3.1 Vadose Zone Characterization

D. G. Horton

This section describes significant vadose zone characterization activities that occurred during fiscal year 2003. These characterization activities were done to further the understanding of physical and chemical properties of the vadose zone and to define existing vadose zone contamination. During the year, soil-vapor sampling and analysis, geophysical logging, and laboratory analysis of chemical and radiological contaminants in soil samples were done to characterize existing vadose zone contaminant plumes and help plan future remedial actions.

Characterization activities further the understanding of physical and chemical properties of the vadose zone.

During fiscal year 2003, baseline spectral gamma logging and neutron moisture logging of boreholes continued at selected past-practice, liquid disposal facilities. The results of this characterization will provide a baseline against which to compare subsequent logging events to monitor for subsurface contaminant movement.

The results of extensive geochemical characterization of core samples from Waste Management Area TX-TY became available in fiscal year 2003. These data allow comparison of contaminated vadose zone sediment with uncontaminated sediment and descriptions of contaminant plumes beneath the single-shell tanks in the vicinity of the boreholes. In addition, two boreholes were drilled and sampled at Waste Management Area T. Those results will become available in fiscal year 2004.

Soil-vapor sampling and analysis were done as part of the remedial investigation for the 200-PW-1 Operable Unit. This activity was done to locate carbon tetrachloride release sites with the potential to impact groundwater in the future. Also, boreholes and test pits were excavated to gather characterization data to support remediation of past-practice liquid disposal facilities in the 200-CS-1 Operable Unit.

Finally, laboratory experiments were completed to help predict the movement of uranium in the vadose zone at water sites in the Hanford Site 300 Area.

3.1.1 Tank Farm Characterization

D. A. Myers, D. G. Horton, S. P. Reidel, R. J. Serne, and K. D. Reynolds

Vadose zone characterization activities at single-shell tank farms in fiscal year 2003 were concentrated at the T, TX, and TY Tank Farms in the 200 West Area. Two new boreholes were drilled at Waste Management Area T through subsurface contaminated soil. Also, data became available from three boreholes drilled in 2002 through subsurface contamination at Waste Management Area TX-TY. A summary of available information is presented in this section.

Boreholes were drilled near tank farms to help locate contamination in the vadose zone. Samples were collected and geophysical logs were run.

Also, during fiscal year 2003, the Tank Farm Vadose Zone Project published an in-depth report, *Field Investigation Report for Waste Management Area B-BX-BY* (RPP-10098). This report documents the extensive investigation of subsurface contamination and includes significant new work on the mobility of contaminants in the Hanford Site subsurface. Major conclusions from this report are summarized in this section. This report is a joint work of CH2M HILL Hanford Group, Inc. and numerous outside collaborators including Fluor Hanford, Inc.; Pacific Northwest National Laboratory; Lawrence Livermore National Laboratory; Oak Ridge National Laboratory; and contributors from numerous universities.

3.1.1.1 Characterization at Waste Management Area T

The CH2M HILL Hanford Group Vadose Zone Project advanced two characterization boreholes (C4104 and C4105) in the T Tank Farm. The boreholes were placed in the

vicinity of tank T-106, the site of the largest documented tank leak in the Hanford Site's history. Tank T-106 lost 435,300 liters of liquid in early 1973. The boreholes advanced and sampled during fiscal year 2003 were designed to provide additional information on the movement and fate of contaminants released during the 1973 leak.

Because these boreholes had a finite probability of intersecting highly concentrated contamination, the boreholes were advanced using a closed-end driven casing. Pre-selected intervals were sampled by driving a split-spoon sampler through the end and ahead of the driven casing. This drilling method successfully advanced borehole C4104 to 38.85 meters below ground surface and borehole C4105 to a depth of 39.89 meters. Advancement of both boreholes was halted within the Ringold Formation when the casings could be driven no further. A total of 21 and 22 samples, respectively, were retrieved and submitted for radiological, chemical, and geochemical analyses. Result of the laboratory analyses will become available in fiscal year 2004 and will be summarized in the next annual groundwater report.

Both characterization boreholes were geophysically logged with a spectral gamma tool. Cesium-137, europium-154, europium-152, tin-126, and cobalt-60 were the manmade radionuclides detected in borehole C4104. Cesium-137, cobalt-60, and europium-154 were the manmade radioisotopes detected in borehole C4105. Table 3.1-1 summarizes the logging results.

3.1.1.2 Characterization at Waste Management Area TX-TY

The CH2M HILL Hanford Group Vadose Zone Project advanced three characterization boreholes (C3830, C3831, and C3832) in the TX Tank Farm in fiscal year 2002. Data from these boreholes became available in fiscal year 2003. Borehole C3830 was drilled to investigate the largest and deepest occurrence of uranium in Waste Management Area TX-TY that is associated with a 1977 leak from tank TX-105. Boreholes C3831 and C3832 were drilled to investigate vadose zone contamination related to a 1984 leak from tank TX-107 in the southwest part of the tank farm.

Advancement of all three boreholes was halted within the Ringold Formation when the casings could be driven no further. Eighteen cores (36 samples) were retrieved from borehole C3830 between depths of 4.54 and 34.6 meters, 20 cores (40 samples) were retrieved from borehole C3831 between depths of 4.54 and 34.77 meters, and 19 cores (38 samples) were obtained from borehole C3832 between depths of 4.94 and 34.89 meters. All cores were submitted for radiological, chemical, and geochemical analyses. A summary of those analyses is presented below.

The magnitude of contamination found in the three boreholes at the TX Tank Farm is not as great as that found in boreholes at other tank farms.

All three characterization boreholes were geophysically logged with a spectral gamma tool. Cesium-137 was the only manmade radionuclide positively identified in borehole C3830; whereas, cesium-137 and cobalt-60 were found in borehole C3831; and cesium-137, cobalt-60, and uranium-238 were found in borehole C3832. Table 3.1-1 summarizes the logging results.

Of the geochemical parameters measured in core samples, pH, electrical conductivity, and concentrations of nitrate, sodium, uranium, and technetium-99 in water extracts are the main indicators of vadose zone contamination. Based on evaluation of these measurements, the borehole data from the TX Tank Farm do not establish the vertical extent of tank contamination, especially in boreholes C3831 and C3832, because contamination was found at the bottom of the boreholes.

The magnitude of contamination found in the three boreholes at the TX Tank Farm is not as great as that found in boreholes at other tank farms. (See Section 3.1 in PNNL-13788 for a summary of contaminants in S and SX Tank Farm boreholes and Section 3.1 in PNNL-14187 for a summary of contaminants in B, BX, and BY Tank Farm boreholes.) Of the three boreholes examined from the TX Tank Farm, borehole C3831 contains the largest amount of contaminants. Figure 3.1-1 shows the depth distribution of pH and electrical

conductivity in borehole C3831. For comparison, Figure 3.1-1 also shows data from a nearby uncontaminated well (well 299-W10-27, located east of the TY Tank Farm) and from a highly contaminated well (299-W23-19, located in the south part of the SX Tank Farm). Figure 3.1-2 shows concentrations of technetium-99, sodium, and nitrate in all three characterization boreholes and a highly contaminated borehole at Waste Management Area S-SX.

