached from this sample material during Tier I testing of the direct push samples. Comparatively,  $7.91\text{E-}03$   $\mu\text{g/g}$  technetium-99 was acid leached from this sample during Tier I testing. Tier II acid extraction of this sample resulted in  $5.93\text{E-}03$   $\mu\text{g/g}$  and  $5.34\text{E-}03$   $\mu\text{g/g}$  technetium-99 in the non-treated and resin-treated samples, respectively. Additionally, the resin-treated technetium-99 could be biased low due to loss of technetium through the treatment process. Finally, resin-treated microwave digests of this sample resulted in an average technetium-99 concentration of  $6.76\text{E-}03$   $\mu\text{g/g}$ . Again, this result could be biased low due to loss of technetium-99 through the separation process. It is difficult to assign quantitative numbers to the Tier II resin-treated data given the poor recoveries and less-than-optimal reproducibility of the data. However, given that large discrepancies in total technetium-99 concentrations among the various extraction techniques (with water extraction consistently being lowest), still existed after resin treatment of the acid extracts and microwave digests, serious thought must be given to the validity of using water-extractable technetium-99 data as the basis for determining total technetium-99 in the sediments.

### 4.3.2 Stable Ruthenium Isotopic Analysis

Two samples from borehole C4104 (emplaced near tank 241-T-106) (Serne et al. 2004b) were processed in conjunction with similar sediments from probe hole C5374 and analyzed for stable ruthenium isotopes via ICP-MS. Ruthenium results from the various aliquots of samples post-resin treatment are presented in Figure 4.19. The data are plotted as the isotopic ratios of ruthenium-102:ruthenium-104 vs. ruthenium-101:ruthenium-104. Also contained in the plot are the isotopic ratio data for natural ruthenium standards that were analyzed as part of the quality control associated with this data set. The plot is a triangle, with each end point of the triangle representing a different source of ruthenium. The three sources include natural ruthenium, ruthenium produced during uranium-235 fission, and ruthenium produced during plutonium-239 fission. The dashed lines contained within the figure represent mixing lines between the respective end members. If ruthenium measured in the samples is present from a single source, the data will plot at the appropriate end member, as was the case for the natural ruthenium standards. However, when samples contain multiple sources of ruthenium, they will plot on one of the mixing lines if their source is a mixture of two components or within the triangle if their source is a mixture of the three components. The data selected for plotting were only those results that had percent relative standard deviations of 7.5% or less based on three replicate analyses. Error bars contained within the plot represent one standard deviation.

All of the sediment water extract data analyzed plot on or near the mixing line between uranium-235 fission and plutonium-239 fission. Further, there appears to be two discrete “groups” of isotopic ratios associated with this data set. The upper group consists primarily of sediment samples collected from

borehole C4104 at depths of approximately 76 and 81 ft bgs. These specific samples from borehole C4104 were chosen for comparison because they bracket the depth of the T Tank Farm direct push samples processed and intercept the same stratigraphic unit (the Cold Creek Unit). Photographs of the samples are presented in Figures 4.20 through 4.24. The lower group contains all of the samples from probe hole C5374 that met the reporting criteria (which were only the 8M HNO<sub>3</sub> column elutions), as well as one of the column elutions from the C4104 borehole sample collected at 76 ft bgs. As discussed in Section 3.3.4, several column fractions were collected as part of the resin treatment process, and each of these fractions were analyzed as discrete samples. As discussed in Section 3.3.4, several of the eluent fractions exiting the ion exchange column were collected as part of the resin treatment process, and each of these fractions were analyzed as discrete samples. This was performed to 1) monitor the samples for ruthenium existing in multiple valence states, 2) investigate isotopic fraction of ruthenium, 3) monitor the samples for mass interferences, which could bias isotopic ratios measured in select fractions.



**Figure 4.19.** Ruthenium Isotopic Data from the T Tank Farm Direct Push Samples and Samples from Borehole C4104



**Figure 4.20.** Photograph of Fine-Grained Upper Cold Creek Unit Sediment Recovered from 81.0 to 81.5 ft bgs in Probe Hole C5374



**Figure 4.21.** Photograph of Fine-Grained Upper Cold Creek Unit Sediment Recovered from 80.5 to 81.0 ft bgs in Probe Hole C5374



**Figure 4.22.** Photograph of Fine-Grained Upper Cold Creek Unit Sediment Recovered from 80.0 to 80.5 ft bgs in Probe Hole C5374



**Figure 4.23.** Photograph of Sediment Recovered from 75.1 to 75.7 ft bgs in Borehole C4104



**Figure 4.24.** Photograph of Sediment Recovered from 80.1 to 80.7 ft bgs in Borehole C4104

It is interesting that the data set that plots lower on the uranium-plutonium mixing line contains all the water extracts that were further treated through the anion exchange resin for the T direct push samples from B1KC40 and one of the C4104 borehole elutants, the nitric acid rinse of the anion exchange column for sample S03072-(A (from 76 ft bgs). However, it does not contain all of the 8M HNO<sub>3</sub> data; the upper group contains data for all of the elutions for the C4104 borehole sample collected from 81 ft bgs (including the 8M HNO<sub>3</sub> elution). This indicates that the isotopic ratios measured in the lower plotting data set have not been biased low due to matrix interferences caused by the 8M HNO<sub>3</sub>. Unfortunately, the total amount of ruthenium present in the T Tank Farm direct push samples was too low for any of the other elutions to contain sufficient ruthenium to provide data that met the reporting requirements (i.e., less than 7.5% relative standard deviation). Quantitative measurement of the column and 5% HCl elutions from the direct push samples would be the best way to show that the lower ruthenium ratios present in these samples are indeed a result of the waste source term and are not associated with sample concentrations or matrices. One way to increase the total amount of ruthenium available for analysis would be to perform 1:1 sediment:water extracts using more sample mass; however, given that these samples were collected using the direct push technique, total sample mass is limited.

Given the shortcomings of the datasets, it is difficult to interpret the results with a high degree of confidence. However, based on the data, it does appear that multiple source terms (at least two) could be present in the C4104 borehole at the interface of the Hanford formation and the Cold Creek Unit. Additionally, one of the sources present at this location has a similar ruthenium isotopic ratio to those measured in the direct push samples collected from probe hole C5374. Since these samples were all collected at the interface of the Hanford formation and the Cold Creek Unit, it is possible that waste from the 241-T-101 tank leak migrated laterally to the southwest and can be observed in the C4104 borehole (Serne et al. [2004b] showed that the strata dip to the southwest in the T Tank Farm). Again, it is difficult to place an exact level of confidence on the interpretation of this data; however, it is supported by the stratigraphy in the area and certainly warrants further investigation.

### **4.3.3 Estimating Recharge Using 1:1 Sediment:Water Extract Chloride Data**

The existing chloride data from the pushes at T Tank Farm are unsatisfactory for use in estimating recharge using the chloride mass balance (CMB) method. Part of what makes the data problematic for CMB is that the chloride profile is incomplete with much of the data being between 43 and 50 ft bgs. Without some knowledge about the chloride profile, it can't be said if the chloride concentrations represent steady-state conditions, whether other transport processes are dominating (i.e., preferential flow), and if the chloride concentrations represent past or current recharge conditions. Another potential complicating factor is if a waste stream such as that resulting from a tank leak or overflow event resides at the sampling depths, the waste could alter the chloride concentration from what would otherwise be considered natural conditions. Obviously, the chemistry data associated with these samples indicates that tank waste constituents are present at the zones sampled by the direct push campaign.

Because the available chloride data is from multiple locations within T Tank Farm, an assumption must be made that conditions that would change recharge, such as evaporation and transpiration conditions, are the same at all vertical and horizontal locations. This is probably a safe assumption in this instance because push locations look to be relatively close to one another (~60 ft) and because the pushes are within a tank farm where the near surface sediment is homogenized backfill and vegetation is kept off. Outside of the tank farms in undisturbed areas, this assumption is not as plausible given that evapotranspiration conditions can vary over small distances. One other assumption that must be made to

make this argument valid (homogeneous backfill material and not vegetated) is that the chloride data from the pushes represents chloride deposited on the soil surface under the current surface conditions. In other words, it represents current recharge conditions.

The CMB method cannot provide insight pertaining to the umbrella or shedding effect of tanks. Assuming the same chloride deposition and evapotranspiration conditions, the concentration of chloride next to the sides of a tank should not be different than the chloride some distance away from the tank. Divergence of water around the tanks will increase the water flux, but the concentration of chloride will not change.

Chloride-36 measurements on these push samples would not provide beneficial information for estimating recharge because the method relies on establishing the chloride-36 peak concentration, meaning that the chloride-36 profile is needed. It is entirely possible that if one were to measure the chloride-36 profile next to the sidewall of a tank and away from the tank, the difference in water flux would be captured. This assumes that the peak chloride-36 deposition (from atmospheric bomb testing) in the mid-1950s post-dates construction of T Tank Farm.

The following types and quantity of samples are necessary in order to obtain a useful CMB dataset:

The collection of many depth-discrete undisturbed core samples is needed so that field moisture content conditions are captured. It's important that field moisture content be accurately determined in order to calculate pore water chloride concentrations.

Continuous, or near continuous, cores collected from near the ground surface to an appropriate depth to capture the chloride peak is necessary. Based on previous Hanford CMB studies, the chloride peak can range from 6 ft to over 30 ft bgs. The majority of the studies identified the chloride peak to be shallower than 30 ft bgs. A helpful guide is to collect cores to a depth of 50 ft, with continuous cores being collected from near the surface to a depth of 30 ft and cores collected every 3 ft from 30 to 50 ft bgs.

## **5.0 Summary and Observations**

In this section, summary information about the characterization of the T and TY Tank Farm direct push sediments is presented. Interpretation of the data has been included to aid in making decisions on what interim actions and future studies are needed to make sound remediation decisions at the T and TY Tank Farms.

### **5.1 T and TX-TY Tank Farms Physical Geology Model**

Assessment of data from nearby boreholes coupled with analysis of material recovered from the direct push holes has led to the interpretation that the deposits beneath the T and TX-TY Tank Farms consist predominantly of the gravel-dominated Hanford formation H1 unit and sand-dominated Hanford formation H2 unit. These facies were deposited onto the giant Cold Creek bar during repeated Pleistocene cataclysmic floods. Beneath the Hanford formation is the Cold Creek unit, which consists of an upper fine sand to silt unit and a lower unit of variably cemented caliche, representing a buried paleosol sequence. Combined, the Cold Creek unit may be up to 40 ft thick and its upper surface has a pronounced dip to the south. Below the Cold Creek unit is a discontinuous layer of Ringold Formation sand (Rtf) underlain by a thick sequence of variably cemented Ringold fluvial gravel (Rwi).

### **5.2 TY Tank Farm Characterization Activities and Data**

The next several sections summarize geochemical and physical characterization data collected on sediment from the direct push holes emplaced within the TY Tank Farm. These characterization activities emphasized tests that provided basic characterization data and were fundamental to determining the distribution of mobile contaminants in the vadose zone sediments. Such information on the direct push sediments included moisture content, total and inorganic carbon content, pH, electrical conductivity (EC), and measurements of major cations, anions, and trace metals (including technetium-99 and uranium-238) in 1:1 sediment:water extracts. Gamma energy analysis (GEA) of the sediments was also performed to search for any detectable man-made gamma-emitting radionuclides. In addition major cations, anions, and trace metals (including technetium-99 and uranium-238) were measured in 8 M nitric acid extracts of the sediments to allow qualitative measurements of constituent mobility by comparing the water leachable to the acid extractable masses for each sample.

#### **5.2.1 Sampling Summary at the TY Tank Farm**

A geochemical investigation in the vicinity of tanks 241-TY-105 (UPR 200-W-152) and 241-TY-106 (UPR 200-W-153) was performed using pairs of direct push probe holes. A total of 31 direct-pushes were driven within the TY Tank Farm; 25 of these holes were logged for geophysical parameters and six were driven for the purpose of retrieving vadose zone sediment for characterization and analysis. The samples were collected around tank 241-TY-105, which was estimated to have leaked 35,000 gal of tributyl phosphate (TBP) waste from the uranium recovery process to the vadose zone in 1960 (Wood et al. 2001), and tank 241-TY-106, which was estimated to have leaked 20,000 gal of the TBP-uranium recovery waste to the vadose zone in 1959.

### **5.2.2 Moisture Content**

Elevated moisture was observed in two of the samples analyzed as part of this study. One of the samples was collected directly south of tank 241-TY-105 (C4624) and the other samples were collected directly south of tank 241-TY-106 (C4604). However, the TY direct samples were collected at the interface between the backfill and Hanford formation; therefore, the elevated moisture measured in these samples could be an artifact of the compaction that occurred at this interface during construction of the tank farm and likely does not indicate the presence of tank-related waste fluids.

### **5.2.3 Contamination Profile around tanks 241-TY-105 and 241-TY-106**

Several parameters, including pH, electrical conductivity, nitrate, technetium-99, sodium, and uranium concentrations in water and acid extracts, and direct GEA of sediment samples were used as indicators to determine the subsurface regions contacted by tank waste that presumably leaked from tanks 241-TY-105 and 241-TY-106. The following paragraphs present the highlights from these tests.

The first parameter measured was the pH of water extracts of the vadose zone sediment. Based on the assumption that tank-related waste fluids are generally caustic and often very caustic (>1 M free hydroxide), elevated pH profiles should be indicative of the near-field region close to the source where the caustic fluid entered the sediments. Nearly all of the samples tested had pH values in the normal range for Hanford sediments (between 7.5 and 8.5). In fact, only one sample (S06001-1A) collected from probe hole C4604 contained slightly elevated soil pH of 8.63. While a soil pH of 8.63 is clearly elevated, it is not indicative of a major tank waste impact zone. Vadose zone sediments collected in close proximity to tank waste discharge points typically have soil pHs well above 9. Therefore, it does not appear that these samples were collected from a location close in proximity to where waste from tank 241-TY-106 entered the vadose zone.

