SGW-44795
Revision 0

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Critical Review of Historical, Field Logging, and Analytical Data for PUREX A Cribs to Estimate Vertical Distribution and Horizontal Spreading of Risk Driving Contaminants

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
under Contract DE-AC06-08RL14788

CH2MHILL
Plateau Remediation Company

P.O. Box 1600
Richland, Washington 99352

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PNNL LETTER REPORT

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Letter Report

CRITICAL REVIEW OF HISTORICAL, FIELD LOGGING, and ANALYTICAL DATA for PUREX A CRIBS to ESTIMATE VERTICAL DISTRIBUTION and HORIZONTAL SPREADING of RISK DRIVING CONTAMINANTS

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May 2, 2008

Prepared for Phil Rogers, Fluor Federal Services,
under Contract DE-AC05-76RLO 1830.

1.0 Objective

Researchers at Pacific Northwest National Laboratory were tasked with developing a best-estimate and likely ranges of contaminant distribution directly beneath the PUREX A Cribs, with a specific focus on the 216-A-4 Crib. This objective was made more difficult since a deep borehole has never been completed within the foot print of the 216-A-4 Crib. However, one deep well (299-E24-23) was drilled (360 ft bgs) and completed adjacent to the 216-A-4 Crib, and the characterization data collected on these samples has been used to support the estimates contained herein. Also included in this scope was the task of estimating the distribution of contaminants below the foot prints of the 216-A-2 Crib, which recently had a borehole drilled through its foot print all the way to the water table (314 ft bgs) and into the aquifer to 322 ft bgs, and the 216-A-21 Crib, which has only been interrogated using one direct push hole emplaced to a depth of 60 ft bgs.

Information used to develop estimates of contaminant distribution below and to the sides (horizontal spreading) of these disposal facilities included historical data on process flow sheets and disposal records (both chemical composition and volumes disposed), borehole geophysical logging data, historical groundwater data present in the HEIS data base, and direct measurements of sediment concentrations of key radionuclides, chemicals, and sediment:water extracts' chemical composition, as well as expert knowledge of geochemical principles and Hanford's subsurface properties.

2.0 Approach

The sediment characterization information considered pertains solely to the following facilities in the 200-MW-1 Operable Unit: the 216-A-2, 216-A-4, and 216-A-21 Cribs, and the 200-E-102 Trench. We did also review the historical groundwater data for 27 monitoring wells in the vicinity of the PUREX A cribs.

We selected the Soil Inventory Model (SIM), Rev. 1 effort [RPP-26744 Rev. 0; Corbin et al. (2005)] as our main source of historical information. The SIM captures information pertaining to facility usage, the total volumes and chemical composition of waste discharged to each facility, and the total inventory of key chemical and radionuclide constituents discharged to each facility. Data on facility dimensions and internal discharge piping were supplied by Fluor Hanford and GRAM, Inc based primarily on information found in the Waste Information Data System (WIDS) and historical Hanford drawings. Field borehole geophysical logs, gross gamma, spectral gamma, and neutron measurements (used to approximate sediment moisture content and lithologic changes) were downloaded from the Stoller Inc. web site http:www.hanford.gov/cp/gpp/data/vzcp. S. M Stoller Corporation used up to three geophysical tools (a spectral gamma logging system, a high rate logging system, and a neutron moisture logging system) to interrogate the drilled and direct push (closed-end steel cased) boreholes. The locations of the three cribs and trench and boreholes for which data were critically reviewed are found on Figure 1 and a more detailed map with the location of for these boreholes is also shown in Figure 5.

Field borehole logging data was supplemented by data derived from the direct measurement of selected constituents in sediments and various extracts of the sediments, and one groundwater sample each obtained before decommissioning borehole C5515 and completing groundwater monitoring well 299-E24-23 (C5301). A deep electrode was buried in borehole C5515 to allow use in future high resolution resistivity field surveys (ERC). These data were generated by Hanford Site laboratories and Hanford-affiliated laboratories and are available in the Hanford Environmental Information System (HEIS) database. Additionally, this report considers recent data generated by PNNL on sediments collected from the area of interest; these data are also available in the HEIS database.

Finally, we incorporated several geochemical resources, such as information in published technical reports and journal articles, and expert opinions from technical staff with tens of years of experience studying Hanford subsurface geology, hydrology, and geochemistry to provide a qualitative to semi-quantitative estimate of the vertical distribution of key contaminants. Our estimates of the horizontal spreading of the fluids and contaminants from each facility are qualitative and rely on the estimates of total fluid disposed, the field borehole spectral gamma log data for Cs-137 from the available boreholes, and the documented geologic stratigraphy of the vadose zone.

This letter report contains eleven sections that attempt to present the assimilated data, our conclusions on the vertical distribution, both historically during active use of the facilities and today in their inactive states, of selected constituents below each facility, the extent of horizontal spreading that might be expected. In the main text of the RI we provided appropriate K_d values to use in future predictive modeling activities. We also provide recommendations on further information or activities that could improve the technical defensibility of the current assessment of the vertical distribution of key risk driving constituents in the subsurface, our estimate of the extent of lateral spreading, and the appropriate K_d's to use in modeling future migration.

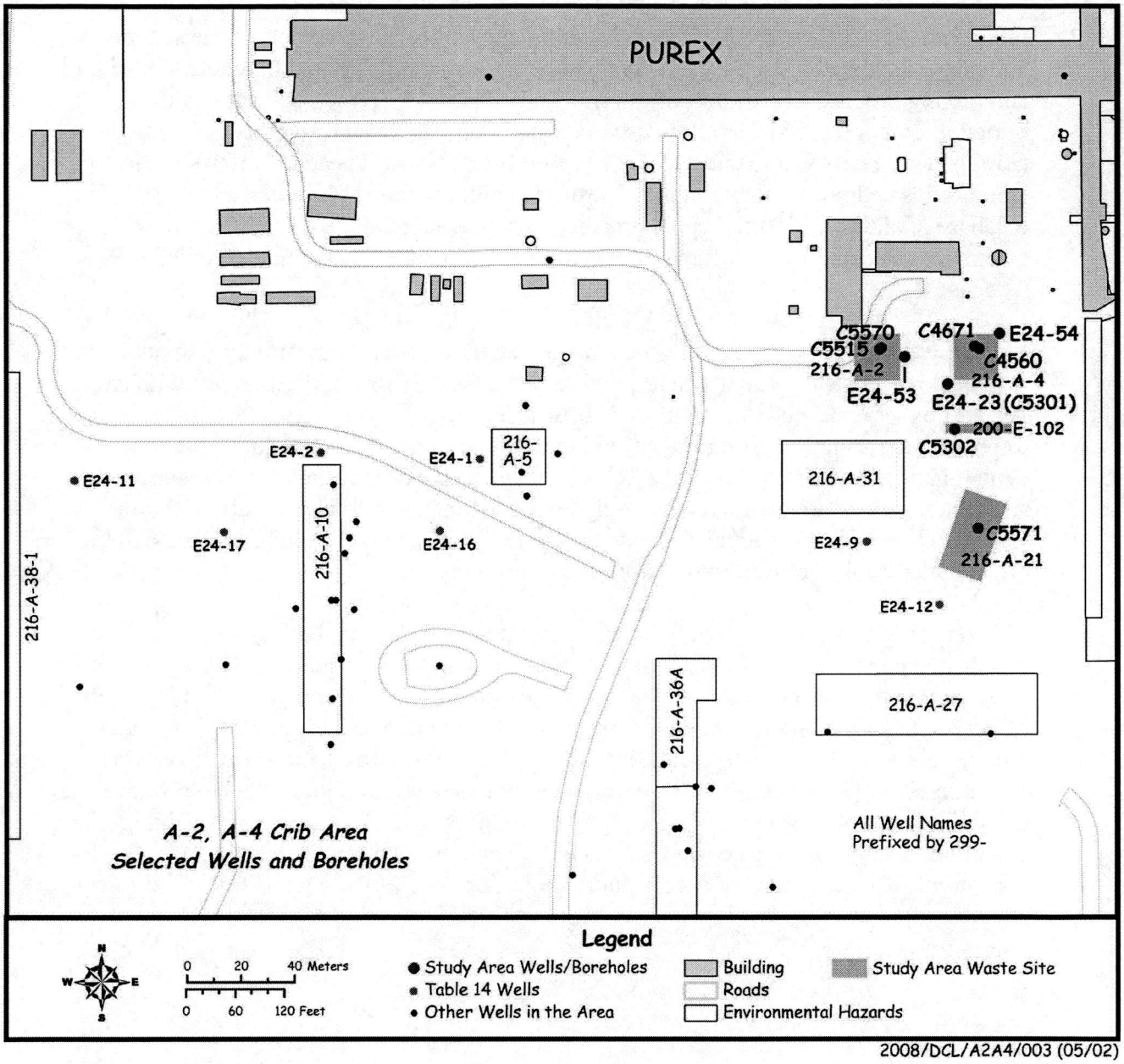

Figure 1. Purex A Crib Location with Facilities and Boreholes of Interest Highlighted

3.0 Facility Information Summarized from the SIM, Rev. 1

The total volumes and chemical composition of the liquid wastes disposed to each of the cribs have been taken from the most recent version of the SIM [Corbin et al. (2005)]. We chose this resource because it represents, in our opinion, the most extensive and most recent assimilation of historical records on the chemical composition of wastes disposed to the various facilities at Hanford. The SIM incorporated information from other models, especially the HDW (Hanford Defined Waste) models that rely on a combination of historical process flow sheet records, records of chemicals purchased, and analytical measurements of actual samples, as well as simple empirical chemical algorithms to estimate the fate of chemicals during the numerous fuel reprocessing and radionuclide recovery operations. The masses or activities of key radionuclides produced during uranium fuel irradiation were estimated using the ORIGEN code as described in Higley et al. (2004). Other key information used in the assessment include the total volume of liquid waste disposed to each facility by year, the years that the cribs were active, the size of the cribs, and the internal structures within the cribs through which the fluids were dispensed. The size of the cribs and details on the internal piping were provided by Fluor Hanford and GRAM, Inc.

Tables 1 through 3 list the total inventory of chemicals and radionuclides disposed to the three cribs and the concentration of the chemicals and radionuclides in the liquid waste as estimated by SIM, Rev 1. The specific SIM designation for the waste stream and the years of operation are also shown in the tables.

Again, we stress that SIM, Rev 1 is the most current assimilation of historical information augmented by the most current versions of various chemical estimation models to allocate both liquid and suspended solids (mostly hypothetically generated from simplified solubility empirical models) that travelled through various fuel reprocessing operations, isotope recovery operations, and waste stream manipulations (concentration of liquid wastes by active large scale evaporators, etc.) and were ultimately disposed to the Hanford vadose zone in cribs, trenches, ditches, or placed in storage tanks, some of which leaked fluids. Other liquids sent to tanks were inadvertently released to the Hanford subsurface during tank filling and tank transfers in events labeled "unplanned releases" (UPRs), many of which have been described in detail in documents archived in Hanford's various libraries/databases.

4.0 Description of Crib Historical Information

The data in Tables 1 through 3 illustrate that the waste streams disposed to the three crib facilities had different chemical compositions and were generated by different activities related to the PUREX process and/or isotope recovery of older wastes.

4.1 216-A-2 Crib

The 216-A-2 crib is located within a larger underground radioactive material area [URM] known as 200-E-103. The site received organic waste from the 202-A building. In addition to waste from the 202-A building, the 216-A-2 crib is associated with the 241-A-151 Diversion Box. The site was deactivated by removing a section of effluent piping when the specific retention capacity of the crib was reached. The unit was replaced by the 216-A-31 Crib. Based on the SIM, Rev. 1, the waste stream disposed to the 216-A-2 Crib does not show charge balance unless the waste stream was acidic or some organic compound was supplying cations to balance the nitrate anion. Note that this waste stream, categorized as PUREX P1 organic waste, contained significant concentrations of tri-butyl phosphate (TBP) and normal paraffin hydrocarbons (NPH). This waste stream is estimated to have contained significant concentrations of Sr-90, Cs-137, and isotopes of plutonium. The 216-A-2 Crib was active from 1956 to 1960 (according to SIM, Rev. 1), and the total volume disposed to the facility is estimated at 0.230 mega liters. Data in WIDS suggests that the start date for waste disposal was January 1956 and the end date was January 1963, with a total volume disposed of 0.23 megaliters. Therefore, there is a discrepancy in the date when no further disposals were made. However, the two estimates for total volume disposed are in agreement. The total volume disposed to this facility was small compared to the other two cribs discussed in this report, as well as many others at Hanford, such that operators must have been concerned about the migration potential of certain contaminants and the "specific retention" concept was used wherein the volume of waste disposed was kept at no greater than 10% of the volume of the facility's cross section multiplied by the depth to the water table. The specific retention concept relied on the vadose zone sediments to be able to retain the fluids via capillary pressure and not allow the fluids to drain to groundwater. This concept that fluids can be held in perpetuity has been shown to be too simplistic [Fayer and Walters (1995), Fayer and Szecsody (2004), Gee (1987), Gee et al. (1992, 2005a, 2005b) and Rockhold et al. (1995)].

The chemical constituents with the largest inventories disposed to the 216-A-2 Crib were TBP (149,200 kg), NPH (63,920 kg), nitrate (2370 kg), and uranium (228 kg) based on SIM, Rev. 1 estimates. The radionuclides with the largest inventories were Sm-151 (27.2 Ci), Pu-239 (7.9 Ci), Pu-241 (6.9 Ci), Cs-137 (1.9 Ci), and Pu-240 (1.6 Ci).

The disposal infrastructure consisted of 15-centimeter (6-inch) perforated vitrified clay pipelines. Two 6.1-meter (20-foot) lengths were formed in a cross pattern horizontally, 6.4 meters (21 feet) below grade. Approximately 1.8 meters (6 feet) of coarse rock with a volume of 140 cubic meters (5,000 cubic feet) was placed around and below the pipes. The excavation above the pipes was backfilled with native overburden. The side slope from the ground surface to 6.4 meters below ground surface (bgs) (21 feet) was 1:1.5 and from 6.4 meters (21 feet) to 8.2 meters bgs (28 feet) was 1:2 (WIDS). The crib's foot print was 20 ft by 20 ft in area with a total depth of approximately 28 ft. This was an open bottom, unlined crib. A schematic of the A-2 crib infrastructure is shown in Figure 2 (taken from RI).

Table 1. 216-A-2 Crib Inventory and Chemical Composition Estimates (based on the SIM, Rev. 1)

Chemicals	Tot. Inventory (kg)	Conc. (mg/L)	Conc. (M)	Charge (+ meq/L)	Charge (- meq/L)	Radio-nuclides	Tot. Inventory (Ci)	Conc. (pCi/L)
Na	**5.966E+00**	2.88E+01	1.25E-03	1.25E+00		H-3	**1.398E-03**	6.75E+03
Al	0.000E+00	0.00E+00				C-14	2.212E-03	1.07E+04
Fe	6.050E-02	2.92E-01		1.57E-02		Ni-63	7.455E-04	3.60E+03
Cr	4.559E-03	2.20E-02			8.46E-04	Co-60	5.378E-03	2.60E+04
Hg	0.000E+00	0.00E+00				Se-79	8.600E-05	4.15E+02
Ni	7.000E-04	3.38E-03		5.76E-05		Sr-90	8.918E-01	**4.31E+06**
Ag	0.000E+00	0.00E+00				Tc-99	2.699E-02	1.30E+05
Mn	0.000E+00	0.00E+00				Sb-125	5.378E-03	2.60E+04
Ca	1.360E-01	6.57E-01		1.64E-02		I-129	1.760E-05	8.50E+01
K	0.000E+00	0.00E+00				Cs-137	1.858E+00	**8.98E+06**
NO3	**2.370E+03**	1.14E+04	1.84E-01		1.84E+02	Sm-151	2.725E+01	1.32E+08
NO2	0.000E+00	0.00E+00				Eu-152	4.068E-03	1.97E+04
CO3	2.036E-01	9.84E-01			3.28E-02	Eu-154	3.023E-01	1.46E+06
PO4	0.000E+00	0.00E+00				Eu-155	1.381E-01	6.67E+05
SO4	2.439E+00	1.18E+01			2.46E-01	Ra-226	4.520E-06	2.18E+01
Si	1.065E-01	5.14E-01				U-235	3.181E-03	1.54E+04
F	0.000E+00	0.00E+00				U-236	1.641E-03	7.93E+03
Cl	1.851E-01	8.94E-01			2.52E-02	U-238	7.623E-02	3.68E+05
Butanol	0.000E+00	0.00E+00				Np-237	6.230E-02	3.01E+05
TBP	**1.492E+05**	7.21E+05				Pu-238	1.950E-01	9.42E+05
NPH	**6.392E+04**	3.09E+05				Pu-239	7.884E+00	**3.81E+07**
NH3	5.155E-02	2.49E-01		1.46E-02		Pu-240	1.585E+00	**7.66E+06**
U-Total	2.283E+02	1.10E+03		9.24E+00		Pu-241	6.947E+00	**3.36E+07**
			Total	**1.05E+01**	**1.84E+02**	Am-241	1.760E-01	8.50E+05
			charge			Cm-242	9.684E-04	4.68E+03
						Cm-244	5.021E-04	2.43E+03

216-A-2 received wastes from 1956 to 1960; waste category is Concentrated Miscellaneous UNH Stream (P1).
Total volume disposed to 216-A-2 Crib was 0.230 mega liters (230,000 liters).
Radionuclide concentrations in SIM, Rev. 1 have been decay corrected to 01/01/2001.
The cation-anion charge balance is very poor which suggests either the waste stream was acidic or there is some error in the waste stream chemical composition. **Major constituents noted in bold red type**.