Because the amount of contamination in the boreholes at the TX Tank Farm is small, the usual indicators of vadose zone contamination (moisture content, pH, electrical conductivity) do not correlate well with zones containing elevated technetium-99, nitrate, sodium, and uranium concentrations.

The moisture content is a direct measure of the mass of fluid in the vadose zone sediment and an increased moisture content, over background values, should represent leaked tank fluids. This does not appear to be the case for samples from the TX Tank Farm boreholes, where higher moisture contents appear more indicative of grain size than contamination.

If it is assumed that tank fluids are generally caustic (often very caustic with >1 M free hydroxide), elevated pH profiles should be indicative of zones of sediment that have been affected by leaked fluids. The pH profile for sediment from borehole C3831 (Figure 3.1-1) shows only slightly elevated pH at 18.6 meters below ground surface, suggesting possible interactions with alkaline tank fluids. This zone also shows relatively high technetium-99, nitrate, and sodium concentrations (Figure 3.1-2). The zone at about 18.5 meters correlates to a clastic dike mapped at a depth of 18.3 to 18.6 meters. The pH data at all other depths in borehole C3831 and at all depths in boreholes C3830 and C3832 show a slight increase over the pH in the uncontaminated borehole (299-W10-27) but do not suggest strong interactions with tank liquids as do the pH values from the highly contaminated borehole (299-W23-19) at the SX Tank Farm.

Electrical conductivity versus depth for the three boreholes from TX Tank Farm is elevated compared to the electrical conductivity of the nearby uncontaminated borehole 299-W10-27 (Figure 3.1-1). However, except for the contaminated sample associated with the clastic dike in borehole C3831, none of the boreholes at the TX Tank Farm show high electrical conductivity indicative of highly contaminated sediment.

Figure 3.1-2 shows the distribution of contaminants with depth for the boreholes at the TX Tank Farm. The highest contamination is associated with the clastic dike identified at a depth of 18.3 meters in borehole C3831. Contamination at all other depths in borehole C3831 and at all depths in the other two boreholes at the TX Tank Farm is much less than that found in highly contaminated vadose zone sediment (compare with well 299-W23-19, Figure 3.1-2).

3.1.1.3 Summary of Significant Findings from the Field Investigation Report for Waste Management Area B-BX-BY

The field investigation report for Waste Management Area B-BX-BY was published in 2003 to fulfill Tri-Party Agreement milestone M-45-55-T02.

The *Field Investigation Report for Waste Management Area B-BX-BY* (RPP-10098) was prepared for the *Resource Conservation and Recovery Act* (RCRA) Corrective Action Program for single-shell tank farms at the U.S. Department of Energy (DOE) Hanford Site. The DOE Office of River Protection initiated the RCRA Corrective Action Program to investigate the nature and extent of contamination and the associated risk of past and potential future tank waste releases to the environment.

The purpose of the B-BX-BY report (RPP-10098) is to:

- Summarize data and evaluations from the site-specific field investigation activities at Waste Management Area B-BX-BY and from other information sources.
- Evaluate the data to determine the potential risk associated with hypothetical exposure to soil and groundwater at the waste management area boundary.

- Recommend one or more interim measures to mitigate the risk or initiate an accelerated corrective measures study to evaluate and compare more complex interim corrective measures, if the potential for near-term risk is excessive.
- Collect data to support waste retrieval and closure of single-shell tanks.

The future impact from waste currently in the vadose zone is not expected to exceed drinking water standards in groundwater.

Major conclusions from the report (RPP-10098) are summarized below:

- The future impact from waste currently in the vadose zone that resulted from past releases from the B, BX, and BY Tank Farms is not expected to exceed drinking water standards in groundwater at or beyond the boundary of the waste management area as long as high-volume liquid discharges to the vadose zone are eliminated. However, high technetium-99 concentrations in groundwater measured east of the BX Tank Farm is most likely due to releases from the tank farm.
- Vadose zone contamination levels were lower than generally anticipated prior to the initiation of the field investigation.
- Estimates of technetium-99 distribution during Hanford Site reprocessing, storage, and disposal and the residue left in the vadose zone have been improved and past assumptions corrected. However, the amount of technetium-99 that was initially discharged to the vadose zone and that has already reached groundwater and may reach groundwater in the future is uncertain.
- Complex hydraulic processes play a major role in contaminant movement in Waste Management Area B-BX-BY. Strong evidence exists of extensive lateral migration in the vadose zone at the waste management area. Lateral migration may have extended into Waste Management Area B-BX-BY from adjacent past-practice discharge sites. Ponding of runoff from natural precipitation in the waste management area may have added significant amounts of spatially confined infiltration.
- Borehole soil characterization performed by the Tank Farm Vadose Zone Project and other laboratory measurements by the Groundwater Remediation Project's science and technology tasks have identified precipitated uranium and strontium-90 phases and sorption sites for uranium and strontium-90 (see PNNL-14187, Section 3.1.2). These data indicate limited future mobility unless abnormally high amounts of infiltration occur. Neither uranium nor strontium-90 is expected to significantly impact groundwater in the current moisture and geochemical environment. However, the precipitated uranium phases may function as a long-term source to percolating water if recharge is not controlled.
- Interim measures (e.g., capping boreholes, cutting off inactive water lines, and building surface run-on barriers and diversions) have been implemented in the waste management area. These are expected to mitigate future contamination risks.

3.1.2 Borehole Geophysics for Vadose Zone Characterization

R. G. McCain

The S.M. Stoller Corporation is responsible for borehole geophysical logging at the Hanford Site. Borehole logging equipment currently in use for vadose zone characterization at the Hanford Site includes the spectral gamma logging system and the neutron moisture logging system. An additional logging system, the radionuclide assessment system, was developed and deployed specifically for monitoring operations in tank farms. Those activities are discussed in Section 3.2.3.

The spectral gamma logging system uses a cryogenically-cooled, high-purity germanium detector to detect, identify, and quantify gamma emitting radionuclides in

the subsurface. Identification of naturally occurring and manmade radionuclides is based on detection of gamma rays that are characteristic of specific radionuclides. A variation of the spectral gamma logging system, known as the high-rate logging system, uses a much smaller detector than the spectral gamma logging system and can collect log data in zones of very high gamma activity where the spectral gamma logging detector is saturated. When used in combination, the spectral gamma logging system and high-rate logging system provide a measurement capability from about 0.1 to 10^9 pCi/g cesium-137.

The neutron moisture logging system uses a 50 mCi americium/beryllium source and helium-3 detector. Neutrons emitted from the source bombard the surrounding formation and are scattered back to the detector. In geologic media, the dominant mechanism for neutron scattering is interaction with hydrogen atoms, and the count rate at the detector is a function of the amount of hydrogen in the formation, which is generally an indicator of the moisture content. Logs from a neutron moisture logging system are useful as an indication of in situ moisture content and for stratigraphic correlation.

Characterization activities are now underway at past-practice disposal sites in the Hanford 200 Areas. Log data and reports are accessible via the internet at http://www.gjo.doe.gov/programs/hanf/HTFVZ.html.