The second parameter that was assessed to investigate proposed tank leaks was the dilution-corrected water extract electrical conductivity (EC) of the sediment samples. The pore water-corrected EC data for all of the samples were dilute and varied little, with a range of 1.71 to 4.62 mS/cm. Based on this, it appears that 1) there is little indication of residual tank waste in the sediments analyzed as part of this study based on elevated dissolved salts and 2) sufficient recharge has likely occurred to drive the bulk of the contamination deeper into the vadose zone. The latter possibility could be evaluated if deeper vadose zone samples were collected.

The third parameter that was used to investigate the extent of tank waste-related contamination in the vadose zone was sodium. Sodium was the dominant water-extractable cation in four out of the five probe holes analyzed (all but probe hole C4604). In the case of probe hole C4604, it is surprising to see a slightly elevated soil pH while still maintaining calcium as the dominant water-extractable cation. Again, this could be an artifact of the sampling technique and the associated poor sample recovery. For the remaining samples, the fact that they did not contain calcium as the dominant cation indicates that the samples have been impacted by a sodium-bearing waste fluid. The source(s) appears to be a moderately concentrated sodium-bearing waste solution that has displaced the natural divalent cations from the sediment cation exchange sites in the sediments. The TBP waste composition that leaked from tanks TY-105 and TY-106 are estimated to contain 4 M sodium, which is adequately high to be readily observed in vadose zone pore waters. The pore water sodium concentrations in the direct push sediment samples is not as high as would be expected if the sediments were significantly contacted with TBP

waste. Thus, the sample locations do not appear to be in the region where most of the leaked fluids percolated. The total vertical extent of the ion exchange front is unknown due to the lack of sediment samples from deeper in the vadose zone.

Mobile constituents, such as water-extractable uranium, technetium-99, and nitrate, are three additional parameters that can be used to investigate subsurface contamination. Naturally occurring uranium is present in a crystalline form that is very recalcitrant to leaching. Therefore, elevated amounts of uranium in the 1:1 sediment:water extracts are typically indicative of contaminant uranium. Technetium-99 and nitrate are both considered highly mobile in the subsurface; therefore, their presence in samples can often be used to estimate the total extent of contaminant plume migration. Of the twelve samples analyzed as part of this study, only one of them contained marginally elevated water-extractable uranium. This sample, which was collected from the shoe at probe hole C4604, contained approximately seven times more uranium ( $7.20\text{E-}03 \mu\text{g/g}$ ) than the background borehole (299-W10-27). The sample collected directly shallower, S06001-1A, did not contain a quantifiable amount of water-extractable uranium. Therefore, the uranium present in the shoe material from probe hole C4604 may be natural uranium that has been leached from the shallower sediment and pushed deeper into the vadose zone. An alternate hypothesis is that the uranium present in this sample was tank related and has been incorporated into soluble calcite precipitates. Quantifiable concentrations of technetium-99 were not measured in any of the TY direct push samples. The relative technetium-99 detection limit for the extraction and analysis of these samples was approximately  $0.17 \text{ pCi/g}$ . Although the water-extractable nitrate values measured in the TY direct push samples were in general higher than the average water-extractable nitrate from borehole 299-W10-27 ( $1.51 \mu\text{g/g}$ ), significantly elevated concentrations of nitrate were not measured. The highest water-extractable nitrate concentration measured ( $6.15 \mu\text{g/g}$ ) was in the shoe material from probe hole C4606. While this sample was elevated with respect to the background borehole, it contained significantly less nitrate than the highest concentration samples from boreholes C3830 (near TX-105), C3831 (near TX-107), and C3832 (near TX-104), which contained 84.1, 847, and  $97.4 \mu\text{g/g}$  nitrate, respectively.

The final indicator used to define the presence of tank-related waste in these samples was direct measurement of sediments for gamma-emitting radionuclides. Only the fission product isotope cesium-137 was detected during gamma analysis of the samples, and it was only observed in one (C4604) of the five direct push sample sets. The shoe material from probe hole C4604 contained  $1.5 \text{ pCi/g}$  cesium-137, while the A-sleeve sample contained  $0.6 \text{ pCi/g}$  cesium-137. The A-sleeve sediment from probe hole C4604 was the only sample with an elevated soil pH. Based on this, it seems likely that the slightly elevated pH in this sample, coupled with the cesium-137 contamination, is a result of contamination from a tank-related waste source. The most probable source of the contamination is the proposed leak from tank 241-TY-106.

#### **5.2.4 Source of Contamination around Tanks 241-TY-105 and 241-TY-106**

After evaluating all the characterization and analytical data, there is no question that the vadose zone surrounding tank 241-TY-106 has been contaminated by tank-related waste; however, the concentrations of waste constituents found are generally very low, suggesting that the sample locations are not near the bulk of the waste fluid released. The direct observance of elevated soil pH and cesium-137 in close proximity to tank 241-TY-106 indicates that the tank or infrastructure associated with the tank is responsible for the contamination. The poor recovery associated with the direct push technique has made it difficult to estimate the lateral spread of the contamination, while the nature of the direct push technique

has made it impossible to discuss the vertical extent of the contamination. However, based on characterization of the three probe holes that were emplaced south of tank 241-TY-106, it does not appear that a significant amount of lateral migration has occurred at the depth sampled. Interpretation of the water extract data associated with these samples suggests 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 the confirmation of this hypothesis.

The vadose zone south tank 241-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 naturally present divalent cations (calcium and magnesium) off the surface exchange sites. The lack of 1) elevated soil pH or 2) direct measurement of gamma-emitting radionuclides indicates that the point source of contamination is not in the direct vicinity of the only probe hole emplaced near tank 241-TY-105. The lack of direct evidence of a point source waste signature near tank 241-TY-105 does not mean the tank did not leak; rather, the vadose zone sample set collected as part of this investigation was not sufficient to either confirm or rebut the supposition that a leak from tank 241-TY-105 led to UPR 200-W-152.

### **5.3 T Tank Farm Characterization Activities and Data**

The next several sections summarize geochemical and physical characterization data collected on sediment from the direct push holes emplaced within the T Tank Farm. Again, these characterization activities emphasized tests that provided basic characterization data and were fundamental to determining the distribution of mobile contaminants in the vadose zone sediments. Such information on the direct push sediments included moisture content, total and inorganic carbon content, pH, electrical conductivity (EC), and measurements of major cations, anions, and trace metals (including technetium-99 and uranium-238) in 1:1 sediment:water and measurement of major cations, anions, and trace metals (including technetium-99 and uranium-238) in 8 M nitric acid extracts. Gamma energy analysis (GEA) of the sediments was also performed to search for any detectable man-made gamma-emitting radionuclides.

#### **5.3.1 Sampling Summary at the T Tank Farm**

A geochemical investigation in the vicinity of tanks 241-T-101 and 241-T-104 was performed using pairs of direct push probe holes. A total of 19 direct-pushes were driven within the T Tank Farm; 14 of these holes were logged for gross gamma using calibrated probes and five were driven for the purpose of retrieving vadose zone sediment for characterization and analysis. The samples were collected around tank 241-T-101, which was estimated to have leaked 7,500 gal of REDOX cladding waste to the vadose zone in 1992.

#### **5.3.2 Moisture Content**

Elevated moisture was observed in several of the samples analyzed as part of this study. The average gravimetric moisture content of all of the samples measured in this study was 7.9 wt%, which was slightly higher than the average moisture content in core samples collected within the Hanford formation H2 unit (3.9%) at the nearby TX Tank Farm characterization site (background borehole 299-W10-27 just east of the TY Tank Farm). However, the Cold Creek Unit was intercepted by several of the T Tank Farm direct push samples, which caused the average moisture content for all of the samples to be biased high when compared to the coarse-grained materials comprising the Hanford formation H2 unit. Therefore, the

elevated moisture measured in these samples was an artifact of the stratigraphic unit (the Cold Creek unit) encountered and does not necessarily indicate the presence of tank-related waste fluids.

### **5.3.3 Contamination Profile around Tank 241-T-101**

Several parameters, including pH, electrical conductivity, nitrate, technetium-99, sodium, and uranium concentrations in water and acid extracts, and direct GEA of sediment samples were used as indicators to determine the subsurface regions contacted by tank waste that presumably leaked from tank 241-T-101. The following paragraphs present the highlights from these tests.

The first parameter measured was the pH of water extracts of the vadose zone sediment. Based on the assumption that tank-related waste fluids are generally caustic and often very caustic (>1 M free hydroxide), elevated pH profiles should be indicative of the near-field region close to the source where the caustic fluid entered the sediments. Nearly one-third of the samples tested had pH values above the normal range for Hanford sediments (> 8.5). The sediments characterized as having an elevated pH were collected from probe holes C4598, C4596, and C5378 at depths ranging from approximately 43 to 63 ft bgs. As mentioned previously, vadose zone sediments collected in close proximity to tank waste discharge points typically have soil pHs well above 9. The three probe holes containing sediments with an elevated pH were the three sample probe holes emplaced closest to tank 241-T-101. Therefore, it appears that waste released from tank 241-T-101 migrated to the southeast in this region of the vadose zone.

The second parameter that was assessed to investigate the proposed tank leak was the dilution-corrected water extract electrical conductivity (EC) of the sediment samples. The pore water-corrected EC data for many of the samples ranged from dilute (1.26 mS/cm) to mildly saline (21.1 mS/cm). All of the samples that exhibited elevated sediment pHs also had elevated porewater conductivities. Not surprisingly, the samples with the highest porewater-corrected conductivities were collected from probe hole C4598, which was the closest sampling hole in proximity to tank 241-T-101. The next highest conductivity was found in samples from probe hole C5378, which was located approximately 5 m to the southeast of tank 241-T-101. These samples were collected at a depth of approximately 63 ft bgs, which was 20 ft deeper than the depth of the C4598 samples. These results again indicate that the initial impact zone from waste released from tank 241-T-101 migrated to the southeast of the tank to at least the location intercepted by probe hole C5378.

The third parameter that was used to investigate the extent of tank waste-related contamination in the vadose zone was sodium. Sodium was the dominant water-extractable cation in all but one of the sample strings (all of the samples except those from probe hole C5374). All three cores from probe hole C5374 contained elevated concentrations of calcium, potassium, magnesium, strontium, and sodium. It was surprising to find elevated calcium, magnesium, and sodium together in the same sample, since the sodium would typically drive the divalent cations off the exchange sites; this phenomenon could indicate that the samples were collected near the leading edge of the ion exchange front. However, it is impossible to confirm this hypothesis given the lack of sample coverage (particularly with respect to depth) in the area.

Water-extractable technetium-99 was found in most of the direct push core samples analyzed; however, it was only significantly elevated in the sediments collected from probe hole C5374. Not surprisingly, these were some of the deepest direct push samples collected as part of the T Tank Farm

sampling campaign. Technetium-99 is generally considered quite mobile in the subsurface, and as such, peak concentrations in the vadose zone are often found well below 115 ft bgs in regions that have been contaminated by tank loss events. Water-leachable uranium-238 was all less than 0.2 µg/g, indicating that there was not a significant amount of contaminant uranium in the vadose zone at these sampling locations. This is compatible with the fact that Tank T-101 released less than a kg of uranium. Water-extractable nitrate was significantly elevated (in excess of 250 µg/g) in the string of cores collected from probe hole C5374 from approximately 80 ft bgs. Probe hole C5374 was emplaced to the south of tank 241-T-101 and adjacent to tank 241-T-104. It is obvious that tank waste has impacted the vadose zone at this location; however, this single set of data does not permit the source of the contamination to be identified.

The final indicator species used to define the presence of tank-related waste in the T direct push samples was direct measurement of sediments for gamma-emitting radionuclides. Direct measurement of sediment samples for gamma-emitting radionuclides showed that the sediments contained natural potassium-40, the activation product cobalt-60, and the fission product isotopes cesium-137, europium-152, europium-154, and europium-155. The samples that contained the manmade gamma-emitting radionuclides were from the four probe holes emplaced closest to tank 241-T-101. Significantly lower activities of gamma-emitting radionuclides were found at these locations than from the previous characterization study performed in the T Tank Farm (Serne et al. 2004b). As much as 40 pCi/g cesium-137 was measured by Serne et al. (2004b) in borehole C4104, while the peak activity measured as part of this study was 16.8 pCi/g. Given the mixed depth sampling frequency that was performed during the direct push campaign, it is difficult to say anything about the relative mobility of the radionuclides; however, it appears that they may have migrated southeast from tank 241-T-101.

### **5.3.4 Tier II Activities Associated with the T Tank Farm Direct Push Samples**

Tier II characterization activities were performed on a subset of the T Tank Farm direct push samples to 1) further investigate the discrepancy between water-extractable and acid-leachable technetium-99 in the direct push samples, 2) see if ruthenium isotopic analyses could be used to identify contaminant source terms, and 3) see if chloride data generated during the 1:1 sediment:water extraction process could be used to investigate the effect of the tank drip line on recharge. Summaries of the results from Tier II tests and analyses are presented in the following sections.

#### **5.3.4.1 Total Extractable Technetium-99**

Extraction of technetium-99 from vadose zone sediments using deionized water, 8M HNO<sub>3</sub>, and microwave-assisted digestion provided mixed results. The %RSDs for the 1:1 sediment:water extract samples that were not resin-treated were excellent, with a range from 0.759% to 2.30% based on one standard deviation of samples analyzed in triplicate. The total technetium-99 analyzed in these samples compared quite well with the total technetium-99 measured in resin-treated sample aliquots. Relative differences between the two data sets for average concentrations of the samples from probe hole C5374 (as measured via the three replicate samples) ranged from 1.42% to 9.97%. These results indicate that technetium-99 reported in the 1:1 sediment:water extracts is indeed technetium-99 (i.e., a matrix interference is not present in these samples). These results show that the additional step of treating the samples with TEVA® resin is not necessary when quantifying technetium-99 in water extract samples.