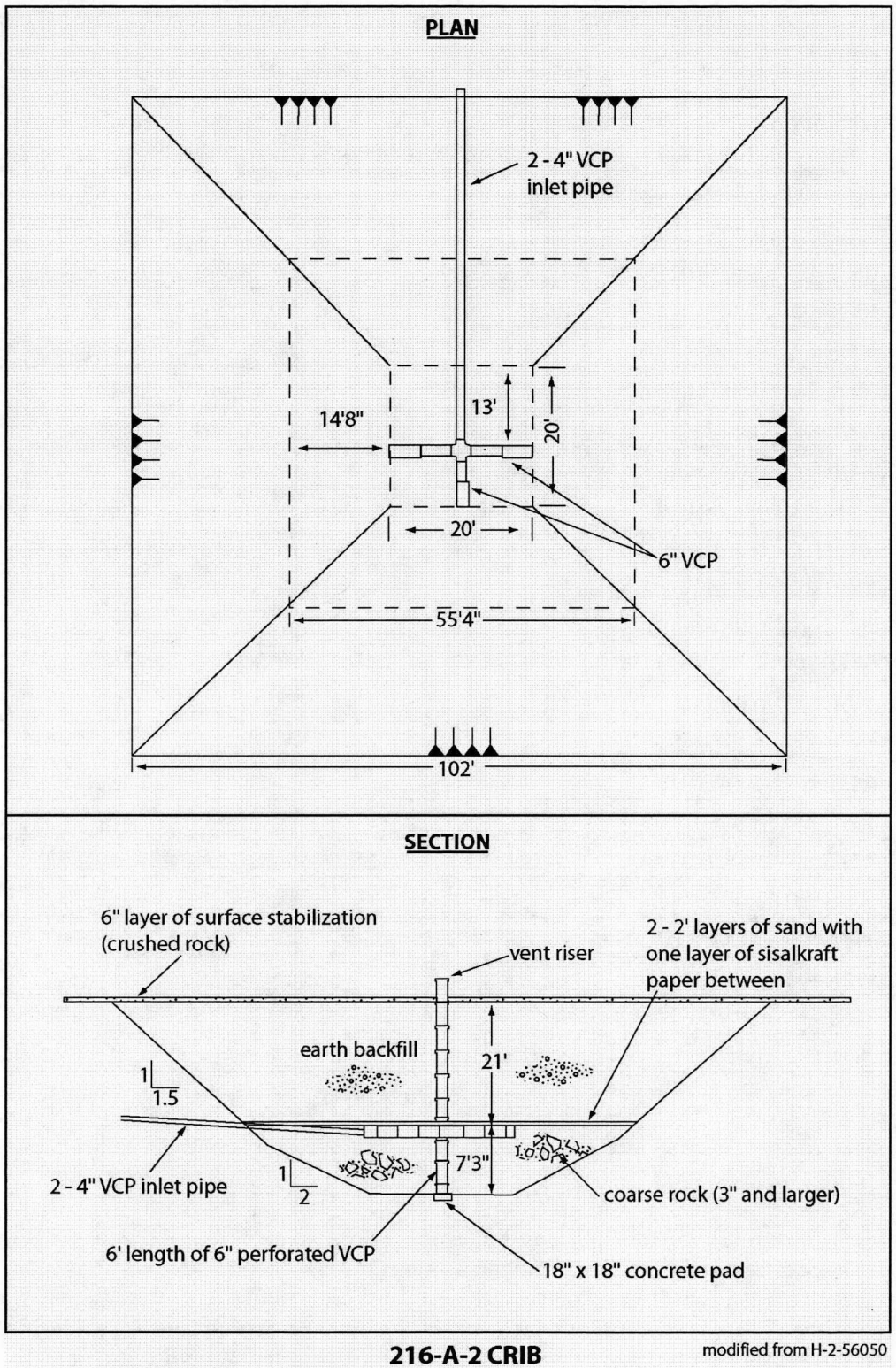

Figure 2. Schematic of the Infrastructure of 216-A-2 Crib. The horizontal inlet pipe(s) are 21 ft bgs and the crib bottom is located 28 ft bgs.

Two borings have penetrated the cross-sectional area of 216-A-2 Crib, one to a depth of 35 ft bgs (C5570) and one all the way to groundwater (C5515). An additional boring was placed ~1.5 m east of the crib and reached a depth of 52 ft bgs (A5910 or 299-E24-53). These three borings are shown on Figures 1 and 5. The field borehole geophysical logging data and direct measurements on sediment samples and water extracts of sediments are tabulated and discussed in later sections.

Based on the volume of waste disposed in the 216-A-2 Crib [~0.23 mega liters], the cross section of the crib foot print [20 x 20 ft; 37.16 m^2], the depth of the current water table [314 ft bgs], and the assumption that the disposed liquid percolated vertically within the foot print and reached a volumetric water content of 10% after contacting the crib bottom, the entire volume of liquid disposed to the crib would have filled the foot print down to a depth of approximately 225 ft bgs. If the disposed liquid percolated at lower volumetric moisture contents or if one considers that the vadose zone pores contain some native water, the depth that would have been wetted would be somewhat deeper. Further, if there was any significant horizontal spreading, the depth at which the disposed water might have stopped after wetting the vadose would have been shallower than 225 ft (69 m) bgs. We will compare these estimates with the near continuous characterization of sediments from borehole C5515 later in this letter report.

4.2 216-A-4 Crib

The 216-A-4 Crib is located directly east of the 216–A-2 Crib within a large gravel area known as the PUREX Stabilized Area (site code: 200-E-103); its location is marked by a large green vent riser extending above the ground surface. The crib received laboratory cell drainage from the 202-A Building and possibly drainage from the 291-A Stack. The 216-A-4 Crib was associated with the 216-A-2 Crib, the PUREX Laboratories, UPR-200-E-15, and 200-E-103. The excavation had 2.4 meters (8 feet) of coarse rock fill with a volume of 280 cubic meters (10,000 cubic feet) and has been backfilled. The side slope from the surface to 5.5 meters (18 feet) deep was 1:1.5 and 1:2 from 5.5 meters (18 feet) to the site bottom at 25 ft bgs. The site was deactivated by blanking the effluent piping when the unit reached its specific retention capacity. (WIDS)

The location of the 216-A-4 Crib is shown in Figure 1. The Crib infrastructure consists of two 6.1 meter (20-ft.) lengths of 15-centimeter (6-inch) perforated vitrified clay pipe, forming a cross pattern horizontally, 5.5 meters (18 ft) below grade. The crib's foot print was 20 ft by 20 ft, with an approximate depth of 25 ft. The 216-A-4 Crib was an open bottom, unlined crib. A detailed schematic of the infrastructure is show in Figure 3.

In December 1958, the crib became plugged and flooded an area between the crib and the 291-A-1 Stack, causing surface contamination. The contaminated soils were removed and disposed in the 200-E-102 Trench, which lies ~ 20 m south of the 216-A-4 Crib. The contaminated sediments disposed in 200-E-102 Trench were covered with 0.3 m (1 ft) of clean material (Baldridge 1959). The 216-A-4 Crib was deactivated in 1958 by blanking off the effluent piping after the crib had reached its specific retention capacity. At the present time, the site is located within a large gravel area, known as the PUREX Stabilized Area (200-E-103). As mentioned previously, only a large green vent riser is visible above ground surface.

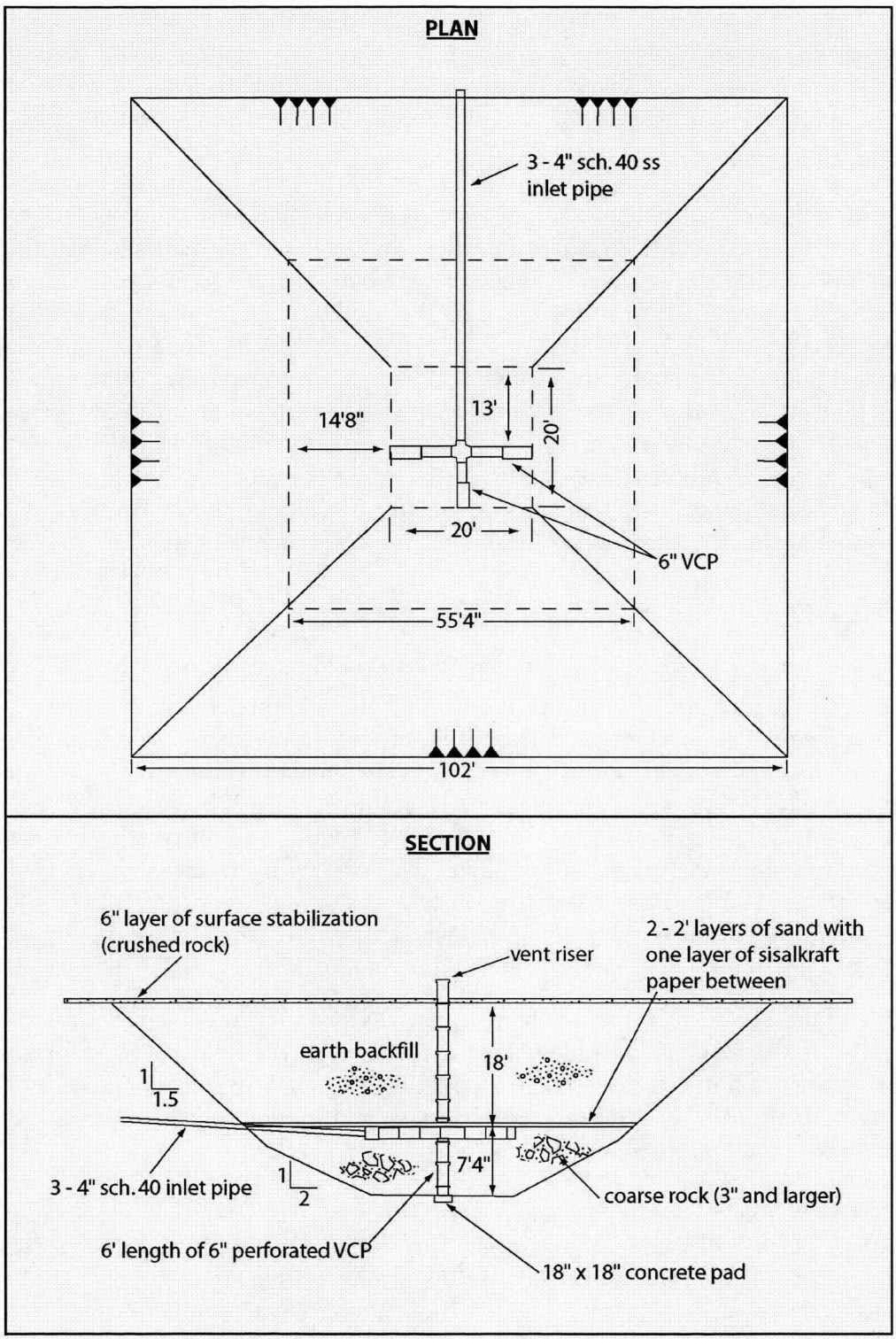

Figure 3. Schematic of the 216-A-4 Crib Infrastructure

Table 2. 216-A-4 Crib Inventory and Chemical Composition Estimates (based on SIM, Rev. 1)

Chemicals	Tot. Inventory (kg)	Conc. (mg/L)	Conc. (M)	Charge (+ meq/L)	Charge (- meq/L)	Radionuclides	Tot. Inventory (Ci)	Conc. (pCi/L)
Na	4.468E+02	7.86E+01	3.42E-03	3.42E+00		H-3	**6.446E+01**	1.16E+07
Al	0.000E+00	0.00E+00				C-14	8.021E-05	1.42E+01
Fe	1.202E+01	2.02E-01	3.62E-06	1.09E-02		Ni-63	1.407E-03	1.30E+02
Cr	2.341E+00	4.17E-01	8.01E-06		1.60E-02	Co-60	5.385E-04	9.56E+01
Hg	2.292E-02	4.11E-03	2.05E-08			Se-79	3.372E-06	5.99E-01
Ni	1.159E+00	1.37E-01	2.33E-06	4.66E-03		Sr-90	**4.144E+00**	7.36E+05
Ag	3.561E-02	3.00E-05	2.78E-10	2.78E-07		Tc-99	5.725E-01	1.03E+05
Mn	5.605E-02	1.00E-02	1.83E-07	3.66E-04		Sb-125	2.624E-04	4.66E+01
Ca	1.251E+02	2.21E+01	5.51E-04	1.10E+00		I-129	0.000E+00	0.00E+00
K	**7.597E+04**	1.36E+04	3.48E-01	3.48E+02		Cs-137	**4.860E+00**	8.63E+05
NO3	**9.537E+04**	1.71E+04	2.76E-01		2.76E+02	Sm-151	1.312E-01	2.33E+04
NO2	3.903E+00	6.91E-01	1.50E-05		1.50E-02	Eu-152	8.400E-05	1.49E+01
CO3	3.562E+00	1.59E-01	2.64E-06		5.29E-03	Eu-154	6.030E-03	1.07E+03
PO4	**1.691E+03**	3.02E+02	3.17E-03		9.52E+00	Eu-155	2.220E-03	3.94E+02
SO4	2.157E+01	3.83E+00	3.99E-05		7.98E-02	Ra-226	2.898E-10	5.15E-05
Si	0.000E+00	0.00E+00				U-235	7.801E-02	1.39E+04
F	1.538E+02	2.76E+01	1.45E-03		1.45E+00	U-236	2.412E-02	4.28E+03
Cl	9.616E+00	1.71E+00	4.82E-05		4.82E-02	U-238	**1.798E+00**	3.22E+05
Butanol	3.114E-02	5.58E-03				Np-237	3.021E-06	5.36E-01
TBP	0.000E+00	0.00E+00				Pu-238	1.226E-01	3.88E+02
NPH	0.000E+00	0.00E+00				Pu-239	**1.085E+00**	3.45E+03
NH3	3.134E-02	5.62E-03	3.30E-07	3.30E-04		Pu-240	3.817E-01	1.20E+03
U-Total	**5.388E+03**	9.64E+02	4.05E-03	8.10E+00		Pu-241	**7.195E+00**	2.28E+04
			total	3.61E+02	2.87E+02	Am-241	5.351E-03	9.50E+02
			meq/L			Cm-242	8.524E-06	1.51E+00
						Cm-244	2.253E-05	4.00E+00

216-A-4 received wastes from 1955 to 1958; waste category is Concentrated Miscellaneous UNH Stream (P1) with low probability of small volumes of PUREX PL1 (P1) waste.
Total volume disposed to 216-A-4 Crib was 6.21 mega liters (6,210,000 liters).
Radionuclide concentrations in SIM, Rev. 1 have been decay corrected to 01/01/2001.
The cation-anion charge balance is fair (23% excess cations) suggesting that hydroxide used for pH adjustment is not being captured in the chemical composition estimates. **Major constituents noted in bold red type.**

Based on the SIM, Rev. 1 information, the waste stream discharged to the 216-A-4 Crib was categorized as a concentrated miscellaneous PUREX UNH (uranium nitrate hexahydrate) waste stream (P1) that did not contain organics (unlike 216-A-2 Crib waste stream which contained significant quantities of organics) and was predominately a potassium nitrate solution with minor amounts of sodium, calcium, phosphate, and fluoride. The charge balance of the estimated solution composition is reasonable, especially if the excess cations are in fact compensated by hydroxide (which is not tracked explicitly in the SIM, Rev. 1). The ionic strength of the waste discharged to the 216-A-4 Crib was about 3 times larger than the solution disposed to 216-A-2 Crib, assuming that the organics in 216-A-2 Crib waste stream were not electrically charged.