Vadose Zone Baseline Characterization in Past-Practice Disposal Facilities. The baseline characterization project for past-practice disposal sites in the Hanford 200 Areas is an extension of the Hanford Tank Farm Vadose Zone Project. Beginning in 2001, spectral gamma logs were collected in existing boreholes associated with past-practice disposal sites in the Hanford 200 Areas. Characterization began in the 200 East Area with a report on the logging results from the 216-B-35 to 216-B-42 trenches, located west of the BX Tank Farm (GJO-2002-322-TAR). This was followed by reports on the 216-B-8 crib and adjacent sites (GJO-2002-343-TAR); the 216-B-5 injection well and 216-B-9 crib and tile field (GJO-2002-358-TAC); and the 216-B-43 to 216-B-50, 216-B-57, and 216-B-61 cribs (GJO-2003-458-TAC). In fiscal year 2003, logging activities were completed in and around Waste Management Area B-BX-BY. Those logging results are being combined with the logging results in the reports cited above and with previous baseline reports for the B, BX, and BY Tank Farms to produce a comprehensive borehole logging report for the entire area.

In fiscal year 2003, spectral gamma logging detected cesium-137, cobalt-60, uranium-238, uranium-235, antimony-125, strontium-90, europium-154, and europium-152 at Waste Management Area B-BX-BY.

Cesium-137, cobalt-60, uranium-238, uranium-235, antimony-125, strontium-90, europium-154, and europium-152 were all detected in Waste Management Area B-BX-BY. The predominant contaminant at the waste management area and adjacent waste sites is cesium-137, which was measured at a maximum concentration of more than 20 million pCi/g in borehole 299-E33-27 (near tank BX-102) and in borehole 299-E33-223 (near tank BX-110). Concentrations of cesium-137 >1 million pCi/g were found above ~45 meters depth in the vicinity of the singe-shell tank farms and in the vicinity of the BY cribs.

Concentrations of uranium-238 from Hanford Site operations were found as high as 1,000 pCi/g east of tank BX-102. Of the 284 boreholes logged, only 17 encountered detectable amounts of manmade uranium-238. The most extensive area of uranium contamination was interpreted as extending downward and to the northeast from the vicinity of tank BX-102, intercepting the groundwater in the vicinity of borehole 299-E33-18. Evaluation of historical log data suggests that the uranium plume reached the groundwater in this area between 1991 and 1997. This is consistent with groundwater monitoring results, which show elevated uranium levels beginning in ~1994. Limited evidence of subsurface uranium contamination was found in the vicinity of other waste sites at which uranium disposal is reported.

The maximum concentration of antimony-127 did not exceed 10 pCi/g. The highest europium-154 concentration encountered was 127 pCi/g near tank BX-101.

In general, contamination that appears to be directly associated with a specific waste site or tank was observed at log depths <46 meters in the immediate vicinity of the waste sites. However, most tank farm boreholes and many boreholes associated with the liquid waste sites are <46 meters in depth, and groundwater occurs at a depth of ~76 meters. Hence, the deeper part of the vadose zone has not been investigated extensively, and the full nature and extent of contamination may not be known. Borehole evidence of vadose zone contamination extending to groundwater does exist for processed uranium originating from the vicinity of tank BX-102 and for cobalt-60 and cesium-137 originating from the BY cribs. Figures 3.1-3 and 3.1-4 show the distribution of cobalt-60 and uranium-238 contamination in the vadose zone in Waste Management Area B-BX-BY and vicinity.

The deeper part of the vadose zone has not been investigated extensively, and the full nature and extent of contamination may not be known.

In addition to wells near the Waste Management Area B-BX-BY, selected boreholes in the 200 West Area that were scheduled for decommissioning were also logged in fiscal year 2003. These boreholes had been identified in the original database for baseline characterization. Log data were collected in 23 of 57 boreholes before they were decommissioned.

Finally, geophysical logging of new and existing boreholes for vadose zone characterization to support ongoing remedial investigation at the Hanford Site was accomplished in fiscal year 2003. These holes were logged as requested, and log plots and log data reports were provided to the remedial investigation projects. In some cases, shallow boreholes were installed specifically for spectral gamma logging, and the results from these boreholes were used to identify locations for more detailed investigations.

3.1.3 Characterization at the 200-PW-1 Operable Unit

V. J. Rohay

Characterization of the carbon tetrachloride vadose zone plume was conducted during fiscal year 2003 as part of the remedial investigation for the 200-PW-1 Operable Unit. The 200-PW-1 Operable Unit waste sites received plutonium-rich and organic-rich waste from several processes located within the Plutonium Finishing Plant complex. A primary component of the organic-rich waste was carbon tetrachloride. The objective of the vadose zone investigation was to locate and characterize the sources of carbon tetrachloride contamination that presently impact groundwater, as well as known and suspect release sites with the potential to impact groundwater in the future.

Soil-vapor sampling was used to explore the dispersed carbon tetrachloride plume in the vadose zone.

Soil-vapor sampling and analysis was used to explore the upper vadose zone in the vicinity of the Plutonium Finishing Plant as Step I of the remedial investigation into the dispersed carbon tetrachloride plume at the 200-PW-1 Operable Unit. The sampling was conducted at engineered structures that had the potential to release carbon tetrachloride to the vadose zone. The engineered structures included liquid waste discharge pipelines, liquid waste discharge sites, and solid waste burial ground trenches. The vadose zone sampling was conducted using either the GeoProbe or cone penetrometer direct push technology. Sampling also was conducted through vent risers into the burial ground trenches. The analyses were conducted using a field-screening instrument. Characterization was performed in accordance with the *200-PW-1 Operable Unit Dispersed Carbon Tetrachloride Vadose Zone Plume Sampling and Analysis Plan – Step I* (DOE-RL-2001-67).

The Step I soil-vapor sampling outside of the Plutonium Finishing Plant Protected Area was conducted between May and October 2002. The sampling methodology and

results are available in the *200-PW-1 Operable Unit Report on Step I Sampling and Analysis of the Dispersed Carbon Tetrachloride Vadose Zone Plume* (CP-13514) and are summarized in Section 3.1.1.3 of PNNL-14187. The Step I soil-vapor sampling inside the Plutonium Finishing Plant Protected Area was conducted in August 2003.

Soil-vapor samples were collected at 17 sites within the Plutonium Finishing Plant Protected Area (i.e., inside the fence) to investigate potential discharge of carbon tetrachloride-bearing waste to the soil column at those sites. A GeoProbe system was used for subsurface access. The maximum depth achieved using the GeoProbe was 14.5 meters. Samples were collected at depths of 4.6 and 7.6 meters and then increments of 7.6 meters until refusal.

Relatively low concentrations of carbon tetrachloride were detected in the vadose zone at the 200-PW-1 Operable Unit.

Relatively low concentrations of carbon tetrachloride (1 to 4 ppmv) were detected in some samples collected at six of the sites. At each of the six sites, the highest concentration was detected in the deepest sample. The relatively low concentrations suggest that there are no active sources of contamination in the upper vadose zone at these locations.

3.1.4 Characterization of the 200-CS-1 Operable Unit

C. S. Cearlock

During fiscal year 2003, characterization activities were performed by Fluor Hanford, Inc. for DOE's Groundwater Remediation Project as part of the 200-CS-1 Operable Unit remedial investigation. The primary objective of the field effort was to characterize the nature and vertical extent of contamination in the vadose zone underlying the 216-A-29 ditch, 216-B-63 trench, and 216-S-10 ditch and pond. Borehole drilling, test pit excavation, surface and borehole geophysical surveys, and analysis of soil samples were conducted during the field activities. Analyses of soil samples are ongoing, and the results will be summarized in the fiscal year 2004 annual report.