The %RSDs for the 8M nitric acid extract samples that were not resin-treated were acceptable, although they weren't as good as those for the water extract samples. For the three sample sets that contained technetium-99 in excess of the limit of quantification for analysis, the %RSDs ranged from 6.39% to 12.5%. Spike recoveries performed as quality control for this data set worked quite well. All three spikes, the blank spike, the background sediment matrix spike, and the direct push sample matrix spike all had recoveries in excess of 85%. These results indicate that technetium-99 is stable throughout the 8M nitric acid extraction process. The %RSDs for the 8M nitric acid extract samples that were treated with TEVA® resin were slightly better than those for the non-treated samples. For the three sample sets that contained technetium-99 in excess of the limit of quantification for analysis, the %RSDs ranged from 3.44% to 12.9%. Unfortunately, spike recoveries for the aliquots of samples that were treated with the resin were quite variable and inadequately low. None of the TEVA® resin-treated spikes had recoveries of 85% or greater. These low recoveries clearly indicate that technetium-99 was lost between the 8M nitric acid extraction step and analysis of the resin-treated eluents. The two most probable steps that could have led to a deficiency in technetium-99 recoveries were heating of the samples to dryness once the 8M nitric acid extracts were complete (this step was performed to change the sample matrix prior to its addition to the TEVA columns), or fouling of the resin columns by the high concentrations of dissolved solids in the acid extract samples.

Although there were issues with the total recovery of technetium-99 through the resin treatment process, the results of this test do allow for some qualifications to be made to the Tier II acid extract data (and subsequently to the Tier I acid extract data). Comparison of the non-resin-treated sample data with the resin-treated data showed good agreement between the analyses. Relative differences between the two data sets for average concentrations of the samples from probe hole C5374 (as measured via the three replicate samples) ranged from 10.3% to 13.3% (the technetium-99 concentrations in the resin-treated samples were consistently lower than those in the untreated samples). There was exceptionally good agreement between the data sets given the low total recoveries measured after resin treatment of the samples. Additionally, it appears that a matrix effect is not the cause of the elevated technetium-99 in the acid extracts vs. the water extracts. These results imply that some credence should be given to the 8M acid extract technetium-99 data. However, before quantitative results are provided, the 8M nitric acid extracts should be taken through the resin treatment process again after the addition of a tracer to monitor recoveries through the purification steps.

The %RSDs for the microwave digests that were not resin-treated were not acceptable, given that technetium-99 was not measured above the limit of quantification for the analysis. Microwave digestion generates greater sample dilution due to a higher solution to solid ratio (100:1 vs. approximately 6:1 for the nitric acid extracts and 1:1 for the sediment:water extracts). On a positive note, spike recoveries performed as quality control for this data set worked quite well. All three spikes—the blank spike, the background sediment matrix spike, and the direct push sample matrix spike—had recoveries in excess of 85%. These results indicate that technetium-99 is stable throughout the microwave digestion process, but higher sample concentrations are necessary to alleviate detection limit issues associated with the technique.

Treatment of the microwave-digested samples with TEVA® resin resulted in quantitative technetium-99 data for all of the direct push samples from probe hole C5374. However, the %RSDs for the microwave-digested samples varied considerably. The %RSDs for the four direct push sample sets ranged from 15.5% to 63.2%. Spike recoveries for the aliquots of sample that were treated with the resin were sporadic. Only one of the TEVA® resin-treated spikes (the background matrix spike) had a recovery

of greater than 85%. As with the acid extract data, these results clearly indicate that technetium-99 was lost between the microwave digestion step and analysis of the resin-treated samples. The same two steps that could have led to a deficiency in technetium-99 recoveries in the 8M nitric acid extracts were the primary culprits with these samples as well.

Although there were issues with the total recovery of technetium-99 with the acid and microwave digestion data sets and no direct method of assuring that all the technetium-99 present in the sediment was water extractable is data set, these results can be used to qualitatively assess the thoroughness of the Tier I water and acid extraction techniques. Comparison of the resin-treated microwave-assisted digestion data to the water and acid extract results shows that significantly more technetium-99 can be extracted via nitric acid or with the aid of microwave digestion than was released using water as the leachant. For example, the two Tier II water extraction tests leached an average of  $2.23\text{E-}03$   $\mu\text{g/g}$  technetium-99 from samples B1KC40C. These results were approximately a factor of two higher than the amount leached from this sample material during Tier I testing of the direct push samples. Comparatively,  $7.91\text{E-}03$   $\mu\text{g/g}$  technetium-99 was acid leached from this sample during Tier I testing. Tier II acid extraction of this sample resulted in  $5.93\text{E-}03$   $\mu\text{g/g}$  and  $5.34\text{E-}03$   $\mu\text{g/g}$  technetium-99 in the non-treated and resin-treated samples, respectively. Additionally, the resin-treated technetium-99 could be biased low due to loss of technetium through the treatment process. Finally, resin-treated microwave digests of this sample resulted in an average technetium-99 concentration of  $6.76\text{E-}03$   $\mu\text{g/g}$ . Again, this result could be biased low due to loss of technetium-99 through the purification process. It is difficult to assign quantitative numbers to the Tier II resin-treated acid extract and microwave digest data given the poor recoveries and less-than-optimal reproducibility of the data. However, given that large discrepancies in total technetium-99 concentrations amongst the various extraction techniques (with water extraction consistently being lowest) still existed after resin treatment of the acid extracts and microwave digests, serious thought must be given to the validity of using water-extractable technetium-99 data as the basis for determining total technetium-99 in the sediments.

#### **5.3.4.2 Analysis of Isotopic Ruthenium**

Several samples from borehole C4104 (emplaced near tank 241-T-106) (Serne et al. 2004b) were processed in conjunction with sediments from probe hole C5374 and analyzed for stable ruthenium isotopes via ICP-MS. The data were plotted as the isotopic ratios of ruthenium-102:ruthenium-104 vs. ruthenium-101:ruthenium-104. All of the sediment extract data analyzed plot on or near the mixing line between uranium-235 fission and plutonium-239 fission. Further, there appears to be two discrete “groups” of isotopic ratios associated with this data set. The upper group (a cluster of data points closer to the U-235 fission end member) consists primarily of sediment samples collected from borehole C4104 at depths of approximately 76 and 81 ft bgs. These specific samples from borehole C4104 were chosen for comparison because they bracket the depth of the T Tank Farm direct push samples processed and intercept the same stratigraphic unit (the Cold Creek Unit). The lower group (a cluster of data points closer to the Pu-239 fission end member) contains all of the samples from probe hole C5374 that met the reporting criteria (which were only the 8M HNO<sub>3</sub> column elutions), as well as one of the 8M HNO<sub>3</sub> column elutions from the C4104 borehole sample collected at 76 ft bgs. Earlier preliminary data indicated that a mass interferent or matrix effect could be biasing the isotopic ratio low (i.e. towards the plutonium-239 fission end member). However, results from these tests indicate that the isotopic ratios measured in the lower cluster of data have not been biased low due to matrix interferences caused by the 8M HNO<sub>3</sub>, suggesting that the isotopic differences measured between the two data clusters could represent isotopic ruthenium from different waste source terms.

Given that there were some analytical shortcomings/challenges associated with this dataset, it is difficult to interpret the results with a high degree of confidence. However, based on the data, it does appear that multiple source terms (at least two) could be present in the C4104 borehole at the interface of the Hanford formation and the Cold Creek Unit. Additionally, one of the sources present at this location has a similar ruthenium isotopic ratio to those measured in the direct push samples collected from probe hole C5374. Since these samples were all collected at the interface of the Hanford formation and the Cold Creek Unit, it is possible that waste from the 241-T-101 tank leak migrated laterally to the southwest and can be observed in the C4104 borehole (Serne et al. [2004b] showed that the strata dip to the southwest in the T Tank Farm). Again, it is difficult to place an exact level of confidence on the interpretation of this data; however, it is supported by the stratigraphy in the area and certainly warrants further investigation.

#### **5.3.4.3 Recharge Estimates**

The existing chloride data from the pushes at the T Tank Farm were unsatisfactory for use in estimating recharge using the chloride mass balance (CMB) method. Part of what makes the data problematic for CMB is that the chloride profile is incomplete with much of the data being between 43 and 50 ft bgs. Without some knowledge about the chloride profile over a much larger depth interval, it can't be said if the chloride concentrations represent steady-state conditions, whether other transport processes are dominating (i.e., preferential flow), and if the chloride concentrations represent past or current recharge conditions.

#### **5.3.5 Source of Contamination around tanks 241-T-101 and 241-T-104**

After evaluating all the characterization and analytical data, there is no question that the vadose zone in the vicinity of tank 241-T-101 has been contaminated by tank-related waste. The direct observance of elevated soil pH, porewater-corrected electrical conductivity, nitrate, technetium-99, elevated water-extractable sodium, and fission product isotopes of europium as well as cesium-137 in close proximity to tank 241-T-101 indicates that the tank or infrastructure associated with the tank is responsible for the contamination. The sparse sample coverage associated with the direct push technique has made it difficult to estimate the lateral spread of the contamination, while the depth limitation of the direct push technique has made it impossible to discuss the vertical extent of the contamination. However, based on characterization of the probe holes that were emplaced to the southeast of tank 241-T-101, it appears that waste from tank 241-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, the lack of depth-discrete samples does not enable the confirmation of this hypothesis.

The vadose zone directly northeast of tank 241-T-104 also has been 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 does not exist to determine if the contamination observed in this region is a result of a loss from tank 241-T-104 or if it is a result of lateral spreading from tank 241-T-101.

## 5.4 Detailed Characterization to Elucidate Controlling Geochemical Processes at the T and TY Tank Farms

Characterization activities of the direct push samples added some insight as to 1) the processes that control the observed distribution of contaminants and 2) the migration potential of key contaminants in the future. The pore waters, calculated by dilution correction of the 1:1 water extracts in the sediment from the direct push samples, were dominated by sodium and bicarbonate for sediments with obvious signs of tank fluids. The most concentrated pore water is shown in Table 5.1 in units of meq/L. Also included in the table for comparison are the maximum pore water concentrations found in other characterization work previously reported for the T, TX, and SX Tank Farms.

For the TY Tank Farm direct push samples, the most saline calculated pore water resided in the H2 unit and had a chemical composition of 80.5 meq/L calcium, 67.2 meq/L sodium, 10.6 meq/L potassium, and trace amounts of magnesium (0.02 meq/L). The cations were balanced primarily by bicarbonate (113 meq/L), with lesser amounts of sulfate (38.6 meq/L), chloride (2.12 meq/L), nitrate (0.999 meq/L), and phosphate (0.422 meq/L). As shown in Table 5.1, the most concentrated calculated pore water from the TY Tank Farm direct push sampling campaign was less concentrated, and in some cases much less concentrated, than pore waters found in the vadose zone sediments from the T, TX, or SX Tank Farms.

For the T Tank Farm direct push samples, the most saline calculated pore water also resided in the H2 unit and had a chemical composition of 193 meq/L sodium with a trace amount of calcium (0.576 meq/L). The cations were balanced almost exclusively by bicarbonate (192 meq/L), with lesser amounts of sulfate (3.05 meq/L), nitrate (1.82 meq/L), and phosphate (1.65 meq/L).

The distribution of the 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. The depth profiles for the divalent alkaline earth cations (calcium, magnesium, and strontium) versus sodium show depleted alkaline earth cation concentrations in the shallow Hanford formation sediments at both locations to depths of up to 80 ft bgs (the terminal depth of the deepest sample emplaced as part of the characterization campaign). 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 the contamination has been present for a sufficiently long period of time to facilitate the migration of more mobile contaminants (i.e., nitrate and technetium-99) 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 supports the premise that mobile contaminants reside much deeper in the vadose zone at both of these locations.

**Table 5.1.** Maximum Pore Water Concentrations in Sediments from the Hanford Formation Unit  
(reported in units of mN)

Tank	Closest Single-Shell Tank and Borehole or Borehole Number						
	TY-106	T-101	TX-107	T-106	SX-115	SX-109	SX-108
Borehole/Probe Hole	C4604	C4598	C3831	C4104	W23-19	41-09-39	W23-64
Na	67.2	193	418	150	35.6	6066	16900
Ca	80.5	0.576	1.2	0.7	281	619	90
Mg	0.02	0	0.2	0.6	94.6	24	10
K	10.6	0	4.7	1.2	3.6	42	92
Sr	0	0	0	0	1.5	4.4	1
UO <sub>2</sub>	0	0	0	0	0	0	0
Total Cations	158	194	424	153	416	6755	17093
NO <sub>3</sub>	0.999	1.82	202	9.2	420	6710	15677
NO <sub>2</sub>	0	0	0	0	0	28	32
SO <sub>4</sub>	38.6	3.05	15.2	5.6	3.3	95	500
CrO <sub>4</sub>	0	0	0	0	100	0	0
PO <sub>4</sub>	0.422	1.65	8.4	1.8	0	0	0
Cl	2.12	0	6.4	3.0	6	119	147
F	0.635	0	0.8	6.4	0	0	0
HCO <sub>3</sub> /CO <sub>3</sub>	113	192	191	220*	7	0	666
Total Anions	155	199	424	246*	536	6952	17022
Dilution Corrected EC (mS/cm)	3.12	21.1	43.3	24.3	33.1	524	1772

\* Suspect data, poor charge balance.