The SIM, Rev. 1 estimates the total volume of waste disposed to the 216-A-4 Crib at 6.21 mega liters compared to the WIDS estimate of 6.21 mega liters. The time period of active disposal was 1955 to 1958 in both the SIM and WIDS databases. Because the volume of waste disposed to the 216-A-4 Crib was about 27 times larger than the volume disposed to the 216-A-2 Crib, the total inventories of radionuclides disposed to the 216-A-4 Crib is larger than the 216-A-2 Crib, despite the concentrations of dissolved radionuclides being lower in the waste stream sent to the 216-A-4 Crib.

The constituents with the largest inventories disposed to the 216-A-4 Crib were nitrate (95,370 kg), potassium (75,970 kg), uranium (5388 kg) and phosphate (1691 kg) based on the SIM, Rev. 1. The radionuclides with the largest inventories disposed to the 216-A-4 crib were tritium (64.5 Ci), Pu-241 (7.2 Ci), Cs-137 (4.86 Ci), Sr-90 (4.14 Ci), and Pu-239 (1.08 Ci).

Two borings have penetrated the cross-sectional area of the 216-A-4 Crib; one to a depth of 23 to 25 ft [~7.3 m] bgs (C4560) and one to 60 ft [18.3 m] bgs (C4671). Two additional borings were placed outside the cross-sectional foot print of the 216-A-4 Crib. The first was approximately 0.5 m from the northeast corner of the crib to a depth of 102 ft [31.1 m] bgs (A5911 or 299-E24-54), and the most recent borehole was placed 2.5 m from the southwest corner of the crib to a depth of 355 ft [108.2 m] bgs (C5301 or 299-E24-23). These four borings are shown on Figures 1 and 5. The field borehole geophysical logging data and direct measurements on sediment samples and water extracts from these boreholes are tabulated and discussed in later sections.

Based on the volume of waste disposed in the 216-A-4 Crib [~6.21 mega liters], the cross section of the crib foot print [20 x 20 ft; 37.16 m^2], the depth of the current water table [314 ft bgs], and assuming that the disposed liquid percolated vertically within the foot print and reached a volumetric water content of 10% after contacting the crib bottom, the entire volume of liquid disposed would have filled the foot print about 19 times over. Thus, without significant horizontal spreading, this crib was filled well beyond the specific retention volume of the vadose zone. A comparison of these estimates with the near continuous characterization of sediments from borehole C5301 is presented later in this letter report.

4.3 200-E-102 Trench

This trench is located inside the surface stabilized Underground Radioactive Material (URM) area south of the PUREX building. The trench is located approximately 68 ft (20.7 m) south of the southern boundary of the 216-A-4 Crib. The 200-E-102 Trench is a rectangle placed in the

east-west direction with dimensions of 80 feet (24.38 m) long by 10 ft (3.05 m) wide, with an approximate depth of 4 ft (1.22 m) based on a description found in Baldridge (1959). Currently, the trench is covered with clean gravel (since 1999) and has no surface markings to identify its location. As mentioned previously, contaminated sediments from the December 1958 flooding event at the 216-A-4 Crib were disposed in the 200-E-102 Trench in 1958. After placing the contaminated sediment in the trench, it was covered with 0.3 m of clean fill. One direct push hole (C5302) was placed in the western-third of this trench. There are no estimates of the waste inventory disposed to this trench in the SIM, Rev. 1. Borehole geophysical logs were obtained through the direct push casing and one sediment sample was obtained at 54.9 ft bgs for direct analysis. The results of both the field logs and direct laboratory measurements on the sediment sample will be discussed in later sections.

4. 4 216-A-21 Crib

The 216-A-21 Crib was built to replace the 216-A-4 Crib, which was deactivated in 1958. The 216-A-21 Crib was an open-bottomed, unlined liquid disposal site located approximately 160 m (525 ft) south of the 202-A Building at PUREX, inside the facility exclusion area fence. The crib site is covered with gravel (crushed rock). The site is associated with the 293-A, 202-A and 291-A buildings. A small surface depression was noted at the site of the 216-A-21 Crib in 1974.

Before June 1958, the unit used a 15-cm (6-in) perforated clay distribution pipe located 4.2 m (13.86 ft) below grade. In June 1958, this pipe failed, and the unit was taken out of service. A new distribution system was installed, and the unit was brought back into service in December 1958 (WIDS). A 10-cm (4-in) stainless steel distribution line ran horizontally through the length of the site, 2.1 m (7 ft) below grade or 3 meters (10 feet) below grade dependent on the source being cited. Branching horizontally from this distribution line were four 1.2 m (4 ft) sections of 10-cm (4-in) piping. Branching vertically at the same locations were four 2.4 m (8 ft) sections of 10-cm (4-in) schedule 40 stainless steel pipe running to the bottom of the site. The bottom 1.5 m (5 ft) of the vertical piping was perforated. The excavation was V-shaped in cross-section with a side slope of 1:1.5; the bottom of the crib was 15.2 m (50 ft) in length. There are 680 cubic m (24,000 cubic ft) of gravel fill in the excavation bottom, to a depth of 1.8 m (6 ft). Above the gravel, the site is backfilled with native overburden sediments.

There are discrepant records on the operational period of the 216-A-21 Crib. One source suggests that this crib was active between June 1965 and September 1970, and the SIM, Rev. 1, in conjunction with information in WIDS, suggests the 216-A-21 Crib was active between 1957 and 1965, which seems more plausible seeing as it was a replacement to the 216-A-4 Crib. When the effluent flow rate exceeded the infiltration capacity, the crib was deactivated by blocking off the inlet pipeline to the unit and rerouting the waste to the 216-A-27 Crib. A schematic of the infrastructure after 1958 is shown in Figure 4.

Based on information from the SIM, Rev. 1, the waste stream disposed to 216-A-21 Crib is categorized as a PASF (P2) waste that did not contain organics and was predominately a sodium nitrate solution with significant amounts of calcium, ammonium, carbonate and chloride. The charge balance of the estimated solution composition is cation rich by 65%, suggesting that the waste stream was basic from hydroxide neutralization, which is not tracked explicitly in the SIM,

Rev. 1. The ionic strength of the waste discharged to the 216-A-21 Crib was about 1.3 times higher than the solution disposed to the A-2 crib, assuming that the organics in 216-A-2 Crib waste stream were not charged, and almost 3 times lower than the waste solution sent to the 216-A-4 Crib.

The SIM, Rev. 1 model estimates the total volume of waste disposed to the 216-A-21 Crib at 77.9 mega liters, compared to the WIDS estimate of 77.9 mega liters. Because the volume of waste disposed to the 216-A-21 Crib was about 340 times larger than the volume disposed to the 216-A-2 Crib, and 13 times larger than the volume disposed to the 216-A-4 Crib, the total inventories of radionuclides disposed to the crib are generally larger than those for the 216-A-2 or 216-A-4 Cribs, regardless of the concentrations of dissolved radionuclides in the individual waste streams. Table 4 lists the total inventories for the radioisotopes that are highest amongst the three waste streams.

The chemical constituents with the largest inventories disposed to 216-A-21 Crib were nitrate (320,000 kg), sodium (108,000 kg), ammonium (66,300 kg), calcium (28,100 kg), and iron (8160 kg) based on SIM, Rev. 1 estimates. A comparison of total inventories of selected chemicals disposed to the three cribs is shown in Table 5. The 216-A-21 Crib has the highest inventories for the chemicals nitrate, sodium, ammonium, calcium, iron, chloride, and carbonate. The 216-A-4 Crib received the highest inventories of potassium, uranium, phosphate, fluoride, sulfate, and nitrite. The 216-A-2 Crib received the highest inventory of organic reagents: TBP and NPH.

Based on the volume of waste disposed in the 216-A-21 Crib [~78 mega liters], the cross section of the crib foot print [50 x 20 ft assumed width of V-shaped trench about a third of the distance up from the bottom where the sisalkraft layer separates the gravel backfill from overburden{see Figure 4}; 92.9 m^2], the depth of the current water table [314 ft (95.7 m) bgs], and assuming that the disposed liquid percolated vertically within the foot print and reached a volumetric water content of 10% after contacting the crib bottom, the entire volume of liquid disposed would have filled the foot print about 94 times. Thus, without significant horizontal spreading, this crib was filled well beyond the specific retention volume of the vadose zone. We can not compare the vertical distribution of constituents within or nearby this crib because no boreholes were drilled to depth near this crib.

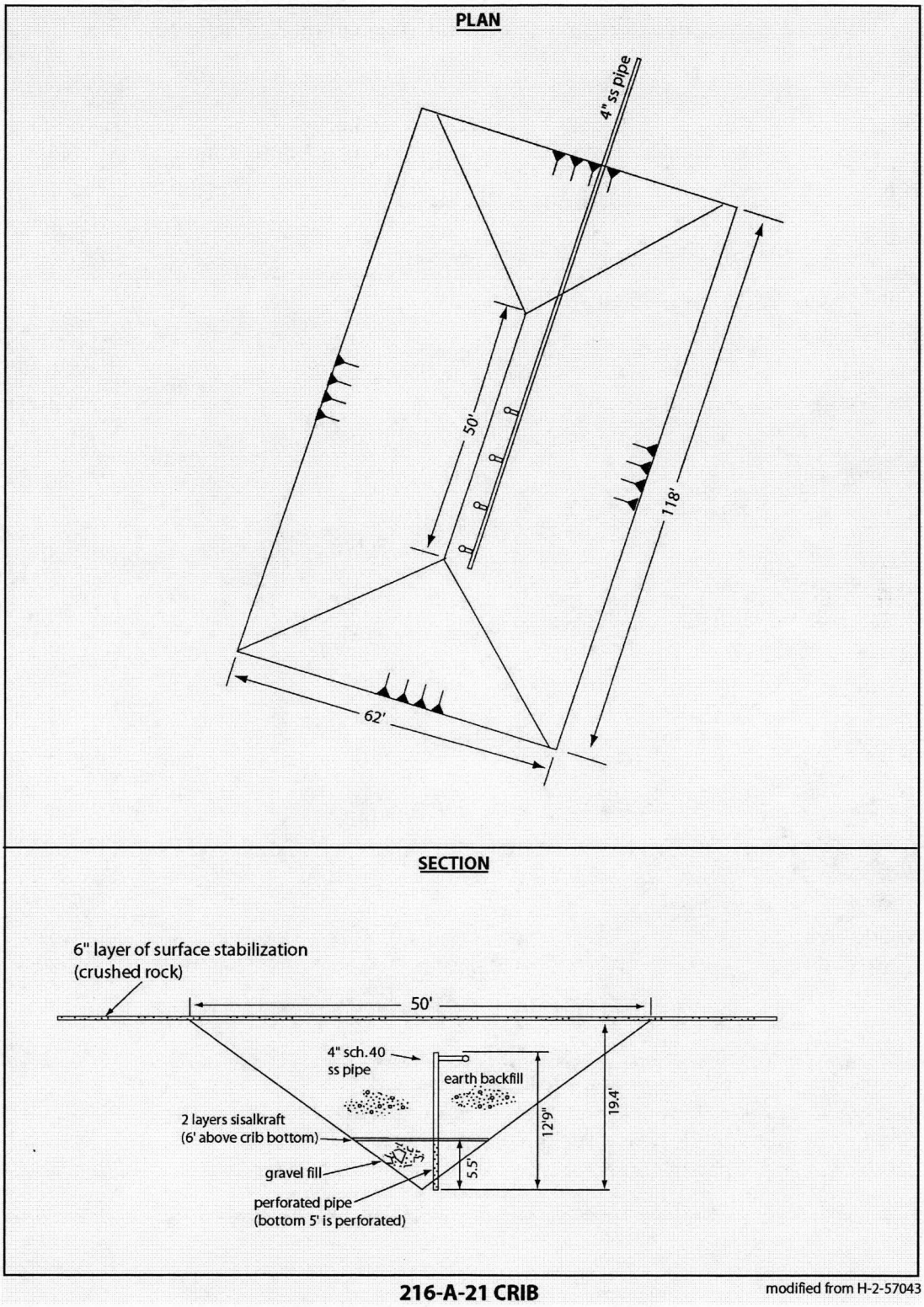

Figure 4. Schematic of the Infrastructure in 216-A-21 Crib

Table 3. . 216-A-21 Crib Inventory and Chemical Composition Estimates (based on SIM, Rev. 1)

Chemicals	Tot. Inventory (kg)	Conc. (mg/L)	Conc. (M)	Charge (+ meq/L)	Charge (- meq/L)	Radionuclides	Tot. Inventory (Ci)	Conc. (pCi/L)
Na	**1.075E+05**	1.53E+03	6.67E-02	6.67E+01		H-3	**4.949E+01**	7.06E+05
Al	0.000E+00	0.00E+00				C-14	0.000E+00	0.00E+00
Fe	8.160E+03	1.16E+02	2.08E-03	6.25E+00		Ni-63	0.000E+00	0.00E+00
Cr	0.000E+00	0.00E+00	0.00E+00		0.00E+00	Co-60	7.714E-02	1.10E+03
Hg	0.000E+00	0.00E+00	0.00E+00			Se-79	1.311E-04	1.87E+00
Ni	0.000E+00	0.00E+00	0.00E+00	0.00E+00		Sr-90	6.063E+00	8.65E+04
Ag	2.814E+00	4.01E-02	3.72E-07	3.72E-04		Tc-99	7.534E-03	1.07E+02
Mn	0.000E+00	0.00E+00	0.00E+00	0.00E+00		Sb-125	0.000E+00	0.00E+00
Ca	**2.809E+04**	4.01E+02	1.00E-02	2.00E+01		I-129	0.000E+00	0.00E+00
K	6.102E+02	8.70E+00	2.23E-04	2.23E-01		Cs-137	**6.374E+01**	9.09E+05
NO3	**3.203E+05**	4.57E+03	7.37E-02		7.37E+01	Sm-151	3.802E-01	5.42E+03
NO2	0.000E+00	0.00E+00	0.00E+00		0.00E+00	Eu-152	9.830E-05	1.40E+00
CO3	2.238E+03	3.19E+01	5.32E-04		1.06E+00	Eu-154	1.141E-02	1.63E+02
PO4	0.000E+00	0.00E+00	0.00E+00		0.00E+00	Eu-155	1.440E-05	2.05E-01
SO4	0.000E+00	0.00E+00	0.00E+00		0.00E+00	Ra-226	3.170E-06	4.52E-02
Si	0.000E+00	0.00E+00				U-235	2.776E-03	3.96E+01
F	0.000E+00	0.00E+00	0.00E+00		0.00E+00	U-236	1.706E-03	2.43E+01
Cl	2.543E+03	3.63E+01	1.02E-03		1.02E+00	U-238	6.497E-02	9.27E+02
Butanol	0.000E+00	0.00E+00				Np-237	2.370E-02	3.38E+02
TBP	0.000E+00	0.00E+00				Pu-238	2.215E-01	3.16E+03
NPH	0.000E+00	0.00E+00				Pu-239	4.607E+00	6.57E+04
NH3	**6.632E+04**	9.46E+02	5.57E-02	5.57E+01		Pu-240	1.130E+00	1.61E+04
U-Total	1.945E+02	2.77E+00	1.17E-05	2.33E-02		Pu-241	**1.005E+01**	1.43E+05
			total	1.49E+02	7.58E+01	Am-241	4.608E+00	6.57E+04
			meq/L			Cm-242	4.271E-03	6.09E+01

216-A-21 received wastes from 1957 to 1965; waste category is PASF (P2)
Total volume disposed to 216-A-21 Crib was 77.9 mega liters (77,900,000 liters)
Radionuclide concentrations in SIM, Rev. 1 have been decay corrected to 01/01/2001.
The cation-anion charge balance has an excess (65%) of cations suggesting that hydroxide used to neutralize acidic PUREX wastes in not being correctly captured in the estimates. Major constituents noted in bold **red** type.