Boreholes and test pits helped characterize the nature and vertical extent of contamination in the vadose zone underlying the 216-A-29 ditch, 216-B-63 trench, and 216-S-10 ditch and pond.

Three boreholes were drilled and nine test pits excavated within the 200 Areas on the Hanford Site. One borehole (B8826) was located within the 216-A-29 ditch east of the AP Tank Farm in the 200 East Area. (Three test pits were completed at this location in fiscal year 2002 and details are provided in BHI-01651.) A second borehole (B8827) and two test pits were dug within the 216-B-63 trench, located east of B Tank Farm in the 200 East Area (Figure 3.1-5). The third borehole (B8828, well 299-W26-14) is adjacent to the 216-S-10 ditch, and three test pits were within the ditch located south of the 233-S Building in the 200 West Area (Figure 3.1-6). Four test pits are within the 216-S-10 pond (Figure 3.1-6). An additional test pit was excavated within the 216-S-10 ditch at the original location of the planned borehole B8828 to gather characterization data below the waste site. The borehole was moved adjacent to the ditch to allow it to be completed as a RCRA groundwater monitoring well. Borehole B8828 was completed as monitoring well 299-W26-14 to support RCRA monitoring needs.

A total of 64 samples were collected from the 9 test pits, and 50 split-spoon samples were collected from the boreholes. These samples are being analyzed for a variety of organic and inorganic constituents and radionuclides. The results of the analyses will become available in fiscal year 2004 and will be reported in the 2004 annual groundwater report.

Geophysical logging was completed at all three boreholes using spectral gamma and neutron-moisture detection methods. The only manmade radionuclide detected was cesium-137 in two of the three boreholes. In borehole B8826, at the 216-A-29 ditch, cesium-137 was detected between depths of 0.9 and 2 meters at concentrations up to

62 pCi/g (at 1.5 meters). Cesium-137 was found between depths of 1.2 and 3.3 meters in borehole B8827, at the 216-B-63 trench, with a maximum concentration of 22.4 pCi/g at 2.7 meters.

3.1.5 300 Area Uranium Leach and Adsorption Studies

R. J. Serne, C. F. Brown, H. T. Schaef, E. M. Pierce, M. J. Lindberg, Z. Wang, P. L. Gassman, and J. G. Catalano

Results of laboratory experiments will be used to model uranium mobility to determine the soil cleanup level in the 300 Area.

The results of laboratory experiments to measure the leaching and adsorption characteristics of uranium in near-surface sediment samples collected from the 300 Area of the Hanford Site were reported in fiscal year 2003 (PNNL-14022). The results will be used to model uranium mobility for the 300-FF-1 and 300-FF-2 Operable Unit waste sites to determine whether the soil cleanup level of 350 picocuries total uranium per gram of soil is protective of groundwater in the 300 Area. This section summarizes the results of the experiments. A complete discussion of the results and the experimental procedures can be found in PNNL-14022.

Uranium is the principal contaminant of concern in the 300 Area of the Hanford Site. Uranium leach rate and distribution coefficient values are key input for modeling contaminant mobility and predicting future impacts to groundwater. (Distribution coefficients are empirical measurements of the ability of sediment to adsorb a contaminant and, therefore, retard the migration of the contaminant through the vadose zone or groundwater.) Literature values for uranium distribution coefficients vary by as much as four orders of magnitude as functions of soil grain size, pH, ionic strength, moisture content, organic matter, and mineralogy (Waite et al. 1994; Kaplan et al. 1998; Hsi and Langmuir 1985). Due to the large variability in uranium distribution coefficients reported in the literature, site-specific studies were performed with sediment from near the surface of the 300 Area.

Eight near-surface sediment samples were collected: three uncontaminated background samples, two uranium-contaminated samples from the 300 Area north process pond, and three uranium-contaminated samples from near the 303-K Building. Physical and chemical properties were characterized for all samples. A series of seven semi-selective chemical extraction techniques were used to determine the percentage of uranium present as various phases in the samples. Table 3.1-2 shows the results of the selective extraction experiments. However, the uranium reported to be extracted by a specific step in the table may include uranium that was not completely extracted by a higher step in the table.

Table 3.1-2 shows that the uranium content in the background sediment is primarily bound tightly in crystalline minerals and is not extractable. The uranium extraction characteristic in samples from the 300 Area north process pond markedly differs from the background sediment. The majority of the uranium in samples from the 300 Area north process pond is present as uranyl carbonates and amorphous iron and aluminum hydrous oxides. About 10% to 20% of the uranium in the samples is leached with the organic matter.

The greatest amount of uranium removed from the samples from the 303-K Building area are associated with amorphous iron and aluminum oxyhydroxide phases followed by uranium associated with carbonates (other uranium [VI] compounds may also be dissolving in this step). Ten to fifteen percent of the total uranium is leached with the organic material.

All five contaminated samples contained uranium that was extractable mostly as uranyl carbonates and amorphous iron and aluminum oxyhydroxides. The next largest

pool of uranium was associated with organic material. Less than a few percent of the total uranium was present in water-leachable and cation-exchangeable phases.

Characterization of the samples was followed by a series of flow-through column leach tests, long-term (154 days) static leach tests, batch adsorption tests, and column flow-through adsorption/desorption tests.

A series of large-column leach tests was done to determine the amount of uranium that could be removed by percolating air-saturated distilled water through the sediments. The results from the tests showed that uranium leaching did not follow a constant solubility pattern. Four of the five near-surface sediment samples showed a large, near instantaneous release of a few percent of the total uranium followed by a slower, continual release that lasted for several months. Steady-state uranium leachate concentrations were never attained, and leaching trends were not consistent among the samples. Dissolution kinetics were slow and the measured leach curves most likely represent slow, kinetically-controlled desorption or dissolution.

Long-term static batch leach tests were used to investigate whether steady-state uranium concentration could be attained, ultimately enabling the determination of a desorption distribution coefficient for the slowly leaching fraction observed in the large column leach tests. Aliquots of sediment were taken from the large leach columns, placed into three containers, and contacted with one of three leaching solutions (deionized water, uncontaminated groundwater, and simulated vadose zone porewater) to determine how much of the remaining uranium could be removed over a 6-month period. Results from the batch leach test showed that <4% of the remaining uranium mass was removed by deionized water, which represented rainwater. The groundwater solution was slightly more effective, leaching as much as 10% of the remaining uranium. The simulated vadose zone porewater solution was the most effective at leaching uranium, removing ~30% of the residual total uranium mass in two out of the five contaminated samples.

Three batch adsorption experiments were done to investigate the effects of uranium solution concentration, pH, and dissolved inorganic carbon concentration on uranium adsorption onto the uncontaminated sediment. Values of the uranium adsorption distribution coefficient ranged from 0 mL/g to >100 mL/g depending on which solution parameter was adjusted.

The solution parameter with the greatest impact on uranium adsorption was the concentration of dissolved inorganic carbon.