## 6.0 Interim Measures Support

Two sets of direct push samples were delivered to the laboratory for rapid turnaround analysis of key constituents. The samples were collected north of the T Tank Farm using the direct push sampling technique; Table 6.1 contains a list of the samples. All eight samples were broken down in the laboratory, characterized by a geologist, digitally photographed, and processed for moisture content. Upon completion of the sample break-down activities, one sample from each probe hole was processed using the 1:1 sediment:water extraction technique described in Section 3.3.2 and analyzed for technetium-99 and nitrate. Results of these analyses, as well as all of the information gathered during sample breakdown, were provided to CH2M HILL Hanford Group, Inc. within 24 hours of receipt of the last sample by the laboratory. Photographs of the samples are contained in Appendix E and geological logs of the samples are presented in Appendix F. Results of the moisture content analysis of select samples from each probe hole are presented in Table 6.2. The 1:1 sediment:water extract nitrate and technetium-99 data are contained in Tables 6.3 and 6.4, respectively.

**Table 6.1.** Sample Inventory from the T Tank Farm Interim Measures Samples

Sample Number	Probe Hole Number	Sample Number	Probe Hole Number
B1NP87C	C5692	B1NP90C	C5694
B1NP87B	C5692	B1NP90B	C5694
B1NP87A	C5692	B1NP90A	C5694
B1NP87	C5692	B1NP90	C5694

Shaded cells indicate grab samples.

**Table 6.2.** Gravimetric Moisture Content of Samples Obtained from the T Tank Farm Interim Measures Activities

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Moisture (%)
B1NP87C	C5692	45.75	4.11%
B1NP87B	C5692	46.25	4.68%
B1NP87A	C5692	46.75	7.41%
B1NP87	C5692	47.25	4.25%
B1NP90C	C4624	53.25	4.94%
B1NP90B	C4610	53.75	6.96%
B1NP90A	C4610	54.25	8.58%
B1NP90	C4606	54.75	4.88%

Shaded cells indicate grab samples.

**Table 6.3.** Sediment:Water-Extractable Nitrate Data for Samples Obtained from the T Tank Farm Interim Measures Activities

Sample ID	Probe Hole ID	Mid-Depth ft bgs	Nitrate ( $\mu\text{g/g}$ )
B1NP87A	C5692	46.75	2.56E+00
B1NP90A	C4610	54.25	1.26E+00

The values for nitrate are considered estimates. The measured value for nitrate in the analytical preparation blank was greater than 5% of the concentration measured in the sample.

**Table 6.4.** 1:1 Sediment:Water-Extractable Technetium-99 Data for Samples Obtained from the T Tank Farm Interim Measures Activities

<b>Sample ID</b>	<b>Probe Hole ID</b>	<b>Mid-Depth ft bgs</b>	<b>Technetium-99 (pCi/g)</b>
B1NP87A	C5692	46.75	<3.56E-01
B1NP90A	C4610	54.25	<3.66E-01
Less than symbol indicates the instrument returned a negative value.			

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## **Appendix A**

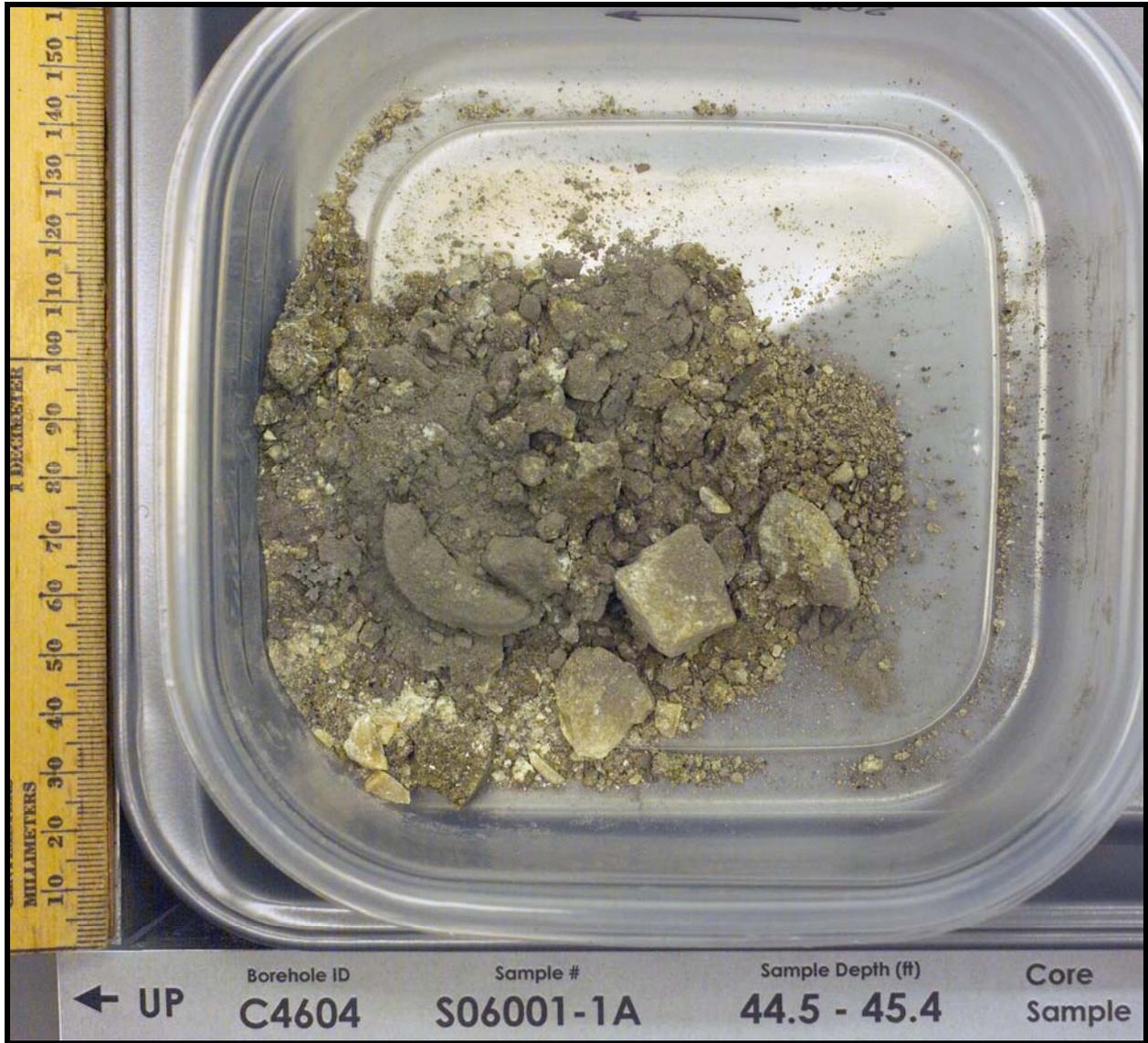
### **Photographs of Core and Grab Samples from the Direct Push Boreholes in the Vicinity of Single-Shell Tanks 241-TY-105 and 241-TY-106**



## Appendix A

### Photographs of Core and Grab Samples from the Direct Push Boreholes in the Vicinity of Single-Shell Tanks 241-TY-105 and 241-TY-106

A.1	Sample S06001-1A from Direct-Push Vertical Borehole C4604 .....	A.2
A.2	Sample S06001-1 from Direct-Push Vertical Borehole C4604 .....	A.3
A.3	Sample S06001-4C from Direct-Push Vertical Borehole C4606.....	A.4
A.4	Sample S06001-4B from Direct-Push Vertical Borehole C4606.....	A.5
A.5	Sample S06001-4A from Direct-Push Vertical Borehole C4606 .....	A.6
A.6	Sample S06001-4 from Direct-Push Vertical Borehole C4606 .....	A.7
A.7	Sample S06001-3A from Direct-Push Vertical Borehole C4610 .....	A.8
A.8	Sample S06001-3 from Direct-Push Vertical Borehole C4610 .....	A.9
A.9	Sample S06001-5 from Direct-Push Vertical Borehole C4622 .....	A.10
A.10	Sample S06001-2B from Direct-Push Vertical Borehole C4624.....	A.11
A.11	Sample S06001-2A from Direct-Push Vertical Borehole C4624 .....	A.12
A.12	Sample S06001-2 from Direct-Push Vertical Borehole C4624 .....	A.13