Table 4. Total Inventory of Select Radioisotopes in Wastes Disposed to the A Cribs

	A-21	A-4	A-2
Isotope	Curies		
Cs-137	**6.374E+01**	4.860E+00	1.858E+00
H-3	**4.949E+01**	**6.446E+01**	1.398E-03
Pu-241	**1.005E+01**	**7.195E+00**	6.947E+00
Sr-90	**6.063E+00**	**4.144E+00**	8.918E-01
Am-241	**4.608E+00**	5.351E-03	1.760E-01
Pu-239	4.607E+00	1.085E+00	**7.884E+00**
Sm-151	3.802E-01	1.312E-01	**2.725E+01**
Pu-240	**1.130E+00**	3.817E-01	**1.585E+00**

Bold type shows the higher values for each isotope.
All values decayed to 01/01/2001

Table 5. Total Inventory of Select Chemicals in Wastes Disposed to A Cribs

	A-21	A-4	A-2
Chemical	kg	kg	kg
NO3	**3.203E+05**	9.537E+04	2.370E+03
Na	**1.075E+05**	4.468E+02	5.966E+00
NH3	**6.632E+04**	3.134E-02	5.155E-02
Ca	**2.809E+04**	1.251E+02	1.360E-01
Fe	**8.160E+03**	1.202E+01	6.050E-02
Cl	**2.543E+03**	9.616E+00	1.851E-01
CO3	**2.238E+03**	3.562E+00	2.036E-01
K	6.102E+02	**7.597E+04**	0.000E+00
U-Total	1.945E+02	**5.388E+03**	2.283E+02
PO4	0.000E+00	**1.691E+03**	0.000E+00
F	0.000E+00	**1.538E+02**	0.000E+00
SO4	0.000E+00	**2.157E+01**	2.439E+00
NO2	0.000E+00	**3.903E+00**	0.000E+00
TBP	0.000E+00	0.000E+00	**1.492E+05**
NPH	0.000E+00	0.000E+00	**6.392E+04**

One recent boring has penetrated the cross-sectional area of the 216-A-21 Crib (C5571) to a depth of 60 ft bgs, and one old borehole (299-E24-12) is located far to the southwest of the crib foot print. The old borehole was logged with a gross gamma probe in 1976. These two borings are shown on Figures 1 and 5. The field geophysical logging data and direct measurements on sediment samples and water extracts of the sediments are tabulated and discussed in later sections.

5.0 Borehole Gamma and Neutron Logs

Several boreholes have been emplaced within the 216-A-2/216-A-4/216-A-21 Cribs region in an attempt to determine the degree of detectable subsurface radiological contamination associated with the various disposal facilities (see Figure 5 and Table 6 for details). Specifically, borehole C5515 and direct push hole C5570 have been emplaced within the 216-A-2 Crib, and an older existing well 299-E24-53 (A5910) is located ~1.5 m east of the crib. Borehole C4560 (which was abandoned during drilling because of high radiological contamination) and direct push hole C4671 were emplaced within the 216-A-4 Crib. Additionally, a new borehole (299-E24-23 or C5301) was placed adjacent to the 216-A-4 crib. Well 299-E24-54 (A5911) is an older existing well that is also adjacent to the 216-A-4 crib. The 216-A-21 Crib has not been as well characterized, with only one direct push hole, C5571, and one older well 299-E24-12 placed rather distant to the south of the crib. Finally, only a single direct push hole (C5302) has been driven through the 200-E-102 Trench. A map showing the region of investigation is provided in Figure 5. Figure 5 also show the top 80 ft of the spectral gamma logs [SGLS] generated from interrogating the steel cased boreholes with various gamma detecting tools. The SGLS logs were cut off at 80 ft bgs because no significant man-made gamma signal was found at deeper depths. The total depths and dates of borehole drilling and logging events are listed in Table 6. The purpose of this section is to assimilate the existing logging data, the available measurements of chemicals and radionuclides in the sediment and sediment:water extracts of the sediments from the boreholes (and wells), and data from the groundwater in the region in an attempt to estimate the distribution of contamination beneath the facilities and the degree of lateral spreading of contaminants in the fluids disposed to the cribs.

Table 6 lists the boreholes that have been drilled near the three cribs and comments on the cased borehole geophysical gamma activity measured in the sediments as a function of depth. The discussion that ensues will emphasize relating the amount and spread of contamination amongst the three primary waste disposal facilities in the area: the 216-A-2, 216-A-4, and 216-A-21 Cribs based mostly on the cased borehole geophysical gamma logs.

According to historical documentation (WIDS), the 216-A-2 Crib received the lowest amount of Cs-137 of the three cribs, at 1.86 Ci. Additionally, this crib received the lowest volume of waste (230,000 L) by a factor of ~20 to ~300 vs. the 216-A-4 and 216-A-21 Cribs, respectively. The estimated concentration of Cs-137 in the liquid waste stream disposed to the 216-A-2 Crib (SIM, Rev. 1) decay corrected to 1-1-2001) was 9.0E+06 pCi/L, which is a factor of ten times more concentrated than the liquid waste streams disposed to the 216-A-4 and A-21 Cribs, respectively. Borehole gamma logging data from mid-2007 is available for two boreholes emplaced within the

foot print of the 216-A-2 Crib [C5515 and C5570]. Both boreholes confirm the presence of high levels of Cs-137 beneath the crib. The total amount of gamma activity in the two boreholes

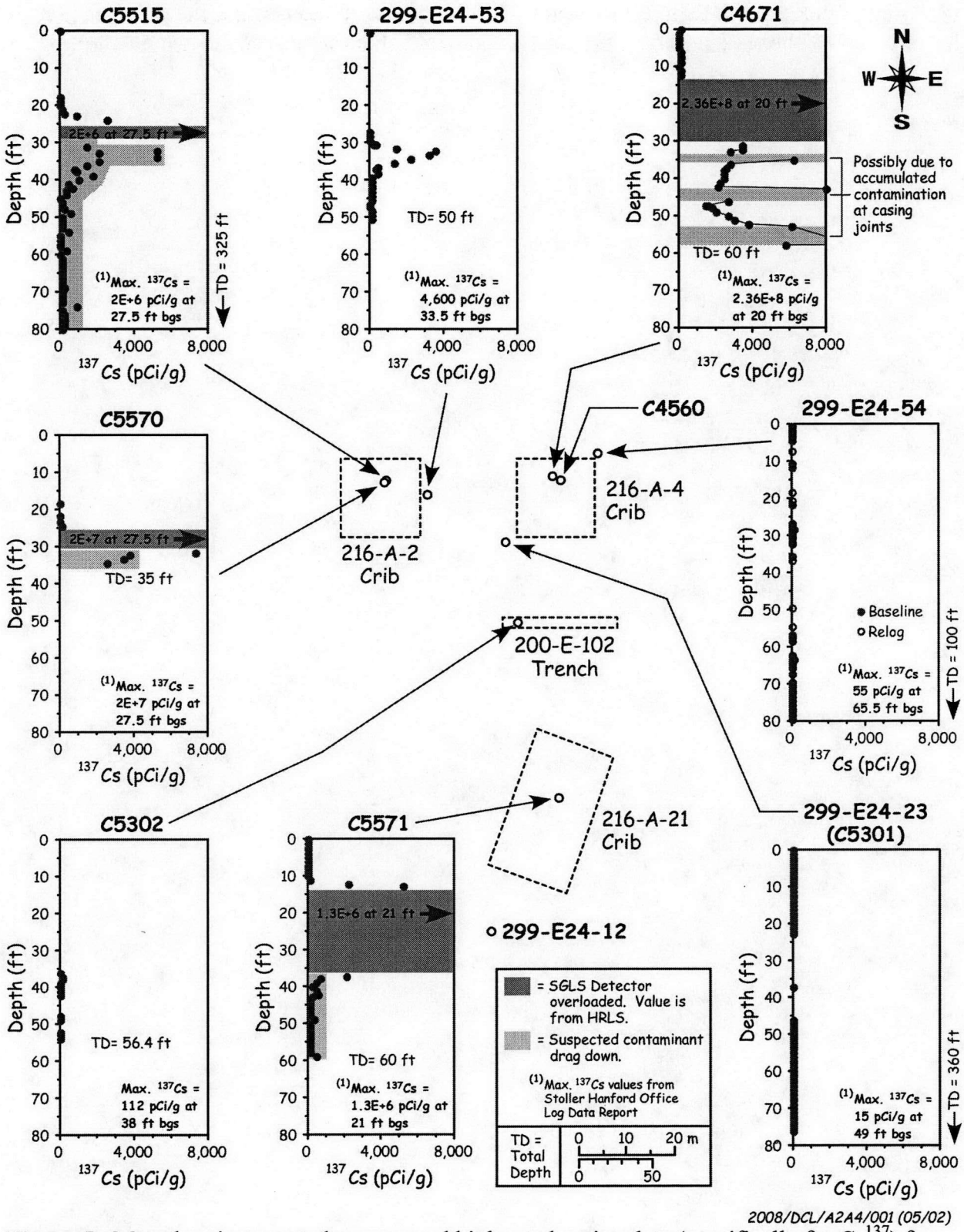

Figure 5. Map showing spectral gamma and high rate logging data (specifically for Cs^{137}) for boreholes emplaced near the 216-A-2, 216-A-4, and 216-A-21 Cribs and the 200-E-102 Trench. See Table 6 for details on the total depths of each borehole/well and the dates of the logging events and discussion on log results deeper than 80 ft bgs.

exceeded the dead time capacity of the spectral gamma tool and as a result, the high rate logging data had to be converted to equivalent Cs-137 activity. Peak Cs-137 activities in the SGLS logs from the two boreholes within the foot print of 216-A-2 Crib ranged from 2E+06 pCi/g (C5515 at 27.5 ft bgs) to 2E+07 pCi/g (C5570 @ 27.5 ft bgs) based on borehole spectral gamma logging. These peak concentration values coincide with the sediment interface between the bottom of the gravel-filled crib and the surrounding native sediment and are in good agreement. Based on the logging data, there appears to be migration of the Cs-137 from the vitreous clay pipes at 21 ft bgs down to the crib bottom (bottom of the gravel fill) at 28 ft bgs and deeper into native sediment.

Determining the maximum depth of the Cs-137 contamination in the two boreholes is more difficult due to apparent casing contamination caused by driving the drill casing (smearing contamination) through and below the peak zone of contaminant detected (~27.5 ft bgs). The spectral gamma log data shows apparent Cs-137 contamination to the bottom of the borehole (~35 ft bgs) in C5570; Stoller Inc. reported that casing contamination was also observed in borehole C5515. This smeared contamination can be differentiated by comparing the geophysical Cs-137 log (C5515) results through the 1st string of casing (driven to ~85 ft bgs) to the 2nd log, which was run through the remainder of the borehole (using a 2nd string of casing) from 85 ft bgs to the total borehole depth. The 1st logging run reveals elevated Cs-137 all the way to the bottom of that 1st casing (~85 ft bgs) with concentrations ranging up to a 1000 pCi/g. However, the interval immediately below this depth and all the way to total depth did not encounter Cs-137 contamination. As reported by Stoller in the log report, this discrepancy between the geophysical log runs strongly suggests that the contamination detected below ~28 ft bgs to the bottom of the 1st casing (~85 ft bgs) is solely due to casing contamination rather than contamination in the formation from crib disposal operations. These data strongly suggest that the depth of Cs-137 contamination maybe limited in depth to no more than about 40 ft bgs.

Sediment grab and core samples retrieved from C5515 showed a few samples with detectable Cs-137 (Table 7). The samples show a sharp peak of Cs-137 [31,000 pCi/g] at 27.5 ft bgs with additional elevated [~>1000 pCi/g] values between 30.2 to 30.3 ft bgs with the next shallower and deeper samples measured at 24.8 and 33.3 ft bgs showing much lower activity. The continuous field logs show the activity peak, with values >10E+04 pCi/g, occurred between 25.5 and 29.5 ft bgs. Thus, the depth discrete grab samples could have missed the most radioactive zone, which appears to be very thin, and only detected near the bottom of the 216-A-2 Crib by the borehole geophysical logging.

The total mass of Cs-137 (in curies) that would be present in the foot print of the facility in the thin extremely concentrated zone between 26 and 29 feet bgs would be ~1000 curies if the total volume contained 2E+07 pCi/g and ~100 curies if the volume contained 2E+06 pCi/g. As shown in Table 4 the total inventory of Cs-137 disposed to A-2 crib was only 1.86 curies. It would thus appear that the extremely radioactive zone does not cover the entire cross-sectional area of the crib. Alternatively, either the spectral gamma activity values are incorrect or the inventory estimate is wrong. One conclusion that can be drawn from this Cs-137 concentration times estimated volume of contaminated sediment analysis is that the inventory of Cs-137 disposed appears to be strongly bound within a very small volume of sediment within a few feet of the crib bottom and that there is more than adequate sediment volume in the crib foot print to have

adsorbed the total inventory disposed given the concentrations of Cs-137 observed by spectral gamma logging and discrete sediment sample analysis.

The sediment samples from borehole C5515 show Cs-137 activities ranging from ~1 to 15 pCi/g at depths in excess of 40 ft bgs. These values are lower than the spectral gamma logging data, which can be explained because the borehole geophysical spectral data is picking up the additional Cs-137 on the contaminated casing. Based on these data, the Cs-137 contamination reaches about 40 ft bgs and the contribution to geophysical log signal from casing contamination below 40 ft bgs accounts for all the deeper apparent activity.

At push hole C5570 the spectral gamma logging suggests there was a high activity, very sharp and thin peak centered at the very bottom of the crib (~28 ft bgs). The moderate vertical and lateral migration of contamination at this crib is confirmed by the geophysical logging data measured in borehole 299-E24-53, which was emplaced 1.5 m outside the crib foot print in 1955. Borehole 299-E24-53, which was logged in 2005, detected Cs-137 from approximately 28.5 ft bgs to the bottom of the borehole (~52 ft bgs); peak Cs-137 activity of 3500 pCi/g was detected at approximately 33.5 ft bgs. In 2007, the spectral gamma logs for borehole C5515 and C5570 showed 1 to 2.6 E+03 pCi/g Cs-137 was present at 39 and 34 ft bgs, respectively. Cs-137, measured via gamma energy analysis, of the actual sediment samples retrieved from comparable depths ranged from 50 to 30 pCi/g, a factor of 10 lower. These differences in Cs-137 concentration data can be explained as casing contamination measured in the geophysical logs below the peak zone of contamination, which would not be seen in the grab samples. Regardless, the activities of Cs-137 dropped 3 to 4 orders of magnitude below the peak interval over 6 to 11 ft vertically. Clearly, based on the spectral gamma log at 299-E24-53 (located outside the crib), some vertical and lateral migration of waste in the range of 13 to 19 ft below the inlet pipes (6 to 11 ft below bottom of crib), and at least ~5 ft of lateral spreading has occurred from this disposal facility at a depth of ~13 ft below the inlet pipe elevation or 6 ft from the crib bottom. Based on the Cs-137 logs from 299-E24-53, the first vertical detection is approximately 29 ft bgs, which is very close (~1 ft) to the crib bottom. The peak Cs-137 activity occurs at approximately 33.5 ft bgs. This old borehole has been logged repeatedly over the years; the available data cover a period from 1982 to 2005 (23 years). Comparison of geophysical log results for that time range indicates no movement or change in concentration for Cs-137. This data suggests that the Cs-137 spread laterally to this area very early on and probably during the time active disposal was occurring to the crib, but has not spread any farther. Assuming that the lateral spread of Cs-137 has reached 5 ft beyond the crib foot print in the easterly direction, the plume foot print could have a cross-sectional area of at least (20 ft X 25 ft; 46 m^2). If the wastes disposed to the 216-A-2 Crib percolated down throughout this larger cross-section, and we use the same assumptions on the volumetric moisture content of 10%, the leading edge of the waste plume would have descended to approximately 185 to 190 ft bgs, which is well above the current water table at ~314 ft bgs.