Results showed that the solution parameter with the greatest impact on uranium adsorption was the dissolved inorganic carbon concentration. Uranium adsorption onto uncontaminated sediment ranged from ~40% at 0.9 mM HCO_3^- to 12 % at 2.2 mM HCO_3^- in solutions with low uranium concentration (500 µg/L). Considerable less sorption was seen in the solution with high uranium concentration (3,000 µg/L), with a range of ~7% at 2.5 mM HCO_3^- to 0% at 12 mM HCO_3^-. The concentration of uranium in solution appeared to have no effect on the uranium distribution coefficient values, a requirement for the use of the linear adsorption isotherm, or distribution coefficient model.

Solution pH was shown to be important in laboratory tests; however, in the field the natural sediment buffers the pH to a nearly constant value, thus minimizing its overall effect. Results from the batch adsorption tests also showed that uranium sorption onto the background sediment is linear up to uranium concentrations of 3 mg/L (holding all other parameters constant), which is well above the values found in the upper unconfined aquifer. Thus, the linear isotherm assumption holds for uranium in the 300 Area sediment/porewater environment.

The chemical composition of vadose zone porewater and groundwater in the 300 Area is not constant. Carbonate concentration, pH, and other constituents vary in space and time because of evapotranspiration, transient rain fall/snow events, and changes in river stage. Therefore, the distribution coefficient for uranium (VI) is not a

constant even though the adsorption of uranium (VI) from a solution with fixed composition follows the linear isotherm. Therefore, the linear distribution coefficient model, but not the constant distribution coefficient model, is defensible in predicting the fate of uranium in the 300 Area aquifer plume.

Uranium sorption onto uncontaminated sediment in the 300 Area is highly variable.

Column adsorption tests were done to assess the sorption of uranium onto the background sediment. This test most closely predicts the fate of uranium-contaminated solutions once they come into contact with "clean" or uncontaminated sediment. Uranium adsorption distribution coefficient values ranged from 1.85 mL/g in a low ionic strength solution (500 µg/L) to 0.86 mL/g in a high ionic strength solution (3,000 µg/L).

Uranium sorption onto uncontaminated sediment in the 300 Area is highly variable and depends on solution conditions. Therefore, predicted distribution coefficient values based on site-specific conditions expected in the 300 Area range from a low of 0 to 1 mL/g in the near-surface vadose zone (which is influenced by evapotranspiration) to 2 to 4 mL/g in unconfined aquifer sediment that is not influenced by dilution with Columbia River water. (For purposes of comparison, a highly mobile constituent such as technetium-99 will have distribution coefficients between ~0 and 0.1 mL/g and a highly immobile constituent such as cesium-137 or lead will have distribution coefficients in excess of 1,000 mL/g [PNNL-13895]). Although not studied in detail, adsorption distribution coefficient values in the saturated aquifer, where dilution due to river water is present (lower total carbonate solution concentration), could be in excess of 7 mL/g.

Table 3.1-1. Summary of Significant Borehole Logging Results from Fiscal Year 2003 Characterization Boreholes at the T and TX Tank Farms

Borehole	Isotope	Depths of Occurrence (m)	Maximum Concentration (pCi/g)	Depth of Maximum (m)
C4104	Cesium-137	0 - 5.5 15 - 15.5	38	15.1
	Europium-154	10.8 - 26	1,960	15.1
	Europium-152	11.3 - 24.8	49	14.5
	Tin-126	13.2 - 15.4	33	15.1
	Cobalt-60	11.1 - 38.8	58	28.5
C4105	Cesium-137	Intermittent depths	0.4	0.15
	Cobalt-60	14.8 - 37.2	15	32.6
	Europium-154	14.8 - 15.5 17.5 - 20.3	21	20.3
C3830	Cesium-137	0 - 3.4	7.5	0.3
C3831	Cesium-137	0 - 1.2	<2.5	0 - 1.2
	Cobalt-60	15.8 - 34.9	61	18.7 and 20.9
C3832	Cesium-137	0 - 0.3 1.2 - 1.4	0.5	0.2
	Cobalt-60	22.9 - 35.0	1.2	24.2
	Uranium-238	30.5 - 33.2	15	32.3

Table 3.1-2. Selective Extraction Results for Uranium in Six Near-Surface Sediment Samples (% of total uranium removed by each extraction)

Extraction Order	Extracted Phases	Background	300 Area North Process Pond		Area Near 303-K Building		
			Sample B11494	Sample B11495	Sample B11BY4	Sample B11BY5	Sample B11BY6
↓	Water soluble	0.01	0.44	0.95	0.22	0.08	0.15
	Ion exchangeable	0.31	0.70	1.57	0.21	0.04	0.29
	Carbonate solids	0.62	30.2	23.9	36.9	20.3	31.1
	Amorphous hydrous oxides	1.82	55.0	28.0	37.2	54.2	45.5
	Organics	0.38	10.1	20.0	12.8	9.19	13.3
	Crystalline oxides	0.36	1.54	2.84	2.77	5.11	2.94
	Strong acid leach	1.05	0.45	0.92	8.38	1.31	6.11
	Residual	95.4	1.58	21.8	1.53	3.18	0.61