**Figure A.1.** Sample S06001-1A from Direct-Push Vertical Borehole C4604



**Figure A.2.** Sample S06001-1 from Direct-Push Vertical Borehole C4604

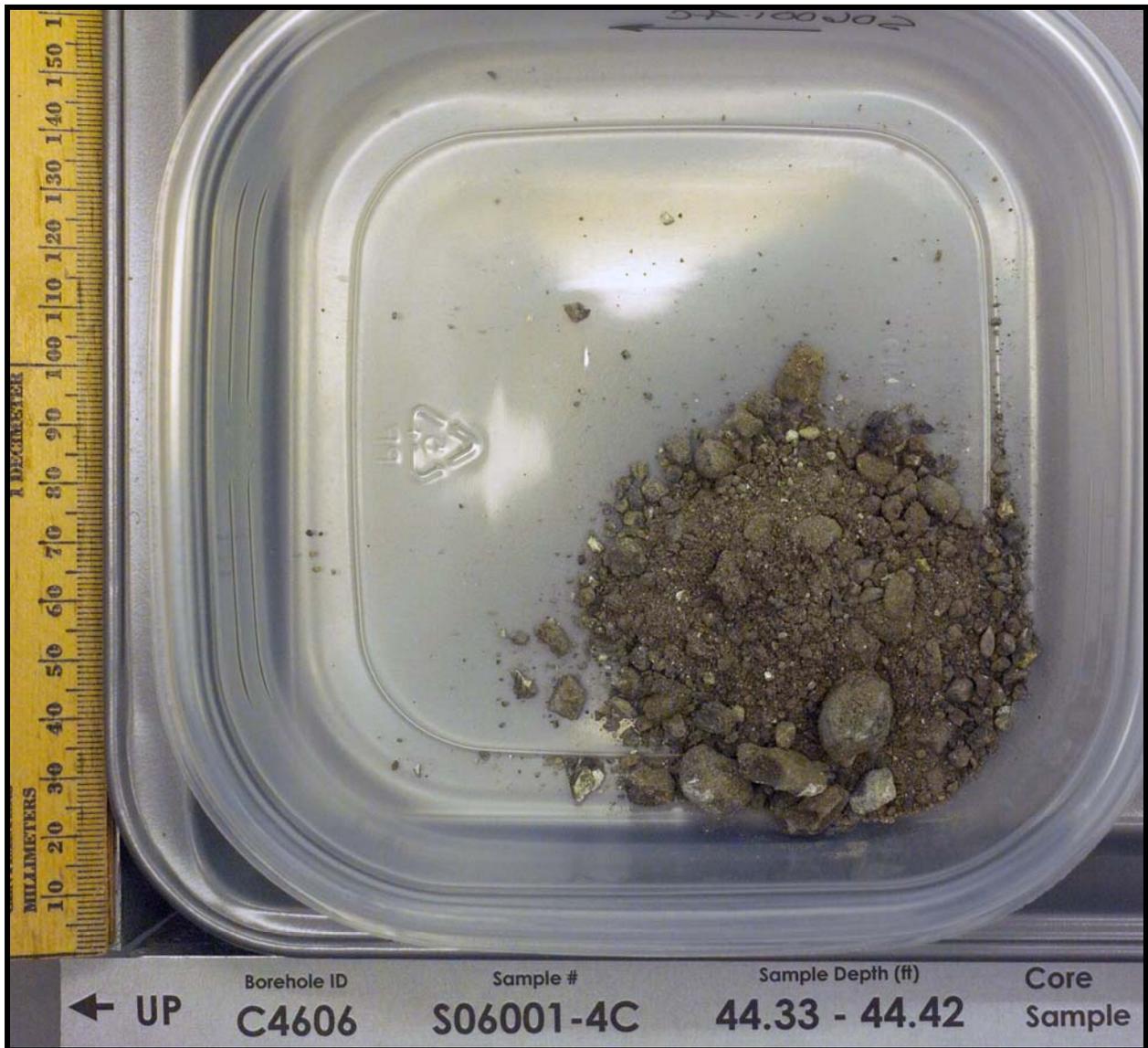


Figure A.3. Sample S06001-4C from Direct-Push Vertical Borehole C4606



**Figure A.4.** Sample S06001-4B from Direct-Push Vertical Borehole C4606



**Figure A.5.** Sample S06001-4A from Direct-Push Vertical Borehole C4606



**Figure A.6.** Sample S06001-4 from Direct-Push Vertical Borehole C4606



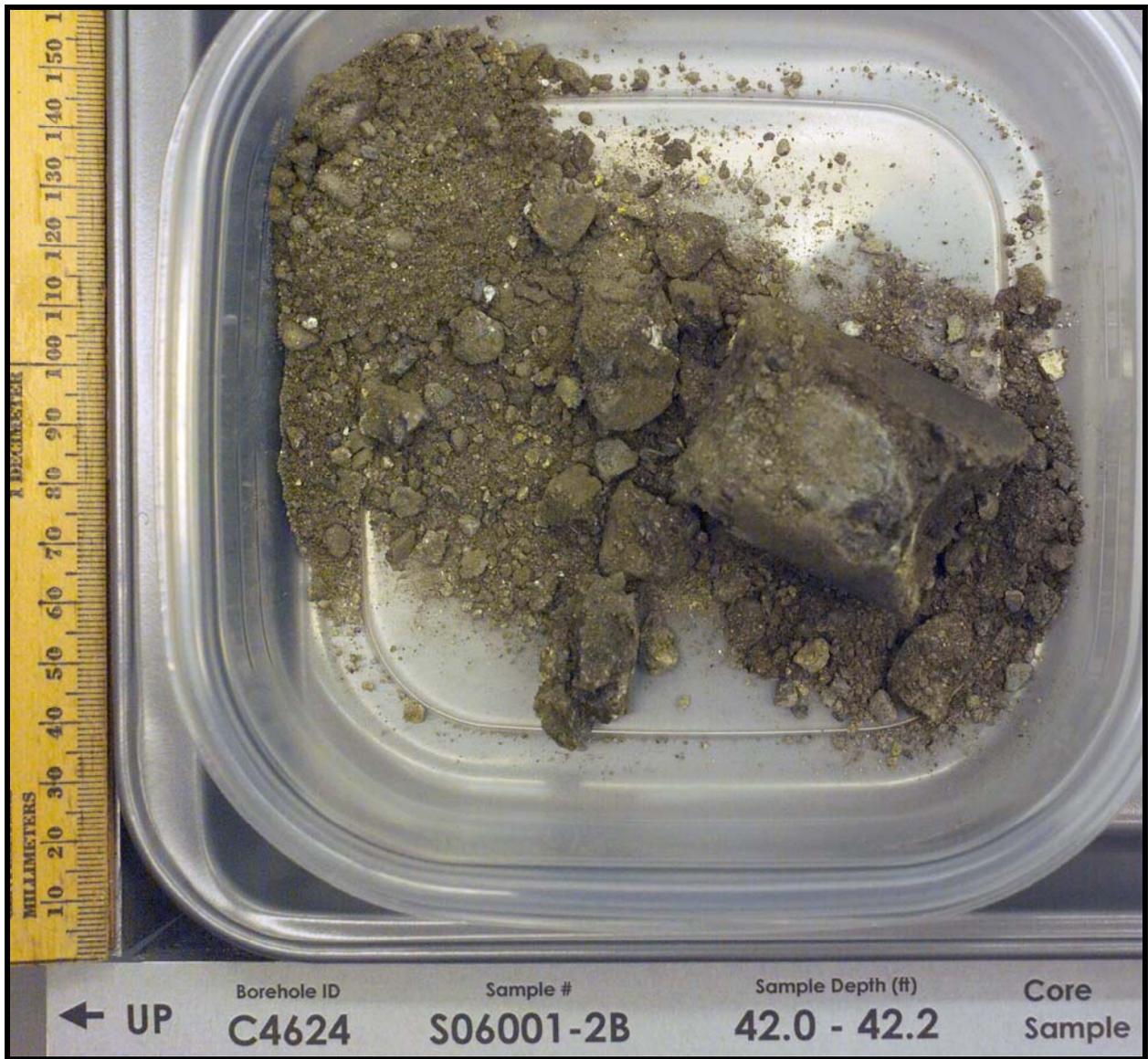
**Figure A.7.** Sample S06001-3A from Direct-Push Vertical Borehole C4610



**Figure A.8.** Sample S06001-3 from Direct-Push Vertical Borehole C4610



**Figure A.9.** Sample S06001-5 from Direct-Push Vertical Borehole C4622



**Figure A.10.** Sample S06001-2B from Direct-Push Vertical Borehole C4624



**Figure A.11.** Sample S06001-2A from Direct-Push Vertical Borehole C4624



**Figure A.12.** Sample S06001-2 from Direct-Push Vertical Borehole C4624



## **Appendix B**

**Logs of Core and Grab Samples from the Direct Push Boreholes in  
the Vicinity of Single-Shell Tanks 241-TY-105 and 241-TY-106**



## Appendix B

### Logs of Core and Grab Samples from the Direct Push Boreholes in the Vicinity of Single-Shell Tanks 241-TY-105 and 241-TY-106

B.1	Core Log for Direct-Push Vertical Borehole C4604.....	B.2
B.2	Core Log for Direct-Push Vertical Borehole C4606.....	B.3
B.3	Core Log for Direct-Push Vertical Borehole C4610.....	B.4
B.4	Core Log for Direct-Push Vertical Borehole C4622.....	B.5
B.5	Core Log for Direct-Push Vertical Borehole C4624.....	B.6

Pacific Northwest National Laboratory		<b>CORE LOG</b>		Boring/Well No <u>C4604</u>		Depth <u>44.5-45.4</u>		Date <u>12-20-05</u>		Sheet <u>1</u> of <u>1</u>				
		Location <u>TY Tank Farm</u>		Project <u>Vadose Zone</u>										
Logged by <u>BN Bjornstad</u>				Drilling Contractor _____										
Reviewed by _____				Date _____				Driller _____						
Lithologic Class. Scheme _____				Procedure _____				Rev _____						
Steel Tape/E-Tape _____				Field Indicator Equip. 1) _____				2) _____						
				Depth Control Point _____										
DEPTH ( )	TIME	SAMPLES		CONTAMINATION		MOIS- TURE	GRAPHIC LOG				LITHOLOGIC DESCRIPTION (particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, etc.)	H <sub>2</sub> O ADDED	CASING	DRILLING COMMENTS (drilling rate, down time, blow counts, water level, drill fluid, etc.)
		TYPE	ID NUMBER	INSTR.	READING		C	Z	S	G				
44											2 SG, 30% G, 60% S, 10% Z, mod rxn w/ HCl, poorly sorted, 2.5/5/4 (lt. olive brn); gravel clasts broken, lgt clast = 2 cm, compact, mod. Consolidated			1.5" diam. s.s. core samples 6" long CPT cores Only one of two liners collected plus shoe sample 1A only had 1-2" of dry powdery gray sediment (crushed).
45			S06001-A			D								
			S06001-1			M								

W = Wet, M = Moist, D = Dry

1998/DCL/PROC/DBL/001

Figure B.1. Core Log for Direct-Push Vertical Borehole C4604

Pacific Northwest National Laboratory		<b>CORE LOG</b>			Boring/Well No <u>C4606</u>		Depth <u>44.33-46.0</u>		Date <u>12-20-05</u>		Sheet <u>1</u> of <u>1</u>			
					Location <u>TY Tank Farm</u>			Project <u>Vadose Zone</u>						
Logged by <u>BN Bjornstad</u>						Drilling Contractor _____								
Reviewed by _____						Date _____								
Lithologic Class. Scheme _____						Procedure _____								
Steel Tape/E-Tape <u>1</u>						Field Indicator Equip. 1) _____ 2) _____								
Rig/Method _____						Depth Control Point _____								
DEPTH ( )	TIME	SAMPLES		CONTAMINATION		MOIS- TURE	GRAPHIC LOG				LITHOLOGIC DESCRIPTION (particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, etc.)	H <sub>2</sub> O ADDED	CASING	DRILLING COMMENTS (drilling rate, down time, blow counts, water level, drill fluid, etc.)
		TYPE	ID NUMBER	INSTR.	READING		C	Z	S	G				
44			S06001-4C			SM	0.5 0.0 0.0 0.0				25G, compact, mod. consolidated,			1.5" dia, 6" long s.s. core
			S06001-4B			M	0.0 0.0 0.0 0.0				2.5 4/2 (dk grayish brn), poorly			liners collected via direct
							0.0 0.0 0.0 0.0				sorted, 1st clast = 3cm, mod			push cone penetrometer
45			S06001-4A				0.0 0.0 0.0 0.0				rxn w/ HCl, 30% G, 60% S,			
			S06001-4				0.0 0.0 0.0 0.0				10% Z, S = 50% basalt, G =			
							0.0 0.0 0.0 0.0				80% basalt			
46							0.0 0.0 0.0 0.0				2g S, 20% G, 70% S, 10% Z, mod.			
							0.0 0.0 0.0 0.0				consolidated, compact,			
							0.0 0.0 0.0 0.0				mod rxn w/ HCl, 2.5 4/4			
							0.0 0.0 0.0 0.0				(olive brn), 1st clast = 2cm,			
							0.0 0.0 0.0 0.0				S = 50% basalt, less gravel			
							0.0 0.0 0.0 0.0				with depth - all most pure			
							0.0 0.0 0.0 0.0				sand, mod sorted			

W = Wet, M = Moist, D = Dry

1998/DCL/PROC/DBU/001

Figure B.2. Core Log for Direct-Push Vertical Borehole C4606

B.3

Pacific Northwest National Laboratory		CORE LOG			Boring/Well No <u>C4610</u> Depth <u>43.67-44.5</u> Date <u>12-20-05</u>			Sheet <u>1</u> of <u>1</u>						
Location <u>TY Tank Farm</u>					Project <u>Vadose Zone</u>									
Logged by <u>BN Bjornstad</u>				Drilling Contractor _____										
Reviewed by _____				Date _____				Driller _____						
Lithologic Class. Scheme _____				Procedure _____				Rev _____						
Steel Tape/E-Tape <u>1</u>				Field Indicator Equip. 1) _____				2) _____						
Depth Control Point _____														
DEPTH ( )	TIME	SAMPLES		CONTAMINATION		MOIS- TURE	GRAPHIC LOG				LITHOLOGIC DESCRIPTION (particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, etc.)	H <sub>2</sub> O ADDED	CASING	DRILLING COMMENTS (drilling rate, down time, blow counts, water level, drill fluid, etc.)
		TYPE	ID NUMBER	INSTR.	READING		C	Z	S	G				
43.5			506001-3A			SM							1.5" diam, 6" s.s. core liners	
44			506001-3			M							collected with direct push cone penetrometer	
						D								

W = Wet, M = Moist, D = Dry

1998/DCL/PROC/DBU/001

Figure B.3. Core Log for Direct-Push Vertical Borehole C4610

B.4





## **Appendix C**

### **Photographs of Core and Grab Samples from the Direct Push Boreholes in the Vicinity of Single Shell Tanks 241-T-101 and 241-T-104**



## Appendix C

### Photographs of Core and Grab Samples from the Direct Push Boreholes in the Vicinity of Single Shell Tanks 241-T-101 and 241-T-104

C.1	Sample B1KC36C from Direct-Push Vertical Borehole C4596.....	C.2
C.2	Sample B1KC36B from Direct-Push Vertical Borehole C4596.....	C.3
C.3	Sample B1KC36A from Direct-Push Vertical Borehole C4596.....	C.4
C.4	Sample B1KC36 from Direct-Push Vertical Borehole C4596.....	C.5
C.5	Sample B1KC35B from Direct-Push Vertical Borehole C4598.....	C.6
C.6	Sample B1KC35A from Direct-Push Vertical Borehole C4598.....	C.7
C.7	Sample B1KC40C from Direct-Push Vertical Borehole C5374.....	C.8
C.8	Sample B1KC40B from Direct-Push Vertical Borehole C5374.....	C.9
C.9	Sample B1KC40A from Direct-Push Vertical Borehole C5374.....	C.10
C.10	Sample B1KC40 from Direct-Push Vertical Borehole C5374.....	C.11
C.11	Sample B1KC37C from Direct-Push Vertical Borehole C5378.....	C.12
C.12	Sample B1KC37B from Direct-Push Vertical Borehole C5378.....	C.13
C.13	Sample B1KC37A from Direct-Push Vertical Borehole C5378.....	C.14
C.14	Sample B1KC38B from Direct-Push Vertical Borehole C5378.....	C.15
C.15	Sample B1KC38B from Direct-Push Vertical Borehole C5378.....	C.16
C.16	Sample B1KC38A from Direct-Push Vertical Borehole C5378.....	C.17
C.17	Sample B1KC38 from Direct-Push Vertical Borehole C5378.....	C.18
C.18	Sample B1LB08C from Direct-Push Vertical Borehole C5380.....	C.19
C.19	Sample B1LB08B from Direct-Push Vertical Borehole C5380.....	C.20
C.20	Sample B1LB08A from Direct-Push Vertical Borehole C5380.....	C.21
C.21	Sample B1LB08 from Direct-Push Vertical Borehole C5380.....	C.22
C.22	Sample B1LB07C from Direct-Push Vertical Borehole C5382.....	C.23
C.23	Sample B1LB07B from Direct-Push Vertical Borehole C5382.....	C.24
C.24	Sample B1LB07A from Direct-Push Vertical Borehole C5382.....	C.25
C.25	Sample B1KC39C from Direct-Push Vertical Borehole C5384.....	C.26
C.26	Sample B1KC39B from Direct-Push Vertical Borehole C5384.....	C.27
C.27	Sample B1KC39A from Direct-Push Vertical Borehole C5384.....	C.28
C.28	Sample B1KC39 from Direct-Push Vertical Borehole C5384.....	C.29