Table 6. Boreholes Emplaced within the 216-A-2, A-4 and A-21 Study Area.

	C5515	C5570	A5910 (299-E24-53)	A5911 (299-E24-54)
Location:	216-A-2 Crib (within Crib)	216-A-2 Crib (within Crib)	216-A-2 Crib (outside Crib)-1.5 m to east	216-A-4 Crib (outside Crib)-0.5 m from NE corner
Date Installed:	July 2007	May 2007	January 1955	January 1955
Total Depth:	322 ft	35 ft	52 ft	102 ft
Depth to Groundwater:	314 ft	NA	NA	NA
Date Logged:	July and August 2007	May 2007	October 2005	April and October 2005
Radionuclides Detected:	Cs-137 from 18 to 86 ft	Cs-137 from 18.5 to total borehole depth (~34.5 ft)	Cs-137 from 29-total depth (~52 ft); Co-60 at 31.5 ft and 36.5-48.5 ft; Eu-154 at 31.5 and 36.5-40.5 ft	Cs-137 from 29-36 ft and 64-91 ft; Co-60 between 29-54 ft and 65-69 ft
Crib Bottom Depth:	28 ft bgs	28 ft bgs	28 ft bgs	25 ft bgs
Peak Activity:	2E+06 pCi/g at 27.5 ft; near bottom where gravel sits on native sediment	2E+07 pCi/g at 27.5 ft; near bottom where gravel sits on native sediment	4600 pCi/g at 33.5 ft (Cs-137); 4 pCi/g at 36.5 ft (Co-60); 6 pCi/g at 36.5 ft (Eu-154); 5.5 ft below crib bottom	55 pCi/g at 65.5 ft (Cs-137); 2 pCi/g at 45.5 ft (Co-60); 30.5 ft below crib bottom
Notes:	Casing was internally contaminated			
	C5301	**C4560 and C4671**	**C5571**	**C5302**
Location:	216-A-4 Crib (outside Crib)-2.5 m SW of crib	216-A-4 Crib (within Crib)	216-A-21 Crib (within Crib)	200-E-102 Trench (inside the western third)
Date Installed:	January 2007	August 2004	July 2007	October 2006
Total Depth:	355 ft	C4560 [~25 ft]; C4671 [60 ft]	60 ft	55 ft
Depth to Groundwater:	314 ft	NA	NA	NA
Date Logged:	December 2006 and January 2007	September 2004	August 2007	October 2006
Radionuclides Detected:	Cs-137 from ground surface to 23 ft and 46-76	C4560 was not logged before abandonment. Cs-137 from	Cs-137 from ground surface to total borehole depth (~59	Cs-137 from 36-42 ft; Eu-154 from 48-to bottom of

	ft	ground surface to total borehole depth (~58 ft) for C4671	ft)	borehole (~54 ft)
Crib/Trench Bottom Depth:	25 ft bgs	25 ft bgs	19.33 ft bgs	19.33 ft bgs
Peak Activity:	15 pCi/g at 49 ft; 25 ft below crib bottom	2.36E+08 pCi/g at 20 ft for C4671; 2 ft below distribution pipes and 5 ft above crib bottom	1.3E+06 pCi/g at 21 ft; 2 ft below crib bottom in native sediment	112 pCi/g at 38 ft (Cs-137); 3 pCi/g at 52.5 ft (Eu-154)
Notes:		Casing was internally contaminated	Casing was internally contaminated	

Table 7. Cs-137 Activity in Grab and Core Samples from Borehole C5515 Emplaced within 216-A-2 Crib, (PNNL analyzed grab samples and others analyzed core samples)

Sample ID	Depth (ft bgs)	Cs-137 (pCi/g)
B1NRH0	14.25	<0.01
B1NPW0	17.8	<0.06
B1NPW3	24.8	0.16
B1NRJ2	27.25	**31,000**
B1NR91	30.2	827; 1070
R1NRH1	30.2	1510; 3700
B1NPW4	30.3	9694; 12700
B1NPW5	31.75	393; 448
B1NR92	33.3	110; 176
B1NRH2	33.3	130
B1NRH3	33.3	90
B1NPW6	34.2	1030; 1700
B1NPW7	37.2	873; 1390
B1NPW8	39.8	16.4; 42
B1NPX0	45.3	2.5
B1NPX1	47.3	9.29
B1NRH4	48.5	14.5
B1NPX3	51.8	0.51
B1NRH7	55.8	5.31
B1NPX5	57.25	6.16; 9.01
B1NPX6	59.8	0.91
B1NPX8	64.3	7.78
B1NPY0	70.3	<0.06
B1NPY1	72.8	<0.06
B1NPY4	79.8	<0.06
All deeper	PNNL samples	<0.06
All deeper	WSCF samples	<0.01

Yellow shading WSCF; Pink shading Eberline; tan shading 222-S lab; white PNNL
Blue type represents GEA of acid extracts of the sediment and black type represents direct sediment GEA counting.

At the 216-A-4 crib, there is one borehole within the crib [C4671] footprint that was spectral gamma logged and one borehole [C4560] that was not logged (but for which one grab sample of sediment was obtained) and two wells outside (0.5m from the NE corner [299-E24-54] and 2.5 m from the SW corner [299-E24-23 (C5301)]) the crib, respectively. The ionic strength of the solution disposed to the 216-A-4 Crib was about 3

times larger than the solution disposed to 216-A-2 Crib, assuming that the organics in 216-A-2 Crib waste stream were not electrically charged. The higher ionic strength of liquid waste disposed to the 216-A-4 Crib should promote migration of Cs-137 to greater distances than Cs-137 migration at the 216-A-2 Crib. Additionally, a larger volume, approximately 6.21 million liters of waste fluids were disposed to the 216-A-4 Crib compared to 216-A-2 Crib, which also would promote more Cs-137 migration. The disposal facility's piping is ~18 ft bgs and the crib bottom is at ~25 ft bgs with gravel placed between the pipes and crib bottom.

The borehole gamma logging data (C4671) inside the 216-A-4 Crib shows very large concentrations of Cs-137 beginning near the depth of the crib piping inlet and increasing to a maximum concentration (2.36E+08 pCi/g) at approximately 20 ft bgs, which is approximately 5 ft above the bottom of the crib. Measurable Cs-137 is found all the way to the total depth of borehole C4671 at 58 ft bgs, but the repetitive and consistently spaced peaks in the geophysical log data at approximately 35, 45, and 55 ft bgs are casing contamination artifacts and most likely not real. The bulk of the contamination appears to drop off in concentration below approximately 35 ft bgs at this location.

In well 299-E24-54 (A5911), located ~0.5 m northeast of the 216-A-4 Crib corner, Cs-137 is detected beginning at approximately 29 ft bgs (excluding a small near surface zone of contamination). The Cs-137 shows two activity peaks of about equal values at approximately 30 ft bgs and 66 ft bgs with a maximum activity near 60 pCi/g and drops below detection at approximately 38 ft bgs. Surprisingly, Cs-137 is again detected deeper, averaging several tens of pCi/g between 64 to 91 ft bgs, with the maximum of 60 pCi/g at 66 ft bgs). The fact that this well is only 0.5 m from the 216-A-4 Crib foot print appears to suggest that lateral migration of Cs-137 from the crib foot print is quite limited. Borehole geophysical logging in this borehole can be traced back to 1963 with the total gamma activity nearly two orders of magnitude higher then than the total gamma activity measured during the 2005 survey. Repeat logging data from this well over the last several decades reveals that, while the total activity (attributed mostly to Cs-137) was much higher in the past (decayed away), the vertical location of the Cs-137 contamination in the well has not changed and not migrated deeper, remaining fixed. The bimodal shape of the spectral gamma logging through the casing at 299-E24-54 suggests that the horizontal spreading of Cs-137 from the crib foot print has been irregular; that is fluids percolating vertically through the crib exhibit irregular horizontal spreading planes most likely caused by subtle differences in grain size in the stratigraphy (finer-grained thin beds are known to promote horizontal spreading).

At the other well, 299-E24-23 [C5301], drilled 2.5 m southwest of the 216-A-4 Crib foot print, detectable Cs-137 was found from the ground surface down to 23 ft and from 46 to 76 ft bgs. The highest Cs-137 activity (15 pCi/g) in the spectral gamma log at well 299-E24-23 (C5301) was found at 49 ft bgs. However, the Cs-137 activity of sediment samples taken from well 299-E24-23 (C5301), as shown in Table 8, does not exceed 9 pCi/g and this maximum value resides in a fine-grained thin lens at 51 ft bgs. The two different measurements (continuous borehole geophysical logging and discrete sediment samples) are likely capturing the small amounts of Cs-137 contained in the thin fine-

grained lens. The fact that the Cs-137 concentrations in both of these boreholes just outside the 216-A-4 Crib footprint [299-E24-54 is only 0.5 m and 299-E24-23 [C5301] is 2.5 m from the 216-A-4 Crib foot print] are up to 10 million times smaller than the maximum Cs-137 activity within the foot print demonstates that lateral migration of Cs-137 from the crib foot print is quite limited. This is corroborated by direct analyses of sediment from 299-E24-23 (C5301), where low concentrations of Cs-137 (<20 pCi/g) are detected below the crib depth from approximately 45 and 76 ft bgs. There are limited measurements of sediment from the C4560 borehole within the crib foot print (shown in Table 8). The Cs-137 content in sediments within the crib foot print down to the maximum depth of the borehole (~25 ft bgs) shows very high concentrations near the bottom of the crib (22.5 ft bgs). Borehole C4560 was never geophysically logged and decommissioned before reaching the planned total depth due to unexpected high levels of Cs-137 contamination encountered during drilling. Borehole C4671 was added near C4560 to collect borehole geophysical data to delineate the extent of the high radiological contamination. The borehole gamma log for borehole C4671, which is right next to borehole C4560, showed a maximum Cs-137 activity of ~2.4 E+08 pCi/g at 20 ft bgs. The value [5 E+06 pCi/g] in C4560 sediment is deemed to be more accurate because it was a direct measurement as opposed to being an estimate based on converting count-rate data from a highly shielded detector through the steel borehole casing (C4671). Either way, there is little doubt that there is a zone of very concentrated Cs-137 near the bottom of the 216-A-4 Crib that does not migrate very far laterally based on the two wells, 299-E24-54 and 299-E24-23 (C5301), which are only 0.5 and 2.5 m outside the crib foot-print, respectively. It also appears that the vertical migration of Cs-137 within the 216-A-4 Crib foot print during active disposal was limited and now appears to be fixed. Between 20 and 32 ft, Cs-137 concentrations decrease to between 10^3 and 10^4 pCi/g and remain in this range to the total depth of borehole C4671 at 58 ft bgs. The very high concentrations at 20 ft bgs, estimated to be 2.4 E+08 pCi/g, appear to be approximately 1 foot thick. Although the leading edge of the Cs-137 plume (vertically) in the crib foot print has not been determined, it does appear to extend below 58 ft. However, the center of mass of Cs-137 disposed to the crib remains near the crib bottom within the gravel between 20 and 25 ft bgs.

Table 8. Cs-137 Activity in Sediment Samples Obtained from Inside and Outside the Foot Print of 216-A-4 Crib

Borehole	Sample ID	Depth (ft bgs)	Cs-137 (pCi/g)
C4560	B195V9	1.75	0.61
	B195W0	13.75	<0.01
	B197F0	19.75	63,600
	B1CLN9-B	22.5	5,630,000
C5301	B1L4Y7	22.25	0.00
	B1L4T7, B1L5N2	30.25	<0.01
	B1L500	30.75	<0.06
	B1L504	39.75	<0.06
	B1L4V2, B1L5N6	44.26	<0.01
	B1M5X1	51	8.56
	all deeper	PNNL samples	<0.06
	all deeper	WSCF samples	<0.01

C4560 is within the crib foot print and C5301 is 2.5 m outside the foot print in the SW corner
Yellow shading WSCF and white shading PNNL data

The Cs-137 spectral gamma data do not indicate that much horizontal spreading or vertical percolation occurred at this site; however, more direct measurement of mobile constituents in the deeper sediments from C5301 borehole, such as nitrate and tritium, suggest that fluids disposed to the 216-A-4 Crib have percolated down to ~300 ft bgs and have spread at least 2.5 meters southwest of the crib's foot print. Based on the estimate that the volume of liquid disposed to the 216A-4 Crib exceeded the specific retention capacity of the crib foot print by 19 times, deep penetration of mobile constituents and horizontal spreading should be expected.

A simple box model of the 216-A-4 Crib with four compartments within the foot print from the depth of the inlet pipes down to 58 ft bgs, the depth of the direct push hole C4671 using a combination of the Cs-137 concentrations estimated by spectral gamma and direct sediment measurement yielded a total inventory of ~115 curies. This assumed that the one-foot thick zone at 20 ft bgs contained 5 E+06 pCi/g Cs-137 based on the direct measurement of sediment as opposed to the estimated concentration of 2.4 E+08 pCi/g from the highly shielded gamma log. As found for the 216-A-2 inventory calculation, this estimate is much larger than the SIM, Rev. 1 estimate for Cs-137 disposed to 216-A-4 [4.86 curies]. The main conclusion is that the observed concentrations of Cs-137 in sediments removed from the shallow in the foot print contain all of the inventory disposed and that the entire crib foot print likely does not contain the high Cs-137 concentrations observed in the sediment sample taken from the center of the crib [borehole C4671]. Further, there are only small amounts of Cs-137

laterally outside the crib foot print as evidenced by samples and gamma logs from wells 299-E24-23 (C5301) and 299-E24-54.

The 216-A-21 crib received the largest amount of Cs-137, 64 total Ci, of the three cribs studied. Additionally, the ~ 78 million liters of fluid disposed to this crib was an order of magnitude more volume than that sent to the 216-A-4 Crib, and more than two orders of magnitude more volume than that sent to the 216-A-2 Crib. Unfortunately, only one shallow borehole within the foot print of the 216-A-21 Crib and no borehole logs outside the foot print [although there is one old monitoring well 299-E24-12 to the southwest] are available to assess the level of contamination associated with the crib. Based on the borehole geophysical logging data for push hole C5571 located within the crib foot print, Cs-137 associated with the 216-A-21 Crib exhibited the largest degree of vertical movement of all three cribs studied. While the peak Cs-137 activity of 1.3 E+06 pCi/g was encountered at approximately 21 ft bgs, which is ~2 ft below the crib bottom, the overall zone of Cs-137 contamination began to increase dramatically at about 10 ft bgs and dropped off around 35 ft bgs. While Cs-137 was detected over the entire length of the direct push borehole, which terminated at ~ 60 ft bgs, there was internal contamination confirmed (Stoller log report) inside the casing and there is no way to determine how much of observed contamination below ~ 35 ft bgs is due to casing contamination carried down the outside of the casing. This relatively continuous, low concentration Cs-137 contamination below the large contaminant peak (10 to 35 ft bgs) is very similar to the drag-down contamination documented in the C5515 borehole at the 216 A-2 Crib. C5571 was a closed end direct push hole with the capability to sample only at a few depths; two sediment samples were obtained at depths of 39.75 and 59 ft bgs, respectively. The Cs-137 contents in these two samples were 3,700 and 180 pCi/g, respectively. The actual measurement of Cs-137 in the sediment at 39.75 ft bgs was about 5 times greater than the borehole geophysical log calculated value, but could be explained by the lack of depth control of where the grab sample actually came from in the pulled back casing. The sample was collected as the casing was pulled back and could have collapsed into the open borehole from a shallower and more contaminated interval. The Cs-137 activity in the sediment sample at 59 ft bgs was consistent with the gamma log calculated value. Based on an inlet pipe depth of approximately 10 ft bgs but with vertical perforated pipes descending to the crib bottom at 19.3 ft bgs, measureable Cs-137 has migrated at least 50 ft below the inlet and 40 ft below the crib bottom. While no boreholes are available to investigate the degree of lateral spreading beyond the foot print of the crib, it is believed that more lateral and vertical spreading would be found at the 216-A-21 Crib than was measured at the 216-A-2 or A-4 Cribs since the volume of waste disposed to the 216-A-21 Crib was larger by a factor of 340 and 13, respectively.