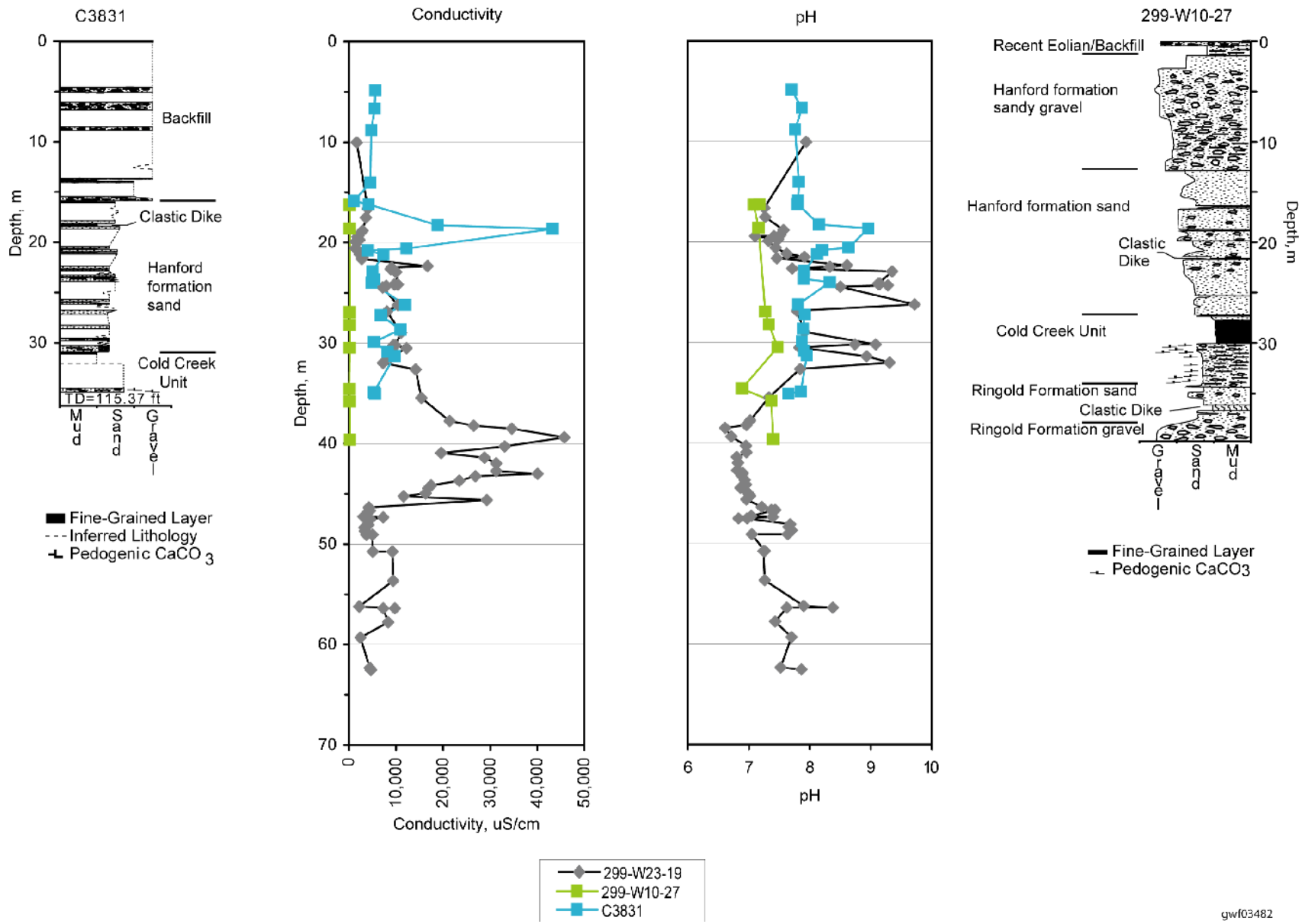

Figure 3.1-1. Electrical Conductivity and pH versus Depth in Characterization Borehole C3831 at TX Tank Farm

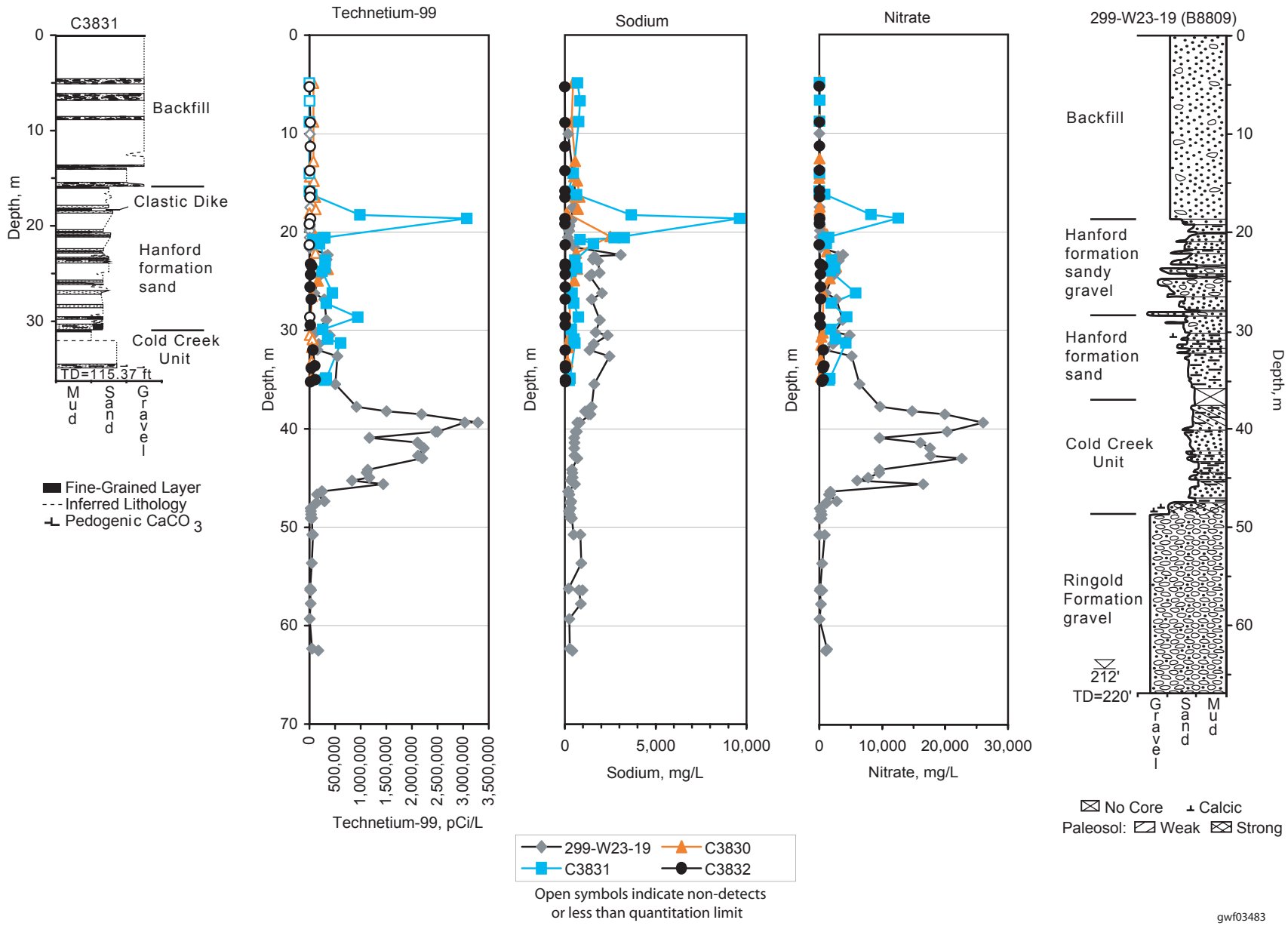

Figure 3.1-2. Concentrations of Contaminant Indicators Technetium-99, Nitrate, and Sodium versus Depth in Characterization Boreholes at TX Tank Farm