Figure C.1. Sample B1KC36C from Direct-Push Vertical Borehole C4596



**Figure C.2.** Sample B1KC36B from Direct-Push Vertical Borehole C4596



Figure C.3. Sample B1KC36A from Direct-Push Vertical Borehole C4596



**Figure C.4.** Sample B1KC36 from Direct-Push Vertical Borehole C4596



Figure C.5. Sample B1KC35B from Direct-Push Vertical Borehole C4598



Figure C.6. Sample B1KC35A from Direct-Push Vertical Borehole C4598



Figure C.7. Sample B1KC40C from Direct-Push Vertical Borehole C5374



Figure C.8. Sample B1KC40B from Direct-Push Vertical Borehole C5374



Figure C.9. Sample B1KC40A from Direct-Push Vertical Borehole C5374



**Figure C.10.** Sample B1KC40 from Direct-Push Vertical Borehole C5374



Figure C.11. Sample B1KC37C from Direct-Push Vertical Borehole C5378



Figure C.12. Sample B1KC37B from Direct-Push Vertical Borehole C5378



Figure C.13. Sample B1KC37A from Direct-Push Vertical Borehole C5378



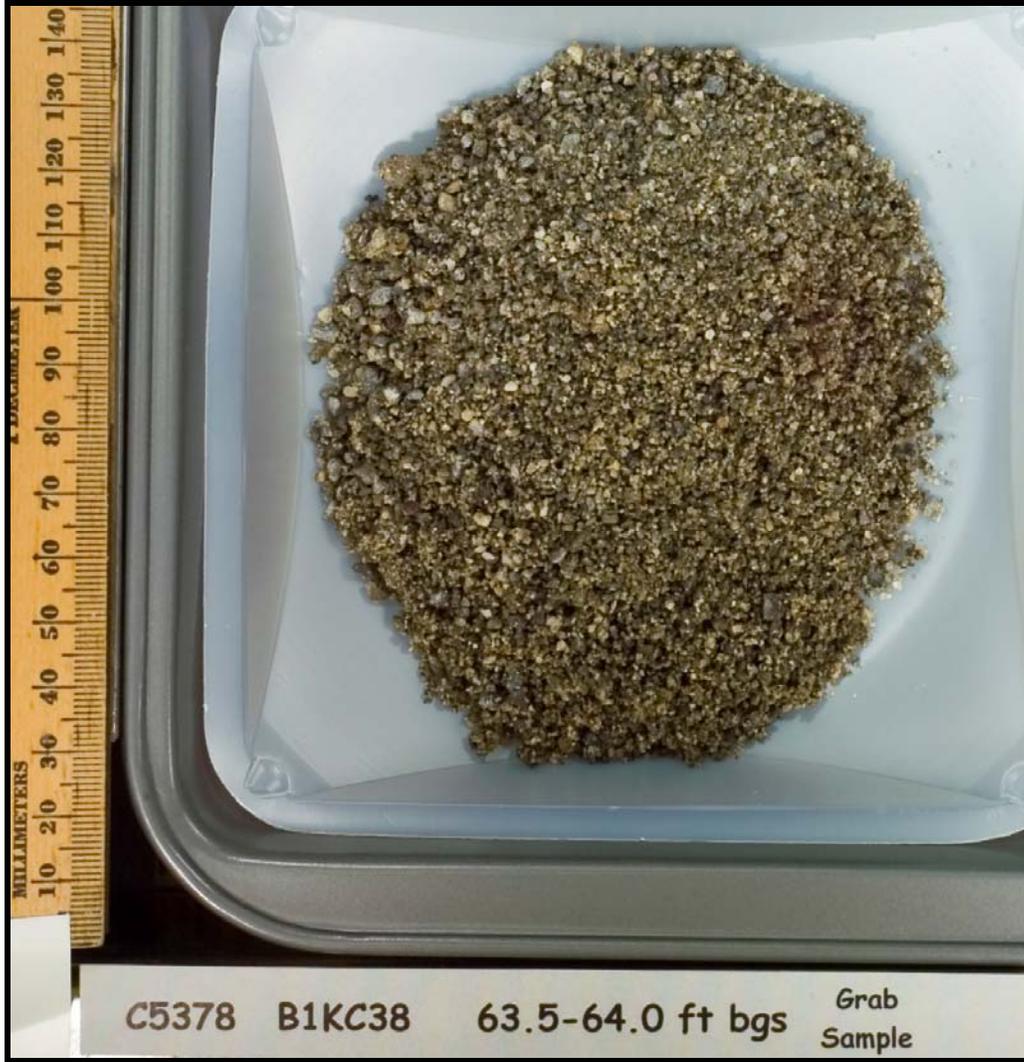
Figure C.14. Sample B1KC38B from Direct-Push Vertical Borehole C5378



**Figure C.15.** Sample B1KC38B from Direct-Push Vertical Borehole C5378



Figure C.16. Sample B1KC38A from Direct-Push Vertical Borehole C5378



**Figure C.17.** Sample B1KC38 from Direct-Push Vertical Borehole C5378



Figure C.18. Sample B1LB08C from Direct-Push Vertical Borehole C5380



Figure C.19. Sample B1LB08B from Direct-Push Vertical Borehole C5380



Figure C.20. Sample B1LB08A from Direct-Push Vertical Borehole C5380



Figure C.21. Sample B1LB08 from Direct-Push Vertical Borehole C5380



Figure C.22. Sample B1LB07C from Direct-Push Vertical Borehole C5382



Figure C.23. Sample B1LB07B from Direct-Push Vertical Borehole C5382



Figure C.24. Sample B1LB07A from Direct-Push Vertical Borehole C5382



Figure C.25. Sample B1KC39C from Direct-Push Vertical Borehole C5384



Figure C.26. Sample B1KC39B from Direct-Push Vertical Borehole C5384



Figure C.27. Sample B1KC39A from Direct-Push Vertical Borehole C5384



**Figure C.28.** Sample B1KC39 from Direct-Push Vertical Borehole C5384



## **Appendix D**

**Logs of Core and Grab Samples from the Direct Push Boreholes in  
the Vicinity of Single Shell Tanks 241-T-101 and 241-T-104**



## Appendix D

### Logs of Core and Grab Samples from the Direct Push Boreholes in the Vicinity of Single Shell Tanks 241-T-101 and 241-T-104

D.1	Core Log for Direct-Push Vertical Borehole C4596.....	D.2
D.2	Core Log for Direct-Push Vertical Borehole C4598.....	D.3
D.3	Core Log for Direct-Push Vertical Borehole C5374.....	D.4
D.4	Core Log for Direct-Push Vertical Borehole C5378.....	D.5
D.5	Core Log for Direct-Push Vertical Borehole C5380.....	D.6
D.6	Core Log for Direct-Push Vertical Borehole C5382.....	D.7
D.7	Core Log for Direct-Push Vertical Borehole C5384.....	D.8

Pacific Northwest National Laboratory		<b>CORE LOG</b>		Boring/Well No <u>C4596</u>	Depth <u>47.0-49.2</u>	Date <u>12-5-06</u>	Sheet <u>1</u> of <u>1</u>				
Logged by <u>B N Bjornstad</u>				Location <u>T Tank Farm</u>		Project <u>Vadose Zone</u>					
Reviewed by _____				Date _____		Drilling Contractor _____					
Lithologic Class. Scheme _____				Procedure _____		Rev _____					
				Driller _____		Drill Method <u>Compenetrometer/direct push</u>					
DEPTH ( )	SAMPLES		MOIS- TURE	GRAPHIC LOG			LITHOLOGIC DESCRIPTION <small>(particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, maximum grain size, consolidation, structure, etc.)</small>	COMMENTS			
	TYPE	ID NUMBER		C	Z	S			G		
47	core	BIKC36C	SM				S, 50% crs, 50% med. grained, well sorted, loose, 25-35% basalt, 2.5-7/2 (lt. gray), lgst clast = crs. sand, wk. mod. rxn. w/ HCl	6" long, 1.5" dia stainless-steel liners - direct push High rad internal			
		36B									
48		36A	M							S, mostly fn sand, laminated, sl. compact, 2.5-6/4 (lt. yellowish brown), well sorted, mod. rxn w/ HCl	
		36	SM								
	grab	36						Poly bottle grab sample			
49											

W = Wet, M = Moist, SM = Slightly Moist, D = Dry

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Figure D.1. Core Log for Direct-Push Vertical Borehole C4596

Pacific Northwest National Laboratory		<b>CORE LOG</b>		Boring/Well No <u>C4598</u>	Depth <u>43.0-43.5</u>	Date <u>12-5-06</u>	Sheet <u>1</u> of <u>1</u>	
Logged by <u>B.A. Bjornstad</u>				Location <u>T Tank Farm</u>		Project <u>T Farm Vadose Zone</u>		
Reviewed by _____				Date _____		Drilling Contractor _____		
Lithologic Class. Scheme _____				Procedure _____		Rev _____		
				Driller _____		Drill Method <u>Cone penetrometer/direct push</u>		
DEPTH ( )	SAMPLES		MOIS- TURE	GRAPHIC LOG			LITHOLOGIC DESCRIPTION <small>(particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, maximum grain size, consolidation, structure, etc.)</small>	COMMENTS
	TYPE	ID NUMBER		C	Z	S		
43		BIK35B						6" long, 1.5" dia. stainless steel liners - direct push
	core	↓	D	↑				35B only contained ~ 2" inches sediment
		BIK35A					m/s, muddy, pebbly sand, v. poorly sorted, 2.5 y 8/2 (white), slough? (g/s, slightly pebbly sand, sand mostly coarse grained, 20-30% basalt, loose, mod. sorted, lgt clast = sm. pebble, 2.5 y 7/2 (lt. gray), wk rxn w/ HCl	
44								

W = Wet, M = Moist, SM = Slightly Moist, D = Dry

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Figure D.2. Core Log for Direct-Push Vertical Borehole C4598

Pacific Northwest National Laboratory		<b>CORE LOG</b>		Boring/Well No <u>C5374</u>	Depth <u>80-82</u>	Date <u>12-5-06</u>	Sheet <u>1</u> of <u>1</u>
Logged by <u>R N Bjornstad</u>				Location <u>T Tank Farm</u>		Project <u>Vadose Zone</u>	
Reviewed by _____				Date _____		Drilling Contractor _____	
Lithologic Class. Scheme _____				Procedure _____		Rev _____	
						Driller _____	
						Drill Method <u>Cone penetrometer direct push</u>	

DEPTH ( )	SAMPLES		MOIS- TURE	GRAPHIC LOG				LITHOLOGIC DESCRIPTION <small>(particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, maximum grain size, consolidation, structure, etc.)</small>	COMMENTS
	TYPE	ID NUMBER		C	Z	S	G		
80	Core	BIK40C	M					ZS, silty fn sand, v. well sorted, micaceous, wkly laminated, 2.5Y6/4 (lt. yellowish brn), compact and cohesive, 20% silt? 80% fn sand, strong rxn w/HCl (calcareous) max part. size = fn sand	6" long, 1.5" dia stainless steel liners - direct push
		↓ 40B						more silt (30-40%?), more compact and cohesive, massive, calcareous	
81		↓ 40A						sharp contact	
	grab	↓ 40	SM					S, fn-md, well sorted, sl. compact, 2.5Y7/2 (lt. gray), laminated, micaceous, lgst part. size = md sand, md sand, well sorted, 2.5Y7/4 (pale yellow), loose,	Poly bottle grab sample
82		↓							

W = Wet, M = Moist, SM = Slightly Moist, D = Dry

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**Figure D.3.** Core Log for Direct-Push Vertical Borehole C5374

Pacific Northwest National Laboratory		CORE LOG		Boring/Well No	Depth	Date	Sheet		
				C5378	46.0-63.5	12-5-06	1 of 1		
				Location	Project				
				T Tank Farm	Vadose Zone				
Logged by				Drilling Contractor					
B N Bjornstad									
Reviewed by				Driller					
Lithologic Class. Scheme				Procedure		Rev			
						Cone penetrometer direct push			
DEPTH ( )	SAMPLES		MOIS- TURE	GRAPHIC LOG				LITHOLOGIC DESCRIPTION (particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, maximum grain size, consolidation, structure, etc.)	COMMENTS
	TYPE	ID NUMBER		C	Z	S	G		
45	core	BIKC37C		Empty				S, mostly medium, mod. sorted, sl. compact, wkly laminated, 1st clast = crs sand, 2.5x6/4 (lt. yellowish brown), coarsens toward bottom, 20-30% basalt at top increases to 30-40% downward, wk-mod. rxn w/ HCl.	6" long, 1.5" dia. stainless steel liners - direct push
		↓	SM						
		37B	↓						
46		↓	↓						
		37A	↓						
		↓		Empty					Bottom of liner empty
				Break					
62	core	BIKC38C	SM					gS, pebbly crs to v. crs. sand, poorly sorted, 15% fn-v. fn pebble 60% crs - v. crs sand, 25% fn-md sand, loose, 1st clast = 1.5 cm, S = 50-60% basalt, G = 80-90% basalt, 2.5x6/2 (lt. brn-ish gray), wk rxn. w/ HCl	
		↓							
		38B							
63		↓							
		38A							
		↓							
	grab	38						S, mostly crs - v. crs, mod. sorted, loose, 2.5x6/2 (lt. brn-ish gray), 40-50% basalt, wk rxn. w/ HCl	Poly bottle grab sample
64	↓	↓	↓						

W = Wet, M = Moist, SM = Slightly Moist, D = Dry

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Figure D.4. Core Log for Direct-Push Vertical Borehole C5378

D.5

Pacific Northwest National Laboratory		<b>CORE LOG</b>			Boring/Well No <u>C5380</u>	Depth <u>50-52'</u>	Date <u>12-5-06</u>	Sheet <u>1</u> of <u>1</u>	
Location <u>T Tank Farm</u>					Project <u>Vadose Zone</u>				
Logged by <u>BN Bjornstad</u>						Drilling Contractor _____			
Reviewed by _____						Date _____			
Lithologic Class. Scheme _____						Procedure _____ Rev _____			
						Drill Method <u>Cone penetrometer direct push</u>			
DEPTH (ft)	SAMPLES		MOIS- TURE	GRAPHIC LOG				LITHOLOGIC DESCRIPTION <small>(particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, maximum grain size, consolidation, structure, etc.)</small>	COMMENTS
	TYPE	ID NUMBER		C	Z	S	G		
50'	core	B12B08C	SM					High rad interval ↓ Poly bottle grab sample	
		↓ 8B							
51'		↓ 8A							
	grab	8							
52'	↓	↓							

W = Wet, M = Moist, SM = Slightly Moist, D = Dry

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Figure D.5. Core Log for Direct-Push Vertical Borehole C5380

Pacific Northwest National Laboratory		<b>CORE LOG</b>			Boring/Well No <u>C5382</u>	Depth <u>78-79.5'</u>	Date <u>12-5-06</u>	Sheet <u>1</u> of <u>1</u>	
Logged by <u>B N Bjornstad</u>					Location <u>T Tank Farm</u>		Project <u>Vadose Zone</u>		
Reviewed by _____					Date _____		Drilling Contractor _____		
Lithologic Class. Scheme _____					Procedure _____		Rev _____		
							Driller _____		
							Drill Method <u>Cone penetrometer direct push</u>		
DEPTH ( )	SAMPLES		MOIS- TURE	GRAPHIC LOG				LITHOLOGIC DESCRIPTION (particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, maximum grain size, consolidation, structure, etc.)	COMMENTS
	TYPE	ID NUMBER		C	Z	S	G		
78	core	B1LB07C	SM	[Hand-drawn lithologic log for sample B1LB07C]				S, md-crs, 60% crs - v. crs sand, 40% fn-md, mod sorted, loose, 30-40% basalt, 2.5Y6/2 (lt. brnsh gray), lgst particle size = v. crs sand, wk-mod rxn w/ HCl	6" long, 1.5" dia stainless-steel liners - direct push
		↓	↓	[Hand-drawn lithologic log for sample 7B]				2S, silty fn sand, v. well sorted, micaceous, cohesive and compact, laminated, 5-10% silt, 2.5Y 7/4 (pale yellow) lgst particle size = med. sand, strong rxn w/ HCl (calcareous)	
79		↓	↓	[Hand-drawn lithologic log for sample 7A]					
		↓	↓	[Hand-drawn lithologic log for sample 7A]					