The fact that the volume of waste disposed to the 216-A-21 Crib exceeded the specific retention capacity of the vadose zone beneath the crib by about 94 times suggests mobile contaminants disposed to this crib have percolated deeply and spread horizontally within the fine-grained layer between 280 and 300 ft bgs and perhaps have broken through to the water table.

Using the same "box model" exercise for calculating the mass of Cs-137 within the 216-A-21 Crib foot print, based on the spectral gamma log and two sediment samples retrieved from push hole C5571, we estimate that sediments within the foot print of 216-A-21 down to 60 ft bgs contain ~60 curies of Cs-137. This compares quite favorably with the SIM, Rev. 1 estimate of 63.7 curies.

The geophysical spectral gamma logging of borehole C5302, located within the 200-E-102 Trench, shows a narrow zone of Cs-137 contamination in the sediment relatively deep beneath the trench from 36 to 42 ft bgs with a maximum concentration of 112 pCi/g at 38 ft bgs. There is a small concentration of Eu-154 (~ 3 pCi/g) found between 48 and 54 ft bgs. There is also an indication of bremmstrahlung radiation between 40 to 47 ft bgs that would be evidence of the presence of Sr-90 based on another similar situation found while logging the casing at a borehole near single-shell tank B-110 for which confirmatory sediment samples were obtained that contained significant concentrations of Sr-90 [see Serne et al. (2002d) for details]. Only one sediment sample was obtained and characterized from borehole C5302 at a depth of 55 ft bgs. The Cs-137 content of this sediment sample was 0.83 pCi/g.

If the disposal history at the 200-E-102 Trench is solely the placement of contaminated sediments removed from the 216-A-4 Crib when it plugged in 1958, it is odd that the three radionuclides, Cs-137, Eu-152, and Sr-90 are found at depths between 36 and 54 ft bgs as opposed to shallower in the vadose zone. Records indicate that the trench's depth was only 4 ft. Additionally, it is documented that a one-foot deep layer of clean fill was placed on top of the trench immediately after the contaminated sediments were placed in it. In 1999, the whole area was covered with clean gravel. Why the gamma emitting radionuclides are found 30 to 50 ft deeper than where the contaminated sediments were buried is unknown. All three of the radionuclides should have partitioned relatively well to Hanford sediments. Therefore, contaminated sediments placed in a trench and then contacted only with natural precipitation should not have caused the bulk of the radionuclides to migrate to depths of 36 to 54 ft bgs.

The spectral gamma logs of this borehole show no radioactivity from the ground surface to a depth of 36 ft bgs. If contaminated sediments were placed in this trench and covered over with clean backfill, then the gamma logs should have detected radioactivity at shallower depths, even if one assumes that contaminated sediments were spread throughout the entire foot print of the trench. The mass of contaminated sediment from around the 216-A-4 Crib that was scraped up and buried in 200-E-102 Trench needs to be further investigated so that the disposal operation at 200-E-102 Trench can be better constrained. Perhaps the 200-E-102 Trench was used earlier for disposal of liquid wastes and the contaminated sediments added latter were in fact not laden with detectable gamma emitters such that the logging signals are showing only past liquid waste generated adsorption patterns for relatively good sorbates. However, the SIM, Rev. 1 database does not include any information for the 200-E-102 Trench, which suggests that this facility did not receive liquid wastes from documented disposal activities. Alternatively, perhaps the contaminated sediments from the 216-A-4 Crib were placed in only the eastern portion of the trench, such that their activity was not detected due to the

placement of borehole C5302. Finally, if the mass of contaminated sediments was very small and it was evenly distributed throughout the trench in a very thin layer, it is possible that the logging technique did not detect the thin zone of 216-A-4 contaminated sediments placed shallow in the trench. A final scenario could be lateral spread of contamination from the 216-A-21 Crib in a northerly direction to intercept the foot print of the 200-E-102 Trench; however, this would appear unlikely given the distances between the two facilities and the small vadose zone lithology dip to the southwest. At this time, the source of the gamma contamination found in borehole C5302 remains unresolved.

All of the borehole geophysical gamma logging and sediment characterization data for the 216-A-2, 216-A-4 and 216-A-21 Cribs can be used to estimate the total mobility of Cs-137 disposed to the cribs. The field gamma logging estimates can be compared to direct analyses of sediments collected as a function of depth at boreholes. The 216-A-4 Crib received 5 Ci of Cs-137 in 6.2 million liters of liquid waste. High levels of Cs-137 have been encountered in both the gamma logs and direct analysis of sediment samples sent to analytical laboratories from boreholes emplaced within the 216-A-4 Crib foot print. The peak Cs-137 activity measured in sediment retrieved from the abandoned borehole (C4560), which was stopped at ~23 ft bgs, was approximately 2E+06 pCi/g at 21 ft bgs.

Direct push borehole C4671, which was stopped at 60 ft bgs, was pushed through a zone of Cs-137 with an activity in excess of 2.4E+08 pCi/g at 20 ft bgs. Beginning at 12 ft bgs, Cs-137 activities increase rapidly to the maximum value at 20 ft bgs. The zone of maximum activity appears to be less than 1 ft thick. Between 20 and 32 ft, Cs-137 activities decreased to between 10^3 and 10^4 pCi/g and remained in this range to the total depth of the borehole (58 ft bgs). Sharp peaks occurred at 35, 45, and 55 ft bgs; this is most likely related to accumulated contamination on the outside of the casing joints, which has been noted at boreholes logged inside tank farms, or from contamination leaking through casing joints that form poor seals. This boring is known to have significant internal contamination, and at least some of the observed contamination can be attributed to internal casing contamination and/or sonde contamination. Thus, it must be noted that significant contamination was found on the inner casing walls in borehole C4671 and could have led to an overestimation of the Cs-137 activity in this borehole. Given that the inlet pipes to the 216-A-4 Crib are 18 ft bgs, finding the maximum concentration of Cs-137 at ~ 20 ft bgs suggest that the bulk of the Cs-137 did not migrate more than a few feet in the vertical direction and probably was sorbed/contained at the backfill-native sediment interface at the base of the crib.

In addition to these two shallow boreholes inside the 216-A-4 foot print, two holes have been emplaced outside the crib foot print. Well 299-E24-54 was emplaced 0.5 m to the northeast of the crib and well 299-E24-23 (C5301) was emplaced approximately 2.5 m southwest of the crib. Spectral gamma logging and actual sediment data from well 299-E24-23 (C5301) identified trace amounts of Cs-137 contamination (see Table 8). Well 299-E24-54's spectral gamma log had two peak activity intervals, one at ~31 ft bgs (~50-60 pCi/g) and 55.3 pCi/g at 65.5 ft bgs. Well 299-E24-23 (C5301) had a peak activity of

50 pCi/g at 49.5 ft bgs. At 299-E24-54, the first and actually more pronounced peak may be associated with the bottom of the crib and is different than the deeper peak at 65.5 ft bgs, which is also similar to the C5301 peak at 49 ft bgs. We speculate that the shallower peak in 299-E24-54 is seeing lateral spread and ~6 ft of vertical migration from the crib bottom. This lobe of Cs-137 activity is not encountered in the C5301 borehole that is farther away from the crib foot print. Also, there is a significant lithologic grain size decrease in a thin zone in the vicinity of 50 to 55 ft bgs and within the sediment below these depths, which would tend to correlate well with where the deeper Cs-137 peaks are located in both boreholes.

While the total depth of Cs-137 contamination at these boreholes is 31 to ~50 ft deeper than the elevation of the inlet pipes, the lack of significant activity in either of these two boreholes in comparison to the millions to hundreds of millions of pCi/g concentrations found inside the crib foot print right below the inlet pipes implies that the Cs-137 is fairly well adsorbed by the sediments. The logging data for the four boreholes within and surrounding the 216-A-4 Crib allow for a qualitative estimate of the lateral spreading as well as the vertical penetration of Cs-137 to be made. The two boreholes outside the 216-A-4 Crib foot print are approximately 2 and 8 ft beyond the foot print. Therefore, Cs-137 did not migrate horizontally more than a few tens of feet and did not migrate vertically more than ~30 ft below the crib bottom, despite the disposal of ~6.2 million liters of waste that would have filled the pore spaces below the crib bottom foot print all the way to the groundwater, a distance of ~290 ft. In addition, repeat geophysical logging in 299-E24-54 dating back to 1982 confirms that there is no change in the Cs-137 activity profile and strongly suggests that there is no vertical movement of Cs-137.

Again the main take home message out of the Cs-137 migration discussion and "box model" calculations based on the observed spectral gamma logs and discrete sediment measurements is that this immobile contaminant binds to sediments within a few tens of feet to maybe 50 ft below and laterally from the facility foot prints. Attempting to determine the total mass of a strongly binding contaminant based on a few discrete sediment samples taken from vertical boreholes, even when combined with the more continuous spectral gamma logs is problematical. In one detailed study of Cs-137 spectral gamma logs using both a slant and vertical borehole and dozens of discrete sediment samples from the two boreholes, Serne et al. (2002 a,b) found Cs-137 concentrations could vary by 4 orders of magnitude over distances of less than 6 inches in both vertical and horizontal distances.

6.0 Effects of Waste Solution Chemical Composition and Total Cs Concentration on Cs-137 Sorption

Because the largest amount of available data to assess the vertical distribution of contaminants below the PUREX A Cribs and the horizontal spreading of contamination is the borehole geophysical logging data, which is complemented by the fewer direct measurements of sediment samples from discrete depths in a few of the boreholes, we will focus on assimilating the Cs-137 data as our first attempt at quantifying the vertical and horizontal extent of contamination below and surrounding the PUREX cribs. Based

on the fact that past comparisons of borehole geophysical spectral gamma logs and direct measurement of Cs-137 activities in discrete sediment samples taken from the same boreholes have universally shown very good agreement [see Serne et al. (2002a,b,c,d and 2004 a,b)], we feel confident that the endeavor is technically valid. Further, the geochemistry of Cs-137 adsorption onto sediments has been studied extensively over the past 50 years. At the Hanford Site, the sorption of Cs-137 has been well characterized, and detailed numerical adsorption models have been produced [Zachara et al. (2002), Steefel et al. (2003), and Lichtner et al. (2004)]. The only drawback to using Cs-137 as the tool to interpret the vertical and horizontal extent of contamination spread is the fact that cesium is quite interactive (adsorbs well) with Hanford sediments. Thus, less interactive contaminants would be expected to travel significantly larger distances both vertically and horizontally in waste fluids that percolate through the vadose zone. However, if we have a good estimate of the distribution of Cs-137 in the subsurface and can accurately quantify the Cs-137's sediment interaction strength, such as by the K_d construct, we have good estimates of the sediment interaction strength of most other contaminants of concern. Using simple one dimensional, or better yet more sophisticated multi-dimensional, transport models based on the K_d construct, and knowledge of water flow rates, one can then estimate the distances that any contaminant might travel. Therefore, we offer the following discussion.

In general, cesium adsorption onto Hanford sediments is controlled by both solution composition and sediment mineralogy/particle size. The key solution constituents that control cesium adsorption are the competing cations potassium, sodium, ammonium (present in some Hanford waste streams including those disposed to the PUREX cribs) and to a lesser extent, calcium and magnesium. The key sediment minerals of importance are clays, such as mica and illite, which have specific adsorption sites on their crystalline structures that are highly specific for adsorbing monovalent cations of the size range in which potassium, rubidium, cesium and the ammonium ions fall. These highly selective mineral adsorption sites are found in limited quantity such that they can become fully saturated with these cations quite quickly; therefore, the concentration of these cations in the solution contacting the sediments must be considered closely. Once the highly selective mineral adsorption sites are saturated, further cesium adsorption follows more common competitive ion exchange on the more abundant "generic" adsorption sites present on all mineral solid phases that constitute sediments. For those interested, there is more discussion in the cited references and in citations found within the cited references describing Cs adsorption models.

For this letter report, we have used Figure 4 from Zachara et al. (2002) to estimate the K_d values for two "environments" within each of the three cribs being studied. The two environments per crib are a near-field condition, wherein the sediments are completely equilibrated with the estimated waste solution disposed at each crib (shown in Tables 1 through 3), and a far-field condition dominated by sediment pore-water concentrations (Tables 9 through 11). The key waste stream variables of importance are the total cesium concentration in solution and the total sodium, potassium (if ammonium is present in the waste stream it was assumed to be equivalent to potassium) and calcium. We have assumed that the Hanford formation sediments in the shallow vadose zone at all three PUREX cribs are similar to the Hanford formation H2 subunit (fine sand) used in all the

cesium adsorption tests performed in Zachara et al. (2002). We used the SIM, Rev. 1 estimates of waste stream composition shown in Tables 1 through 3 for the macro cations sodium, potassium (includes any ammonium) and calcium. For determining the total concentration of cesium in the waste stream, we took the Cs-137 activity and converted it to mass. Using nuclear fission tables, Dresel et al. (2002) and Evans et al. (2002) concluded that "fresh" Hanford reprocessed irradiated fuel waste streams contained on a mass basis about 33% each Cs-133 (stable), Cs-135 (long-lived) and Cs-137 (30 yr half life). Thus, the total mass of cesium in a Hanford waste at the time of reprocessing would be ~3 times as large as that calculated from the Cs-137 activity. Because Cs-137 activities are very commonly measured in waste solutions, this value is generally available. The SIM, Rev. 1 also estimates Cs-137 activity in each waste stream (decay corrected to 1-1-2001) as shown in Tables 1 through 3. Because there is essentially no loss of Cs-135 to decay and no loss for the stable Cs-133, we must correct the Cs-137 activity value available "today" back to the time the fuel was reprocessed or in this case, back to the date that the SIM, Rev 1 modeling calculations chose: 01/01/2001. For simplicity and conservatism, we used one half-life decay of Cs-137 in our corrections. Thus we took the SIM, Rev. 1 estimated Cs-137 values in the three waste streams and multiplied by 6 [2 divided by 0.33 to account for Cs-137 being only one-third of the mass of cesium produced] to get an estimate of the total cesium mass concentration in the waste streams. For now, the following calculations are deemed accurate enough to estimate reasonable K_d values for Cs-137 in both the waste stream equilibrated sediments and the current vadose zone pore water and/or current groundwater-aquifer sediment environments.

Table 12 shows the estimated concentrations of the key cations in the waste streams based on the SIM, Rev. 1 and the vadose zone pore waters based on direct measurements of water extracts of sediments from the one borehole placed in or near each of the three cribs investigated. Table 12 also presents the K_d values for Cs-137 that were generated by extracting K_d values using Figure 4 presented in Zachara et al. (2002) that plots the values obtained from systematic and detailed laboratory batch tests used to generate the sophisticated model presented in the paper. The figures in Zachara et al. (2002) show results for binary cation exchange reactions for Cs vs Na, Cs vs K, and Cs vs Ca. One can combine the numerical results of such binary tests to estimate adsorption for ternary systems such as Na, Ca, Cs or quaternary systems such as Na, K, Ca, and Cs. The similarity of potassium and ammonium sorption competition with Cs allows one to assume additivity of their concentrations in either the numerical model or the figures cited. The same is true for magnesium and calcium sorption competition with Cs. Thus, a complex natural or waste stream chemical composition can be modeled to estimate cesium K_d values. In the future, if warranted, the sophisticated numerical model can be modified to produce a simple EXCEL macro to calculate Cs K_d values from inputting solution compositions including Cs mass concentrations and estimates of the cation exchange capacities of both the more ubiquitous general exchange sites and the much less abundant highly selective mono-valent sorption sites.