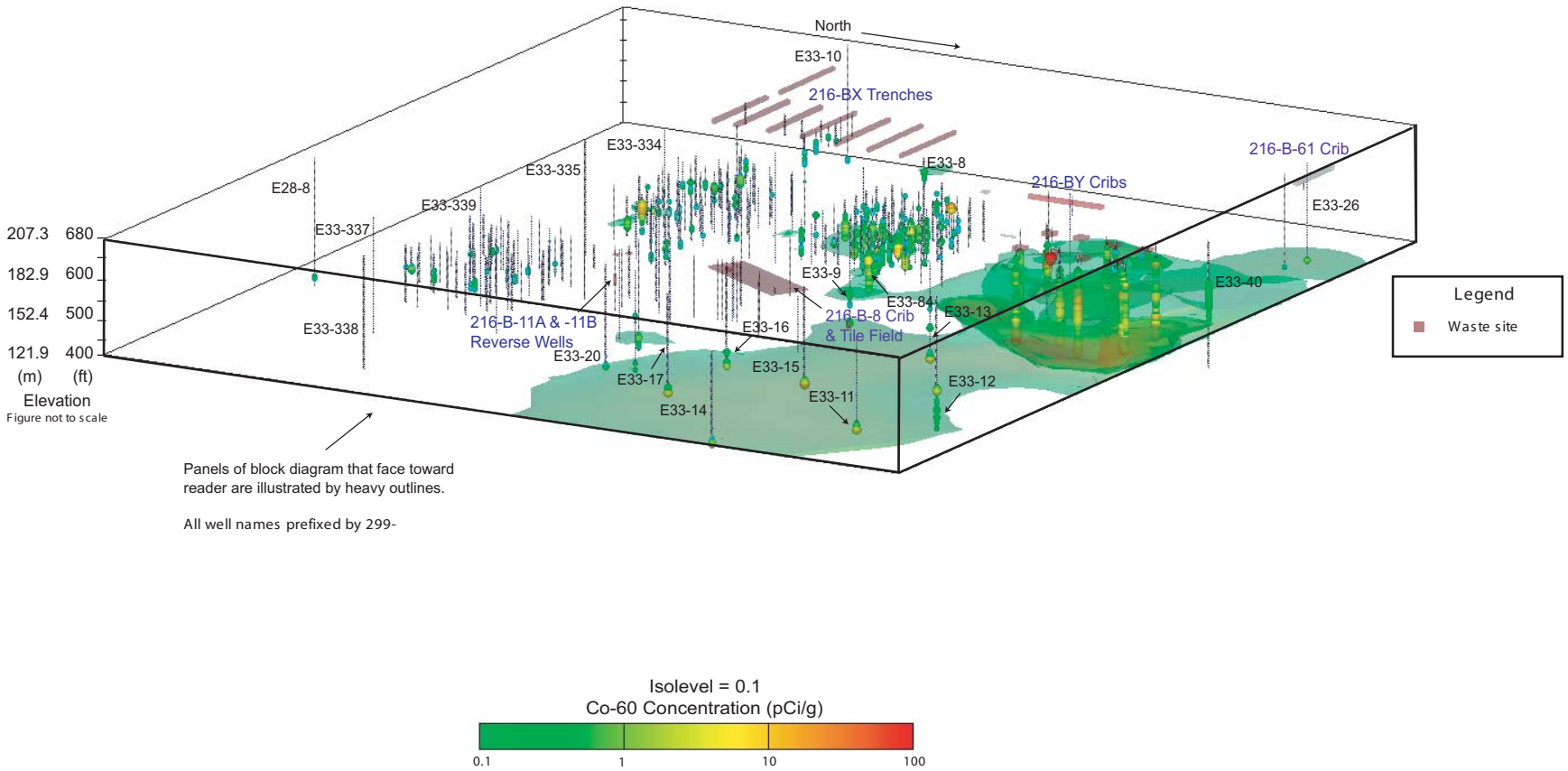

Figure 3.1-3. Cobalt-60 Contamination in the Vadose Zone Near Waste Management Area B-BX-BY

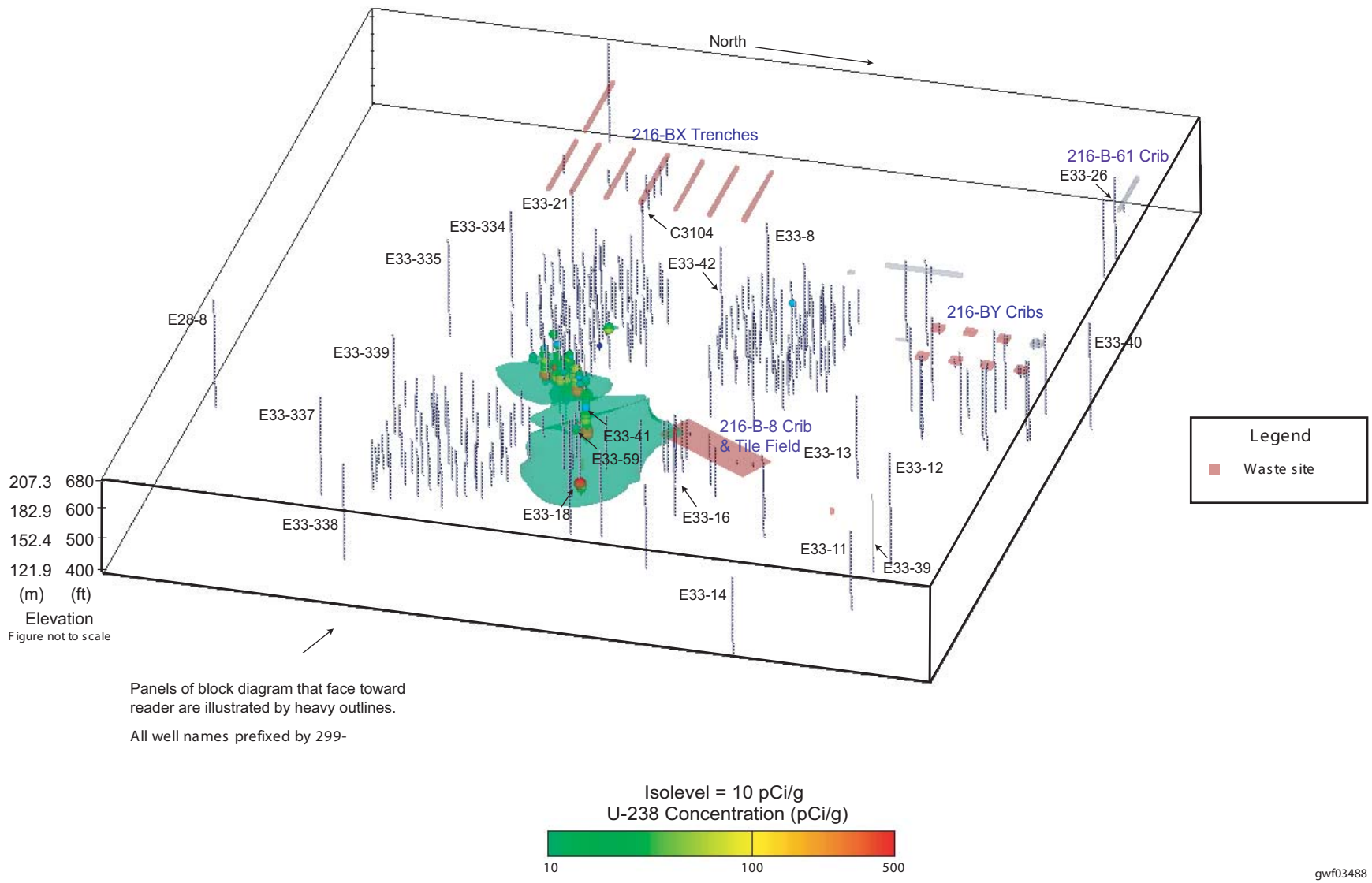

Figure 3.1-4. Uranium-238 Contamination in the Vadose Zone Near Waste Management Area B-BX-BY