W = Wet, M = Moist, SM = Slightly Moist, D = Dry

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Figure D.6. Core Log for Direct-Push Vertical Borehole C5382

Pacific Northwest National Laboratory		CORE LOG			Boring/Well No	Depth	Date	Sheet
					C5384	44.0-46.0	12-5-06	1 of 1
Logged by <u>BN Bjornstad</u>					Drilling Contractor _____			
Reviewed by _____					Driller _____			
Lithologic Class. Scheme _____					Drill Method <u>Cone penetrometer direct push</u>			
DEPTH (ft)	SAMPLES		MOISTURE	GRAPHIC LOG			LITHOLOGIC DESCRIPTION (particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, maximum grain size, consolidation, structure, etc.)	COMMENTS
	TYPE	ID NUMBER		C	Z	S		
44	core	81K39C	SM	[Hand-drawn lithologic log showing a column of dots representing sand]			mgS, v. poorly sorted, v. compact = slough? S, md-crs, loose, mod sorted, 2.5 7/2 (lt. gray), msv, 30-40% basalt, WK rxn w/HCl	6" long, 1.5" dia stainless steel liners - direct push
		↓ 39B					50% crs sand, 40% md sand, 10% fin sand	
45		↓ 39A						
		↓ 39					fn sand, 2.5 1/4 (lt. gel. brn), well sorted, mod. rxn w/HCl	
46	grab	↓ 39	↓					Poly bottle grab sample

W - Wet, M - Moist, SM - Slightly Moist, D - Dry

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Figure D.7. Core Log for Direct-Push Vertical Borehole C5384

D.8

## **Appendix E**

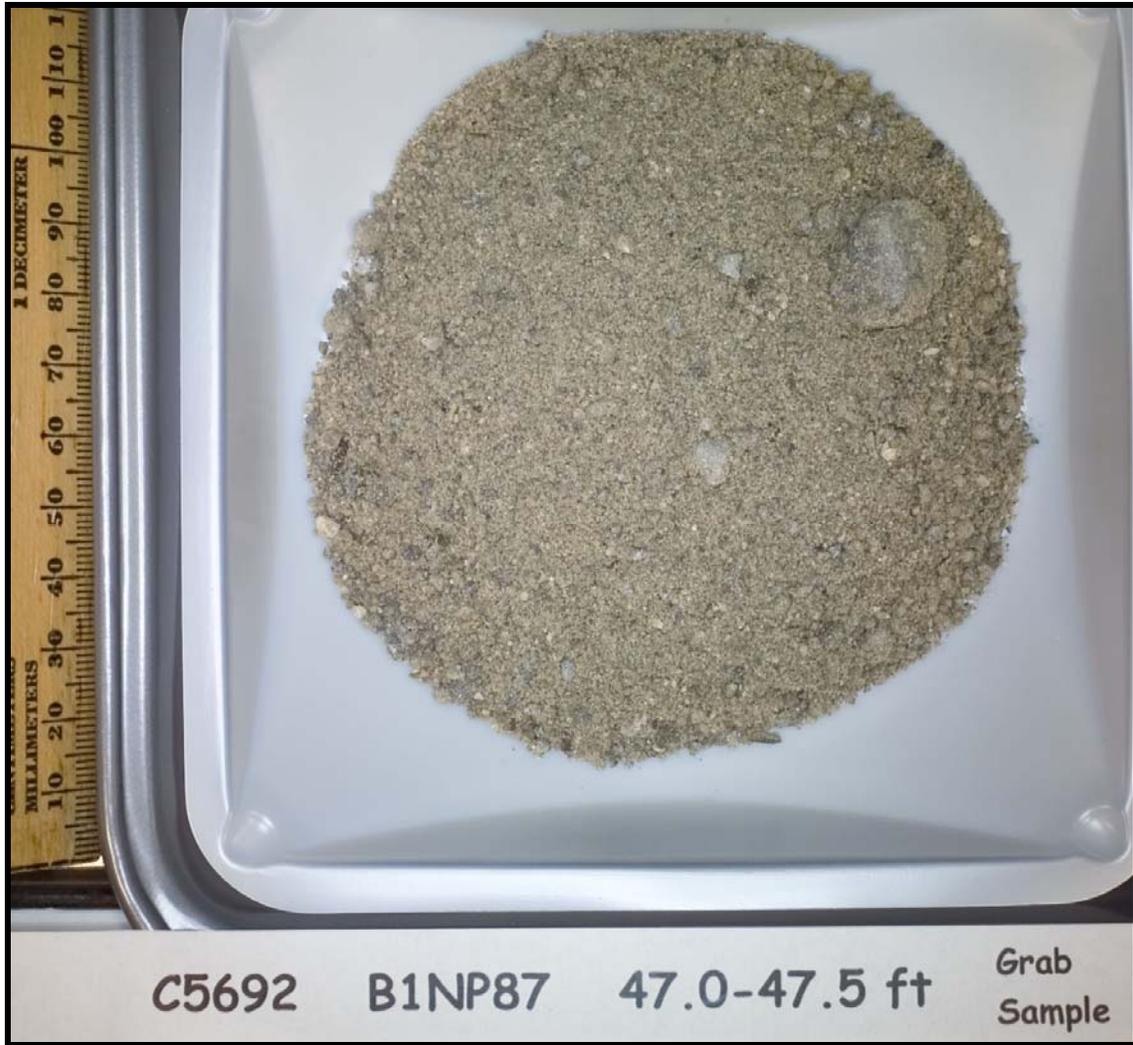
### **Photographs of Core and Grab Samples from the Interim Measures Direct Push Boreholes Collected North of the T Tank Farm**



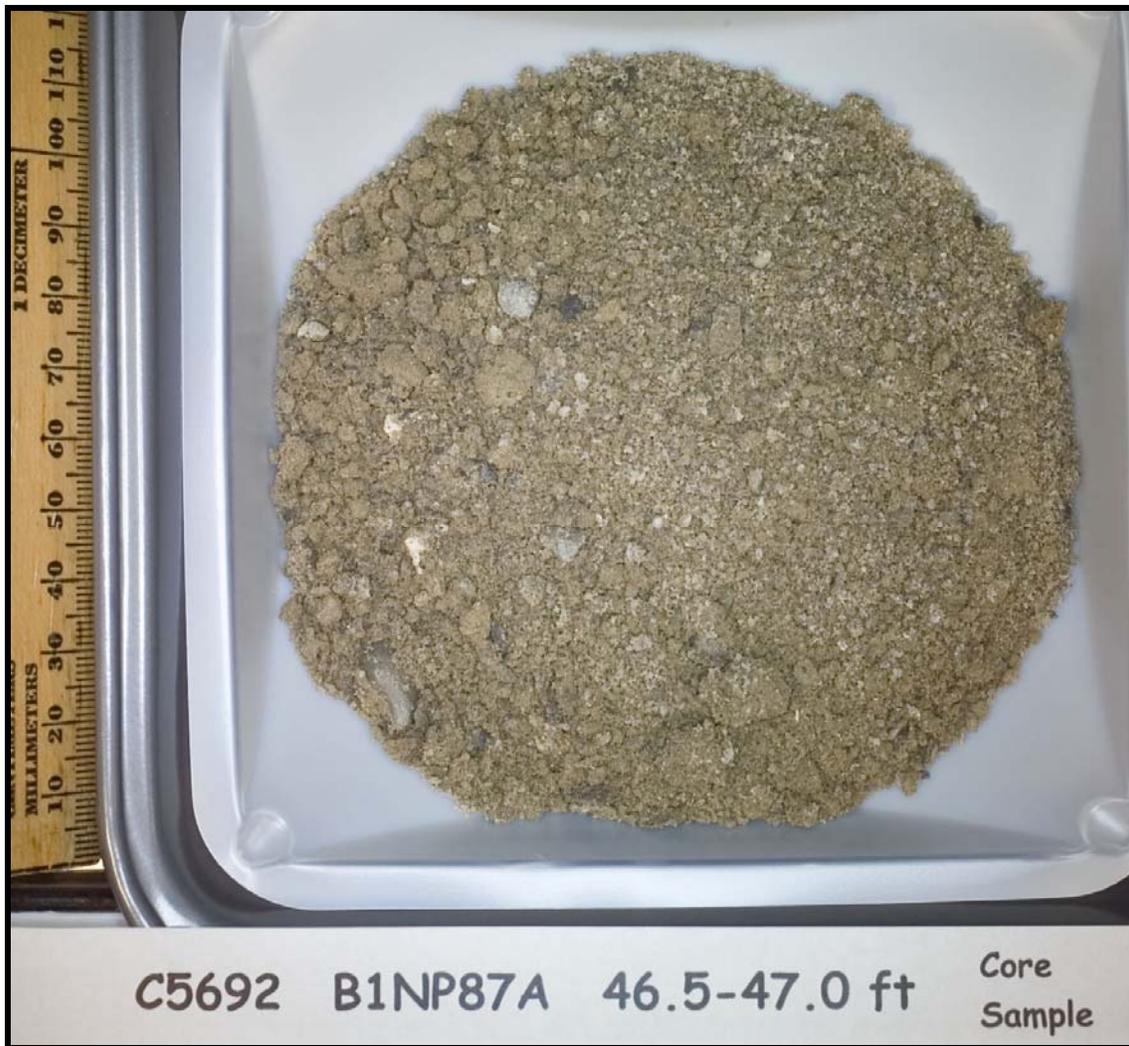
## Appendix E

### Photographs of Core and Grab Samples from the Interim Measures Direct Push Boreholes Collected North of the T Tank Farm

E.1	Sample B1NP87 from Direct-Push Vertical Borehole C5692 .....	E.2
E.2	Sample B1NP87A from Direct-Push Vertical Borehole C5692 .....	E.3
E.3	Sample B1NP87B from Direct-Push Vertical Borehole C5692 .....	E.4
E.4	Sample B1NP87C from Direct-Push Vertical Borehole C5692 .....	E.5
E.5	Sample B1NP90 from Direct-Push Vertical Borehole C5694 .....	E.6
E.6	Sample B1NP90A from Direct-Push Vertical Borehole C5694 .....	E.7
E.7	Sample B1NP90B from Direct-Push Vertical Borehole C5694 .....	E.8
E.8	Sample B1NP90C from Direct-Push Vertical Borehole C5694 .....	E.9



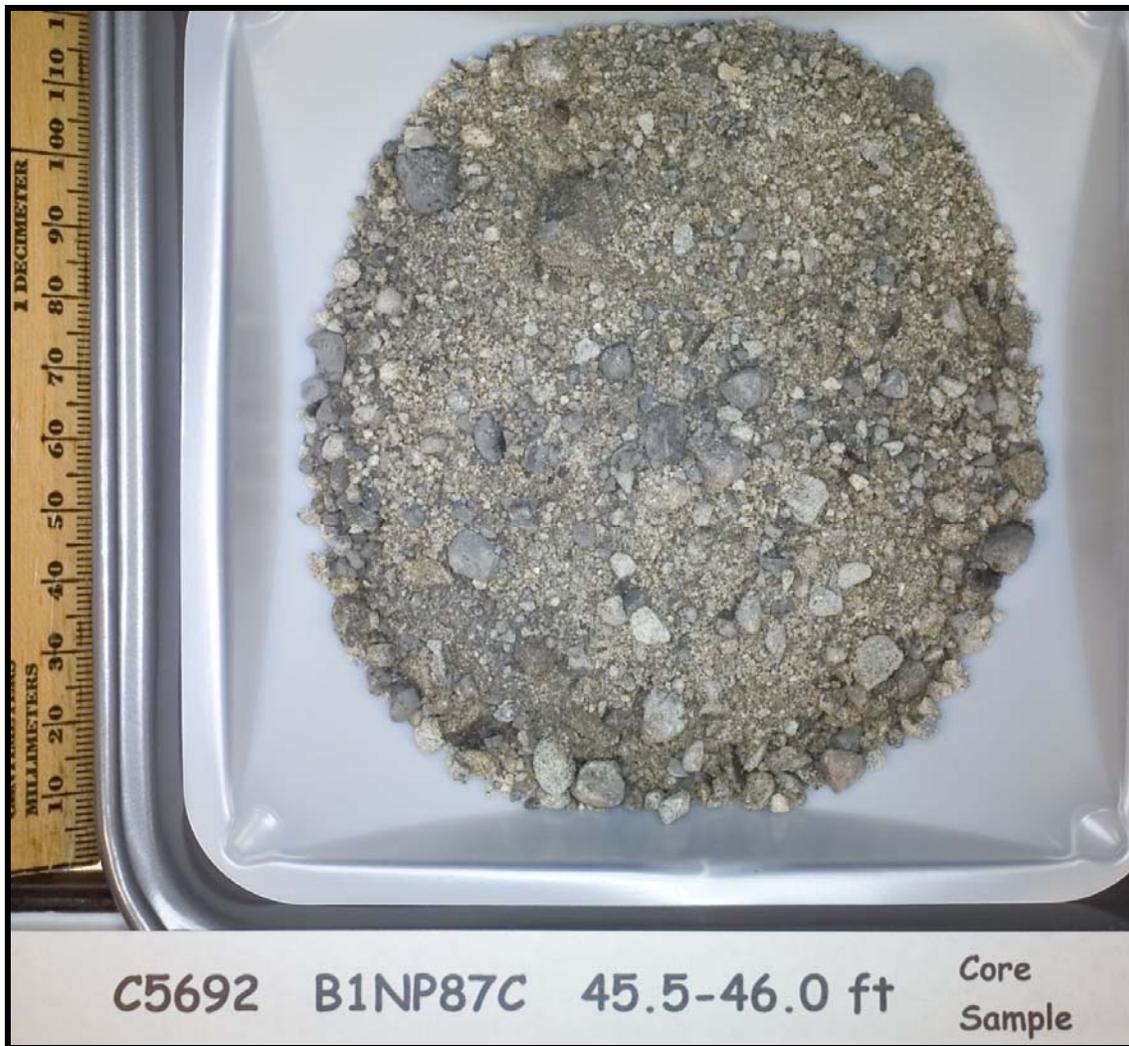
**Figure E.1.** Sample B1NP87 from Direct-Push Vertical Borehole C5692