The data in Table 12 show that the cesium K_d values for sediments in equilibrium with the waste streams are generally lower than the K_d values for sediments more distant

(either deeper in the foot print or laterally at any depth outside the foot print) from the inlet source; except perhaps 216-A-21 Crib, where the measured sediment pore water ionic strength was in fact higher than that in the waste liquids. The influence of higher total Cs in a given waste solution, which would tend to lower the K_d if all other factors were equal, is shown by the 216-A-2 Crib waste stream having a K_d value of 1,800 mL/g versus the 216-A-21 Crib waste stream (cesium K_d of 2,500 mL/g), which contained a factor of ten less total cesium and a lower total cation composition. A more dramatic example of cesium K_d suppression is shown for the 216-A-4 Crib waste stream composition estimate alternatives used. In one case, we assume that potassium and ammonium constitute the bulk of the dissolved cations in the 216-A-4 Crib waste and in the second case, we assume that the waste composition is mostly sodium. The SIM, Rev. 1 estimated that the 216-A-4 Crib liquid waste contained high concentrations of potassium; however, the water extracts and acid extracts of the shallow sediments from boreholes C4560 (inside the crib) and C5301 (just outside the crib foot print) did not show any elevated potassium, and as more commonly found around Hanford disposal facilities, slightly elevated concentrations of sodium were found. Potassium and ammonium compete more strongly for the highly selective adsorption sites in the Hanford sediments than sodium does. So for solutions at the same molarity, a potassium/ammonium solution drives the cesium K_d as low as 8.5 mL/g, versus 700 mL/g for the same molarity sodium solution. If the solution was calcium dominated at this molarity, the cesium K_d would be even larger than 700 mL/g. For the pore water compositions measured in the water extracts from sediments from boreholes C5515, C5301, and C5571 [see Tables 9 through 11], the Cs K_d values are all fairly large and show mainly the effects of total cation concentration. For example, a sodium-dominated pore water at 0.45 M lowers the cesium K_d to 450 mL/g versus a sodium-dominated pore water at 0.02 M, which yields an equilibrium K_d value of 10,000 mL/g. For all pore waters analyzed from the borehole sediments, the dissolved Cs-137 concentration and thus, the total cesium concentration, was not detectable. Therefore, assumed total cesium concentrations in vadose zone sediment pore waters are very low ($<10^{-11}$ M), and the sediments being encountered deep in the sediment profile or laterally away from the crib foot prints have adequate highly selected adsorption sites available to adsorb cesium and yield the highest K_d values possible. This causes cesium to be readily adsorbed by sediments distal to the waste source locations, in effect, stopping cesium migration from reaching large distances.

Using the Table 12 cesium K_d estimates, the total volumes of liquid disposed to each crib, and the estimated concentrations (activities) of cesium in the waste streams to compare with the distribution of cesium in the borehole geophysical gamma logs at the various boreholes, we make the following observations.

Table 9. Calculated Porewater Composition of Sediments from the 216-A-2 Borehole (C5515).

Sample ID	Depth (ft bgs)	Anions (meq/L)	Cations (meq/L)	Charge Difference (%)	Total Charge (meq/L)	Anion Contribution Ionic Strength (M)	Cation Contribution Ionic Strength (M)	Total Ionic Strength (M) A2 Waste Stream I = 0.084M
B1NPW0	17.8	2.30E+01	1.79E+01	2.48E+01	4.09E+01	2.29E-02	1.37E-02	3.66E-02
B1NPW3	24.8	4.47E+01	4.01E+01	1.08E+01	8.47E+01	4.46E-02	2.75E-02	7.21E-02
B1NPW4	30.3	1.56E+02	1.09E+02	3.53E+01	2.65E+02	1.84E-01	5.60E-02	2.40E-01
B1NPW8	39.8	5.43E+01	4.65E+01	1.55E+01	1.01E+02	5.51E-02	3.85E-02	9.36E-02
B1NPX0	45.3	3.15E+01	2.38E+01	2.78E+01	5.53E+01	3.38E-02	1.81E-02	5.19E-02
B1NPX1	47.3	2.93E+01	2.17E+01	2.99E+01	5.10E+01	3.05E-02	1.67E-02	4.72E-02
B1NPX3	51.8	4.33E+01	3.62E+01	1.78E+01	7.94E+01	4.34E-02	3.04E-02	7.39E-02
B1NPX6	59.8	3.82E+01	3.33E+01	1.35E+01	7.15E+01	3.76E-02	2.83E-02	6.58E-02
B1NPX8	64.3	3.87E+01	3.51E+01	9.87E+00	7.38E+01	3.59E-02	3.04E-02	6.63E-02
B1NPY0	70.3	7.30E+00	6.37E+00	1.36E+01	1.37E+01	7.29E-03	5.39E-03	1.27E-02
B1NPY1	72.8	3.36E+01	2.96E+01	1.26E+01	6.33E+01	3.32E-02	2.45E-02	5.77E-02
B1NPY4	79.8	4.93E+01	4.36E+01	1.23E+01	9.28E+01	4.83E-02	3.54E-02	8.36E-02
B1NPY4 DUP	79.8	5.20E+01	4.51E+01	1.40E+01	9.71E+01	5.06E-02	3.68E-02	8.75E-02
B1NPY7	86.8	4.34E+01	4.54E+01	4.61E+00	8.88E+01	4.27E-02	3.79E-02	8.06E-02
B1NPY9	92.8	4.43E+01	4.04E+01	9.38E+00	8.47E+01	4.23E-02	3.28E-02	7.51E-02
B1NR05	106.8	4.09E+01	3.27E+01	2.23E+01	7.36E+01	3.97E-02	2.59E-02	6.56E-02
B1NR16	132.3	2.63E+01	2.39E+01	9.78E+00	5.02E+01	2.58E-02	1.95E-02	4.53E-02
B1NR24	152.3	2.98E+01	2.31E+01	2.53E+01	5.28E+01	2.88E-02	1.84E-02	4.72E-02
B1NR30	167.3	3.59E+01	3.04E+01	1.64E+01	6.63E+01	3.51E-02	2.29E-02	5.81E-02
B1NR36	182.3	2.98E+01	2.52E+01	1.67E+01	5.49E+01	2.85E-02	1.96E-02	4.81E-02
B1NR41	194.8	2.81E+01	2.04E+01	3.14E+01	4.85E+01	2.67E-02	1.59E-02	4.26E-02
B1NR44	202.3	2.70E+01	2.23E+01	1.90E+01	4.93E+01	2.62E-02	1.61E-02	4.23E-02
B1NR51	219.8	2.91E+01	2.32E+01	2.28E+01	5.23E+01	2.92E-02	1.91E-02	4.83E-02
B1NR51 DUP	219.8	2.81E+01	2.20E+01	2.45E+01	5.01E+01	2.82E-02	1.82E-02	4.64E-02
B1NR58	237.3	2.45E+01	2.09E+01	1.57E+01	4.54E+01	2.42E-02	1.65E-02	4.07E-02
B1NR63	250.3	2.39E+01	2.03E+01	1.62E+01	4.42E+01	2.34E-02	1.61E-02	3.95E-02
B1NR69	265.8	1.98E+01	1.75E+01	1.26E+01	3.73E+01	1.96E-02	1.49E-02	3.45E-02

Sample ID	Depth (ft bgs)	Anions (meq/L)	Cations (meq/L)	Charge Difference (%)	Total Charge (meq/L)	Anion Contribution Ionic Strength (M)	Cation Contribution Ionic Strength (M)	Total Ionic Strength (M) A2 Waste Stream I = 0.084M
B1NR76	282.3	4.04E+01	3.32E+01	1.95E+01	7.35E+01	4.01E-02	2.70E-02	6.70E-02
B1NR77	284.8	1.45E+01	1.44E+01	6.51E-01	2.90E+01	1.26E-02	1.32E-02	2.58E-02
B1NRP7	289.5	1.41E+01	1.44E+01	2.24E+00	2.86E+01	1.22E-02	1.38E-02	2.60E-02
B1NR82	297.3	2.66E+01	2.60E+01	2.46E+00	5.26E+01	1.85E-02	2.27E-02	4.12E-02
B1NR84	302.3	2.95E+01	2.92E+01	1.19E+00	5.87E+01	2.01E-02	2.46E-02	4.47E-02

Table 10 Calculated Porewater Composition of Sediments from the 216-A-21 Borehole (C5571).

Sample ID	Depth (ft bgs)	Anions (meq/L)	Cations (meq/L)	Charge Difference (%)	Total Charge (meq/L)	*Anion Contribution Ionic Strength*	*Cation Contribution Ionic Strength (M)*	Total Ionic Strength (M) A21 Waste Stream I = 0.106M
B1P3M1	39.6	1.29E+02	1.30E+02	6.29E-01	2.60E+02	9.53E-02	9.85E-02	1.94E-01
B1P3M2	59.1	5.10E+02	4.91E+02	3.91E+00	1.00E+03	2.72E-01	3.17E-01	5.89E-01

Table 11. Calculated Porewater Composition of Sediments from the 216-A-4 Borehole (C5301)..

Sample ID	Depth (ft bgs)	Anions (meq/L)	Cations (meq/L)	Charge Difference (%)	Total Charge (meq/L)	Anion Contribution Ionic Strength	Cation Contribution Ionic Strength (M)	Total Ionic Strength (M) A4 Waste Stream I = 0.3 M
B1L14Y7	22.3	1.63E+01	1.82E+01	1.09E+01	3.45E+01	1.57E-02	1.07E-02	**2.65E-02**
B1L500	30.8	2.71E+01	3.11E+01	1.37E+01	5.82E+01	2.67E-02	1.98E-02	**4.65E-02**
B1L504	39.8	1.83E+01	1.87E+01	2.45E+00	3.70E+01	1.93E-02	1.27E-02	**3.20E-02**
B1M5X1	51.0	2.30E+01	3.36E+01	3.74E+01	5.67E+01	2.29E-02	2.80E-02	**5.08E-02**
B1L512	59.3	3.67E+01	4.57E+01	2.18E+01	8.24E+01	3.64E-02	3.06E-02	**6.70E-02**
B1L517	62.5	5.02E+01	5.42E+01	7.53E+00	1.04E+02	4.99E-02	3.82E-02	**8.81E-02**
B1L519	77.3	5.16E+01	5.80E+01	1.16E+01	1.10E+02	5.16E-02	4.12E-02	**9.28E-02**
B1L524	90.3	4.39E+01	4.82E+01	9.48E+00	9.21E+01	4.00E-02	3.58E-02	**7.58E-02**

Sample ID	Depth (ft bgs)	Anions (meq/L)	Cations (meq/L)	Charge Difference (%)	Total Charge (meq/L)	Anion Contribution Ionic Strength	Cation Contribution Ionic Strength (M)	Total Ionic Strength (M) A4 Waste Stream I = 0.3 M
B1L528	100.0	3.20E+01	3.45E+01	7.63E+00	6.64E+01	2.81E-02	2.75E-02	**5.56E-02**
B1L531	108.5	4.11E+01	4.55E+01	1.01E+01	8.66E+01	3.63E-02	3.66E-02	**7.29E-02**
B1L531 DUP	108.5	3.98E+01	4.22E+01	5.93E+00	8.20E+01	3.54E-02	3.36E-02	**6.90E-02**
B1L536	119.8	4.35E+01	4.93E+01	1.26E+01	9.28E+01	4.00E-02	4.09E-02	**8.08E-02**
B1L540	130.8	3.61E+01	3.84E+01	6.33E+00	7.45E+01	3.25E-02	2.82E-02	**6.07E-02**
B1L543	137.3	2.87E+01	3.04E+01	5.71E+00	5.91E+01	2.61E-02	2.24E-02	**4.84E-02**
B1L547	147.3	2.59E+01	2.48E+01	4.14E+00	5.07E+01	2.50E-02	1.83E-02	**4.32E-02**
B1L553	162.8	2.83E+01	2.70E+01	4.82E+00	5.53E+01	2.76E-02	2.02E-02	**4.78E-02**
B1L553 DUP	162.8	2.72E+01	2.52E+01	7.66E+00	5.24E+01	2.65E-02	1.86E-02	**4.51E-02**
B1L557	172.3	3.70E+01	3.26E+01	1.27E+01	6.95E+01	3.59E-02	2.53E-02	**6.13E-02**
B1L562	185.3	3.34E+01	3.47E+01	3.75E+00	6.81E+01	3.31E-02	2.59E-02	**5.90E-02**
B1L568	199.8	3.94E+01	3.63E+01	8.29E+00	7.56E+01	3.39E-02	2.84E-02	**6.23E-02**
B1L570	204.8	3.91E+01	3.34E+01	1.58E+01	7.24E+01	3.14E-02	2.60E-02	**5.74E-02**
B1L577	222.3	4.99E+01	4.45E+01	1.14E+01	9.43E+01	3.80E-02	3.65E-02	**7.45E-02**
B1L582	234.8	4.23E+01	3.95E+01	6.93E+00	8.18E+01	3.18E-02	3.29E-02	**6.47E-02**
B1L587	247.3	4.91E+01	4.65E+01	5.51E+00	9.56E+01	3.69E-02	3.91E-02	**7.59E-02**
B1L592	259.8	4.52E+01	4.33E+01	4.35E+00	8.84E+01	3.41E-02	3.67E-02	**7.08E-02**
B1L596	269.8	4.55E+01	4.57E+01	3.82E-01	9.12E+01	3.81E-02	3.46E-02	**7.27E-02**
B1L5B1	282.8	2.44E+01	2.63E+01	7.34E+00	5.07E+01	1.60E-02	2.47E-02	**4.07E-02**
B1L5B1 DUP	282.8	2.34E+01	2.67E+01	1.32E+01	5.01E+01	1.47E-02	2.51E-02	**3.99E-02**
B1L5B3	287.3	2.51E+01	2.57E+01	2.31E+00	5.08E+01	1.68E-02	2.30E-02	**3.98E-02**
B1L5B5	292.3	2.37E+01	2.67E+01	1.20E+01	5.05E+01	1.59E-02	2.31E-02	**3.90E-02**
B1L5C0	304.8	5.48E+01	5.16E+01	6.00E+00	1.06E+02	4.83E-02	3.53E-02	**8.36E-02**
B1L5C4	314.8	3.80E+01	3.82E+01	4.61E-01	7.61E+01	3.22E-02	2.80E-02	**6.02E-02**

Table 12. Waste and Pore Water Compositions Used to Estimate Cs-137 Kd Values

		Waste Composition						Pore Water Composition				
Crib	Waste Type	Na	K,NH_4	Ca	Cs	Cs K_d	Porewater	Na	K,NH_4	Ca, Mg	Cs	Cs K_d
		M	M	M	M	mL/g	Type	M	M	M	M	mL/g
A2	PUREX (P1) Organic	**0.2**[*1]	1.50E-06	1.60E-05	4.50E-09	1800		0.01	<0.05	9.75E-03	trace	*5
A2							Ca	0	0	**0.02**	trace	14,000
A2							Na	**0.02**	0	0	trace	10,000
A4	Conc Misc UNH (P1)	3.40E-03	**0.348**	5.50E-04	4.40E-10	8.5		0.01	<0.05	9.75E-03	trace	*5
A4		**0.3514**[*2]	3.30E-07	5.50E-04	4.40E-10	700	Ca	0	0	**0.02**	trace	14,000
A4							Na	**0.02**	0	0	trace	10,000
A21	PASF (P2)	6.67E-02	5.59E-02	1.00E-02	4.60E-10	*5		0.4	0.01	0.04	trace	*5
A21		**0.14**[*3]			4.60E-10	2500	Na	**0.45**			trace	450
A21			**0.14**[*4]		4.60E-10	25					trace	

*1 assumed in order to get charge balance on nitrate
*2 if potassium estimate is not correct assumed really was sodium
*3 assumed end member with all Na cation (will yield highest K_d)
*4 assumed end member with all K, NH_4 cation (will yield lowest K_d)
*5 actual estimated composition but can't select K_d off figures for ternary solution

One question that has been raised is "Are the apparent concentrations (high radioactivity and dose readings) in sediments from boreholes inside the foot print of the 216-A-4 Crib reasonable given the assumed waste stream that was disposed?" At equilibrium, the amount of Cs-137 that can be adsorbed on a sediment is equal to the K_d value times the equilibrium concentration in solution. Following is the standard equation that defines the relationship

$$S = K_d * C \qquad (1)$$

Where S is the amount of contaminant adsorbed on the sediment (pCi/g), K_d is in this case the sorption coefficient for Cs-137 (units mL/g), and C is the concentration (pCi/mL) of Cs-137 in the liquid waste stream disposed in the crib.