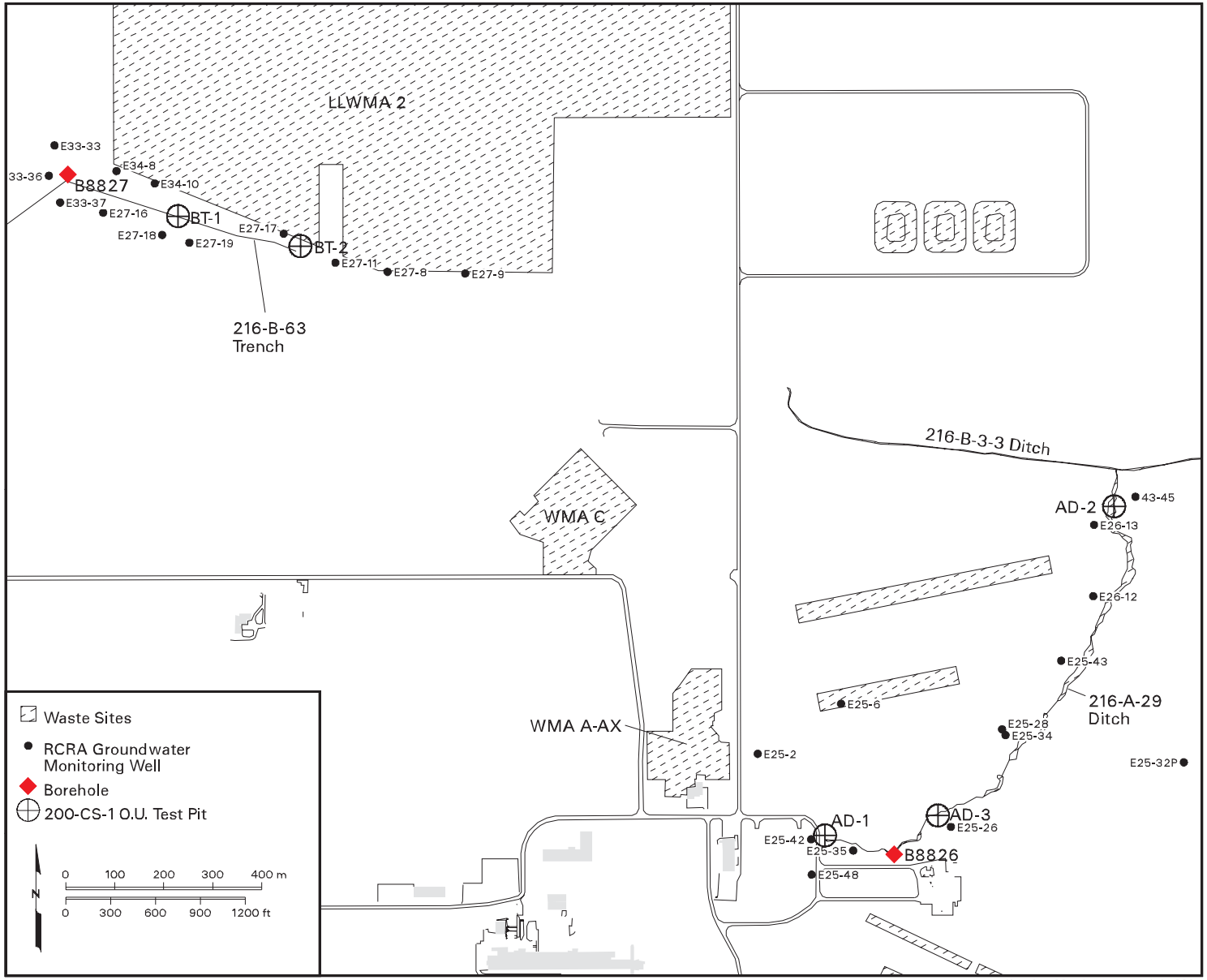

Figure 3.1-5. Locations of Boreholes and Test Pits (designated BT) for Characterization of the 216-A-29 Ditch and 216-B-63 Trench

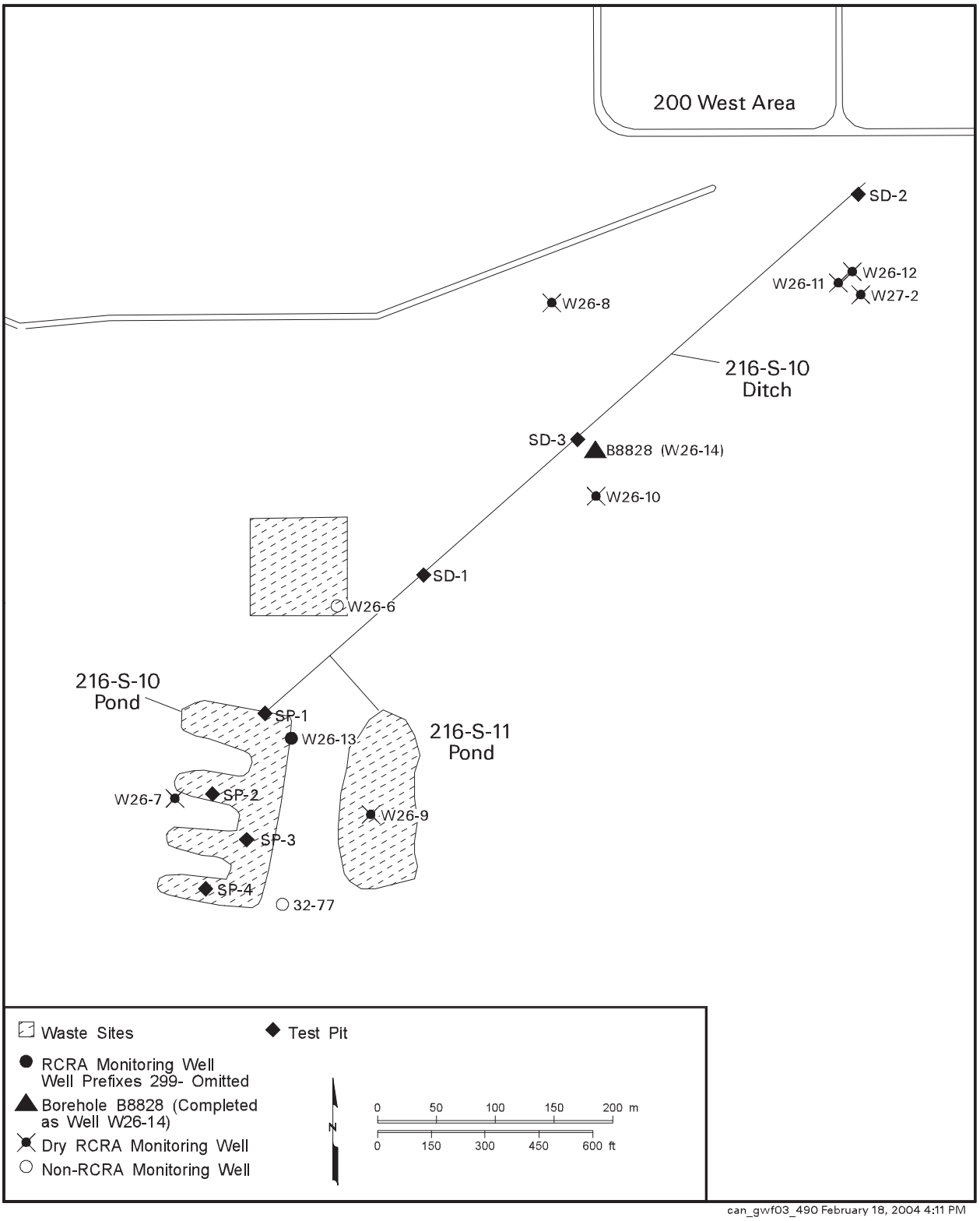

Figure 3.1-6. Locations of Borehole B8828 and Test Pits (designated SP and SD) at the 216-S-10 Ditch and Pond System