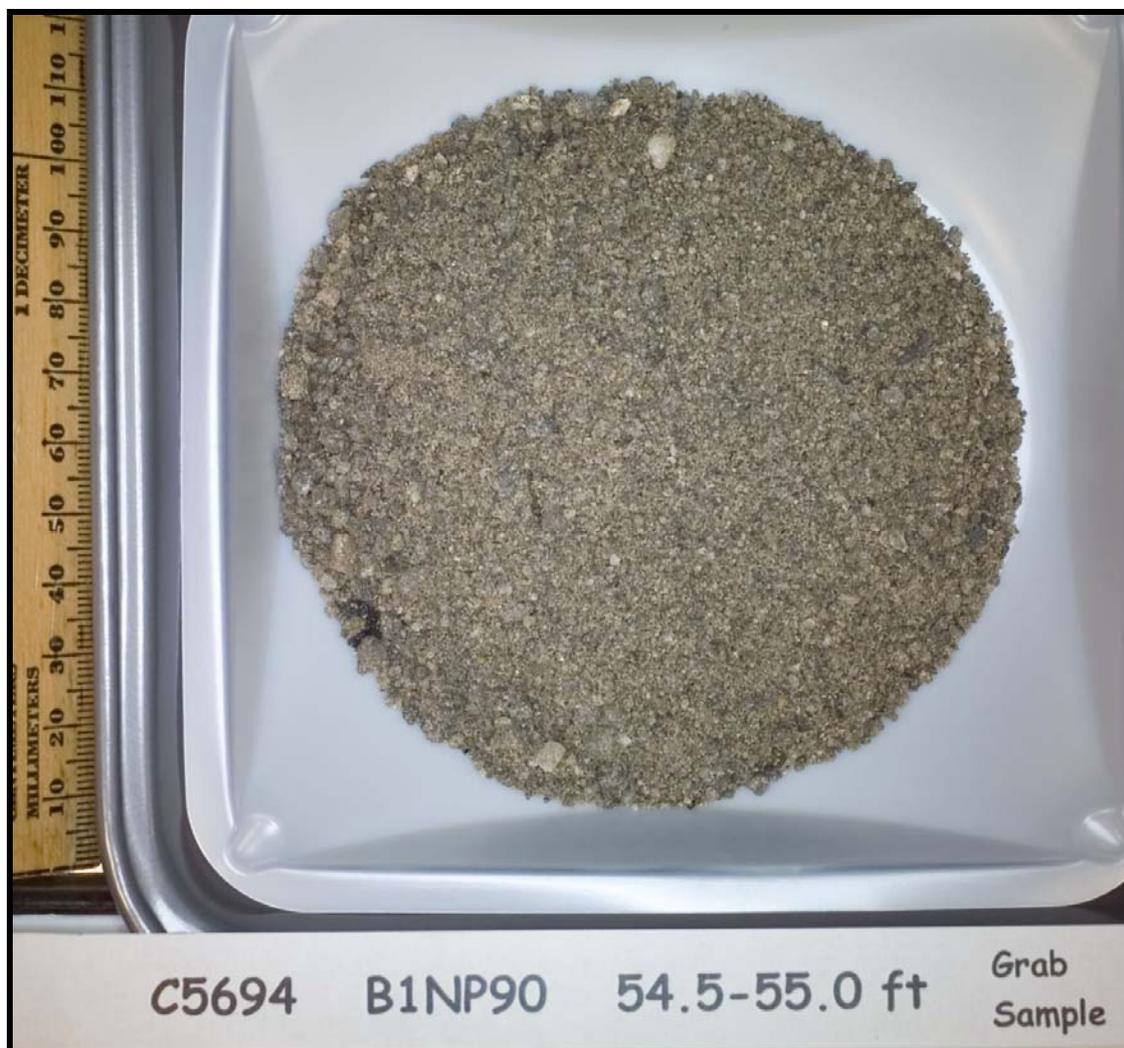
**Figure E.2.** Sample B1NP87A from Direct-Push Vertical Borehole C5692



**Figure E.3.** Sample B1NP87B from Direct-Push Vertical Borehole C5692



**Figure E.4.** Sample B1NP87C from Direct-Push Vertical Borehole C5692



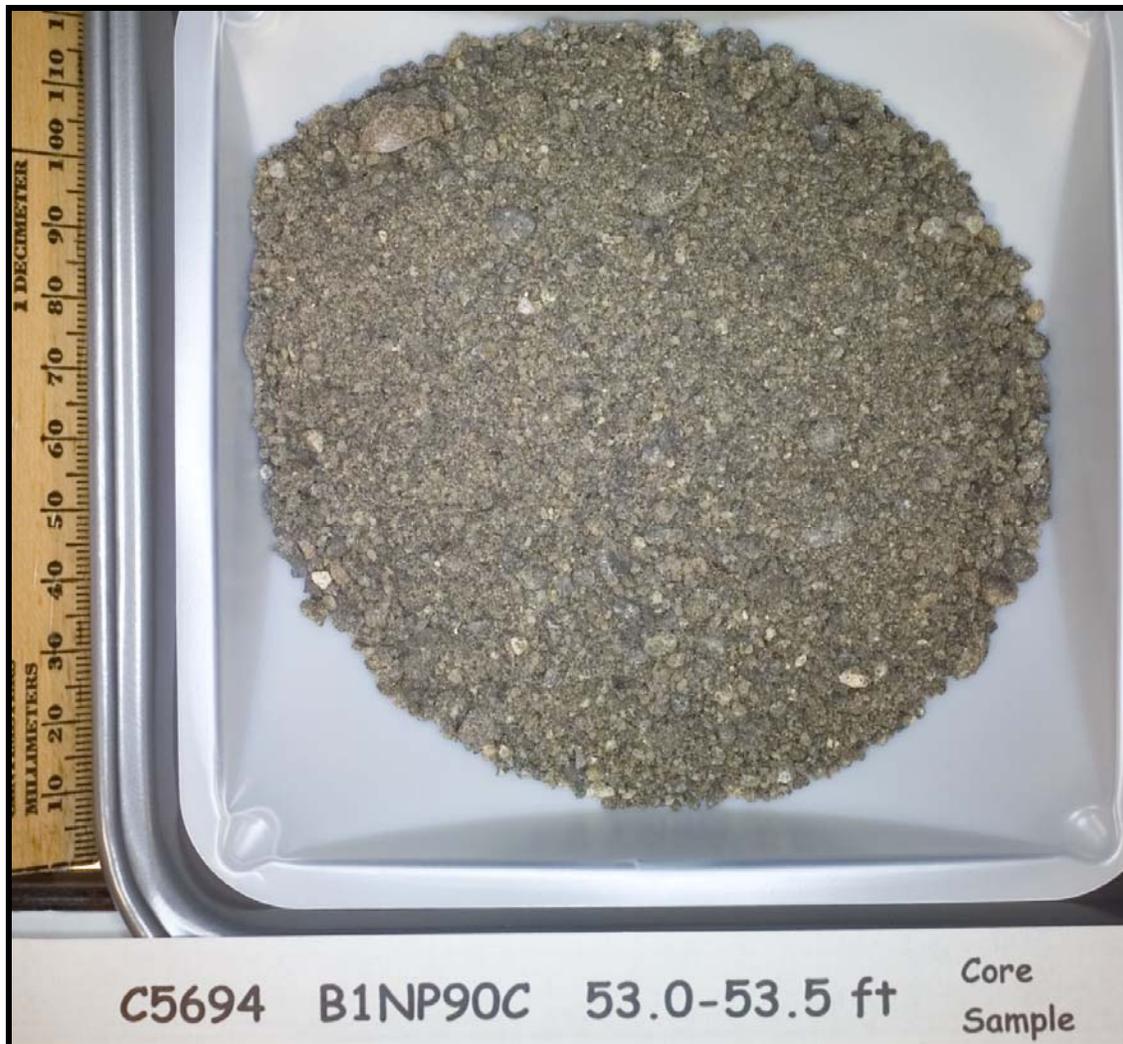
**Figure E.5.** Sample B1NP90 from Direct-Push Vertical Borehole C5694



**Figure E.6.** Sample B1NP90A from Direct-Push Vertical Borehole C5694



**Figure E.7.** Sample B1NP90B from Direct-Push Vertical Borehole C5694



**Figure E.8.** Sample B1NP90C from Direct-Push Vertical Borehole C5694



## **Appendix F**

### **Logs of Core and Grab Samples from the Interim Measures Direct Push Boreholes Emplaced North of the T Tank Farm**



## **Appendix F**

### **Logs of Core and Grab Samples from the Interim Measures Direct Push Boreholes Emplaced North of the T Tank Farm**

F.1	Core Log for Direct-Push Vertical Borehole C5692.....	F.2
F.2	Core Log for Direct-Push Vertical Borehole C5694.....	F.3

Pacific Northwest National Laboratory		<b>CORE LOG</b>		Boring/Well No <u>C5692</u>	Depth <u>45.5-47.5</u>	Date <u>5-30-07</u>	Sheet <u>1 of 1</u>
Location <u>T Tank Farm</u>				Project <u>Vadose Zone</u>			
Logged by <u>B N Bjornstad</u>				Drilling Contractor _____			
Reviewed by _____				Date _____		Driller _____	
Lithologic Class. Scheme _____				Procedure _____		Rev _____	
				Drill Method <u>Cone penetrometer</u>			

DEPTH ( )	SAMPLES		MOIS- TURE	GRAPHIC LOG			LITHOLOGIC DESCRIPTION (particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, maximum grain size, consolidation, structure, etc.)	COMMENTS
	TYPE	ID NUMBER		C	Z	S		
45								
	DP	B1NP87C	D	o	o	o	SG, sandy granule-pebble gravel, 60% fn-crs sand, 35% granule-sm pebble, 5% silt, loose, poorly sorted, 1st clast = 2 cm, S = 30-40% basalt, G = 80-90% basalt, 2.5Y5/2 (grayish brn), most gravel clasts v. angular = crushed during drilling?, wk rxn w/ HCl (g)S, slightly granular-pebble sand, 5-10% granule to sm. pebble, 80-90% fn-crs sand, 5-10% silt, mod. sorted, loose, 1st clast = 2 cm, 2.5Y6/2 (lt. brnish gray), S = 30-40% basalt, wk rxn w/ HCl, siltier and more calcareous (mod rxn w/ HCl) with depth	DP = direct push samples in 1" ± 0.6" long s.s. liners Collected 5-23-07
46	↓	" 87B	↓	o	o	o		
	↓	" 87A	↓	o	o	o		
47	Grab	" 87	↓	o	o	o		

W = Wet, M = Moist, SM = Slightly Moist, D = Dry

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Figure F.1. Core Log for Direct-Push Vertical Borehole C5692

Pacific Northwest National Laboratory		CORE LOG			Boring/Well No	Depth	Date	Sheet
					C5694	53.0-55.0	5-30-07	1 of 1
Logged by		B N Bjornstad			Location		Project	
Reviewed by					T Tank Farm		Vadose Zone	
Lithologic Class. Scheme		Procedure			Rev		Drill Method	
							Cone Penetrometer	
DEPTH ( )	SAMPLES		MOIS- TURE	GRAPHIC LOG			LITHOLOGIC DESCRIPTION (particle size distribution, sorting, mineralogy, roundness, color, reaction to HCl, maximum grain size, consolidation, structure, etc.)	COMMENTS
	TYPE	ID NUMBER		C	Z	S		
53	DP	B1NP90C	D	0	0	0	gS, 30% granule-sm pebbles, 70% fn-v.crs sand, mostly crs sand, loose, S=50-60% basalt, G=80-90% basalt, 2.5YNS/ (gray), lgst clast = 1.0 cm, SA-SR, poorly sorted, wk-mod rxn w/HCl	DP = direct push samples in 1" ID 6" long s.s. liners
		" 90B		0	0	0		
54		" 90A		0	0	0	zgS, 10-20% silt, 60-70% fn-crs sand, 5-10% granule-sm pebble gravel, clumps held together with lt. gel.	Collected 5-29-07
	Grab	" 90		0	0	0	brn silt, poorly sorted, lgst clast = 0.5 cm, mod. rxn w/HCl	
55				0	0	0	gS, 20-25% granule to sm pebble, 70% fn-crs sand (mostly mid-crs), 5% silt, loose, mod. sorted, S=30-40% basalt, G=60-70% basalt, tr. caliche clasts, 2.5Y5/2 (grayish brn), SA-SR, mod. rxn w/HCl	

W = Wet, M = Moist, SM = Slightly Moist, D = Dry

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Figure F.2. Core Log for Direct-Push Vertical Borehole C5694



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W. Um	P7-22
M. M. Valenta	P7-22
J. M. Zachara	K8-96
Hanford Technical Library (2)	P8-55