Based on data contained in Tables 1-3 and 9-11, sediment near the crib inlets of the liquid waste stream should build up sediment concentrations [S] in the above equation as shown in Table 13. The results of using the SIM, Rev. 1 waste stream conceptualization and the Cs K_d conceptual model suggests that the maximum Cs-137 concentrations predicted to build up in the sediments right near the crib inlets within the foot print of the three cribs agree with the observed borehole geophysical gamma logging and the few discrete sediment samples that happened to be obtained near the peak concentrations for the 216-A-2 and 216-A-21 Cribs.

The predicted maximum activities for Cs-137 build up on the sediments near the inlet of the 216-A-4 Crib were significantly lower than the value calculated by borehole geophysical spectral gamma logging. Additionally, the predicted maximum concentrations for Cs-137 in the 216-A-4 Crib sediments were also a factor of ten lower than those measured in a sediment sample collected at 22 to 23 ft bgs within the crib foot print. This analysis approach does corroborate the fact that observed Cs-137 activities near the 216-A-4 Crib bottom are surprisingly higher than expected based on historical records of the types of waste disposed. Further, the predicted waste composition of the concentrated miscellaneous UNH (P1) waste stream is dominated by potassium at ~0.35 M. If this was the case, the Cs-137 K_d would be relatively low [<10 mL/g] and the distribution of sorbed Cs-137 should be rather diffuse [a thick zone] compared to the sharp, thin, intensely concentrated plumes generally observed in the vadose zone below disposal facilities. Note that when the spectral gamma plots versus depth are re-plotted on a linear concentration scale as was done in Figure 5 versus the traditional log concentration scale used by S. M. Stoller Corp., the vertical distributions become even more pronounced and sharp (very thin peaks) in appearance. The borehole geophysical spectral gamma log for borehole C4671 within the foot print of the 216-A-4 Crib shows a distinctly sharp vertical distribution, and the two boreholes outside the crib foot print [C5301 and A5911 (299-E24-54)] show little evidence of lateral spreading of Cs-137, despite the disposal of 6.21 million liters of waste. The water and acid extracts of the sediments throughout the vertical extent of well 299-E24-23 (C5301) also do not show any elevated potassium concentrations above natural background amounts. The total estimated inventory of potassium disposed to the 216-A-4 Crib was ~76,000 kg, yet no anomalously high potassium concentrations were found outside the crib foot print. No

potassium data was collected on sediments within the crib foot print. We thus question whether the correct waste stream composition was assigned to the 216-A-4 Crib by the SIM, Rev. 1 staff or alternately, the chemical algorithm used to assign chemical compositions might be erroneous.. We base our skepticism on two different points: lack of elevated potassium observed in sediments proximate to the crib and the very sharp vertical distribution of the Cs-137 distributions inside the crib coupled with the lack of any evidence of lateral spread of Cs-137 in the sediments right outside the crib foot print.

Conversely, the vertical and horizontal spread of Cs-137 observed in the sediments within the foot print and just outside the eastern edge of the 216-A-2 Crib seem significant compared to the estimated Cs-137 K_d values for both the waste stream (1800 mL/g) and the pore water (10,000 to 14,000 mL/g) measured inside the foot print throughout the C5515 borehole profile. The total volume of waste disposed to the 216-A-2 Crib was only 0.230 million liters, and given the high predicted K_d values, we would not expect the observed relatively large lateral and vertical movement of Cs-137 at this location. Recall that the 216-A-2 Crib waste stream was laden with TBP and NPH, and the calculated charge balance of the modeled composition was very poor. Based on our geochemical experience and understanding, neither TBP nor NPH should have a chemical impact on Cs interactions with sediments. However, these organics may dramatically alter solution viscosity, sediment particle surface wetting properties, and water flow characteristics. Finally, the SIM, Rev. 1 chemical composition estimate for waste disposed to 216-A-2 Crib, which showed a poor charge balance that we arbitrarily "fixed" by adding sodium, may be wrong. Additionally this may have been a poor assumption to use, as adding sodium to compensate for missing cation charge forces the cesium K_d estimates to large values (compared to values if potassium or ammonium were used to reach charge balance) and thus, the predicted mobility of cesium would be minimized versus using the unbalanced cation-anion composition listed in SIM, Rev. 1.

At the 216-A-21-Crib, the vertical extent of cesium migration (maximum observed at 21 feet bgs and significantly elevated values down to 40 ft bgs within the foot print of the 216-A-21 Crib below the inlet pipes [situated somewhere between 7 and 10 ft bgs dependent on historical document cited]) in our opinion, seems appropriate based on the range of estimated K_d values and the large volume of fluid disposed (77.9 million liters) to the crib. There are no boreholes off to the sides of the 216-A-21 Crib that could be logged to investigate horizontal spreading to see if the large volume of waste liquid disposed did indeed lead to horizontal spreading.

Table 13. Calculated Maximum Cs-137 Activities Expected vs K_d and Waste Stream Conceptual Model

		Waste Composition						
Crib	Waste Type	Na	K,NH_4	Ca	Cs-137	Cs Kd	Calc. Max Cs-137 Sorbed on Sediment	Cs-137 measured in Gamma Logs or Directly in Sediment
		M	M	M	pCi/L	mL/g	pCi/g	pCi/g
A2	PUREX (P1) Organic	**0.2**[*1]	1.50E-06	1.60E-05	8.98E+06	1800	1.62E+07	0.2 to 2E+07 (2 logs)
A4	Conc Misc UNH (P1)	3.40E-03	**0.348**	5.50E-04	8.63E+05	8.5	7.34E+03	2.4E+08 (log) @ 20' bgs and 5.6E+06 (sed) @22 to 23'bgs
A4	Conc Misc UNH (P1)	**0.3514**[*2]	3.30E-07	5.50E-04	8.63E+05	700	6.04E+05	2.4E+08 (log) @ 20' bgs and 5.6E+06 (sed) @22 to 23' bgs
A21	PASF (P2)	**0.14**[*3]		1.00E-02	9.09E+05	2500	2.27E+06	1.0E+06 (log) @ 21' bgs
A21	PASF (P2)		**0.14**[*4]	1.00E-02	9.09E+05	25	2.27E+04	1.0E+06 (log) @ 21' bgs

Discrepancy highlighted in pink shading.

7.0 Comments of the Utility of Available Direct Sediment and Sediment Extracts Data to Estimate Vadose Zone Contaminant Vertical and Lateral Distributions and Total Vadose Zone Inventories

Past CERCLA inactive-facility field studies at and around cribs have relied on taking sediment core samples at several pre-selected depths and analyzing the sediment samples for a select list of chemical species focused more so on determining the total concentrations of regulated chemicals and radionuclides (more commonly referred to as contaminants of concern) than species that would allow the geochemical environment to be adequately characterized. In our opinion, it is equally important to measure and define the geochemical environment in the vadose zone sediment-pore water system as it is to measure total concentrations of selected regulated chemicals and radionuclides. Knowledge of the geochemical environment present in the subsurface, (obtained from direct measurement of the major chemical species in the pore water or calculating the pore water composition and pH from water extracts of sediment samples as well as determining some of the properties of the sediments (including calcium carbonate content, moisture content, particle size, bulk sediment and clay size fraction mineralogy, cation exchange capacity, and hydrous ferric oxide content) allows geochemists to understand the major processes that control sediment-pore water interactions. The major soil chemical constituent's interactions with pore water, in general, dominate and control the interactions of the trace quantities of contaminants present in contaminated systems. If one only measures the total concentrations of contaminants, it is difficult to evaluate their fate over future times.

The characterization paradigm that gives equal emphasis to measuring the concentrations of major constituents in the water and solid phases, as well as determining the same for the regulated contaminant species, has been recently used at two boreholes in the PUREX crib region, C5515 and C5301. The former is inside the foot print of the 216-A-2 Crib and the latter is 2.5 m outside the southwest corner of the 216-A-4 Crib. In this more detailed sediment characterization scheme, grab samples and some intact cores were collected about every 2 to 5 feet depth and, after performing some fundamental characterization on all samples, a much smaller subset that covers the entire vertical extent of the borehole (ground surface to water table) were characterized further to gain some preliminary understanding on key contaminant and key geochemical properties and their vertical distributions. Additional samples at depths where the key contaminants were observed or where large gradients in geochemical properties (e.g., ion exchange fronts between native pore water and waste solutions when evident) were then characterized until the entire vertical distribution of key contaminants and the zones where key geochemical parameters were evolving/changing were delineated. This characterization scheme is iterative and somewhat unique for each borehole as opposed to being locked in based on *a priori* assumptions, historical information about the site, and expert opinion.

One of the key parameters to measure on vadose zone sediments is gravimetric moisture content. Figure 6 shows the moisture content profiles for C5515 and C5301. We have found from numerous vadose zone characterization studies that elevated moisture

contents correlated strongly with the presence of fine-grained sediments and that thin fine-grained lens can act as horizontal spreading planes. As can be seen in Figure 6, there are two depths at which there are significantly elevated moisture zones. The shallow elevated moisture zone in C5515 (in the 216-A-2 Crib foot print) occurs at ~70 ft bgs and is no thicker than 6 ft. The zone of elevated moisture is perhaps thinner that 6 ft; however, this single data point was not confirmed via neutron moisture logging of the borehole and we do not have more sample coverage in this region to provide confirmation via laboratory analysis. At C5301, which was emplaced right outside the southwest corner of the 216-A-4 Crib, a thin (<2 ft thick) zone of elevated moisture was found at 51 ft bgs. Both zones contained about ~13 to 16 wt% water, and both could be acting as horizontal spreading planes. A much thicker zone (20 to 22 ft) of elevated moisture is found in both boreholes between the depths of ~280 to 305 ft bgs. This deeper moist zone correlates exactly with a very fine-grained sand to silt interval and is located approximately 15 ft above the current water table. It is most likely an efficient perching horizon or horizontal spreading plane for fluids that were disposed to the cribs. As will be discussed below, this deep and relatively thick zone of fine-grained sediment contains elevated concentrations of several mobile contaminants at this time.

One key question that comes to mind is whether the contaminants in this elevated moisture zone beginning at ~280 to 282 ft bgs represent residual material left behind when the regional high water table subsided after active disposal of millions of liters of liquid wastes to the cribs. The coverage of old wells from which one can get historical water level data in the vicinity of the PUREX A cribs and in general south of the PUREX fuel reprocessing building is quite sparse. Only two wells, 299-E17-1 (somewhat south and significantly west) and 299-E25-36 (somewhat north and significantly east) [see Figures 1 and 7 for location of wells and A cribs], had water table elevation data that has been collected for many years. The well hydrographs (water table elevation vs. time) and gross beta concentrations in the groundwater vs. time are shown in Figures 8 and 9. The water table elevations in these two wells were not available until the mid 1960s for 299-E17-1 and mid-1988 for 299-E25-36. Because the most active time of liquid disposal to the A crib area was the mid 1950s to mid 1960s, it is possible that the highest (shallowest) water table was not captured. However, the two plots show that the water table in the past from the mid 1960s to the present has dropped only about 10.7 ft (3.25 m) since the highs observed in the late 1980s. Unless there was a large mound formed below the A cribs in the mid 1950s to mid 1960s that raised the water table another ~20 ft from the high water table in ~1988 measured in these two wells, the fine-grained strata at ~280 ft bgs in the two new boreholes is too shallow to have ever been within the water table. Thus, a more plausible explanation for the contamination found in this fine-grained strata is vertical descent through the vadose zone below the A cribs and horizontal spreading within the strata.

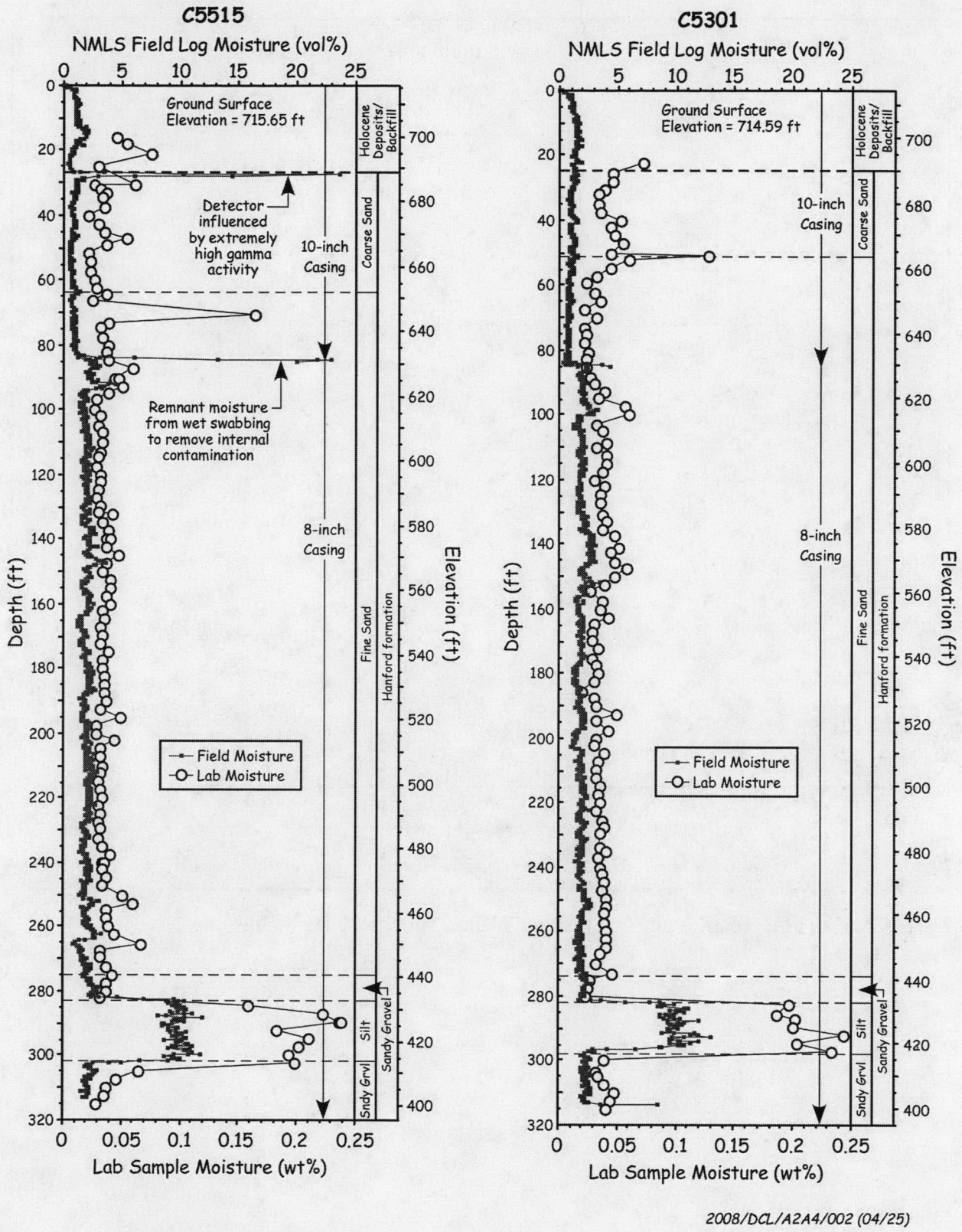

Figure 6. Moisture Content vs. Depth for Boreholes through 216-A-2 and near 216-A-4 Cribs

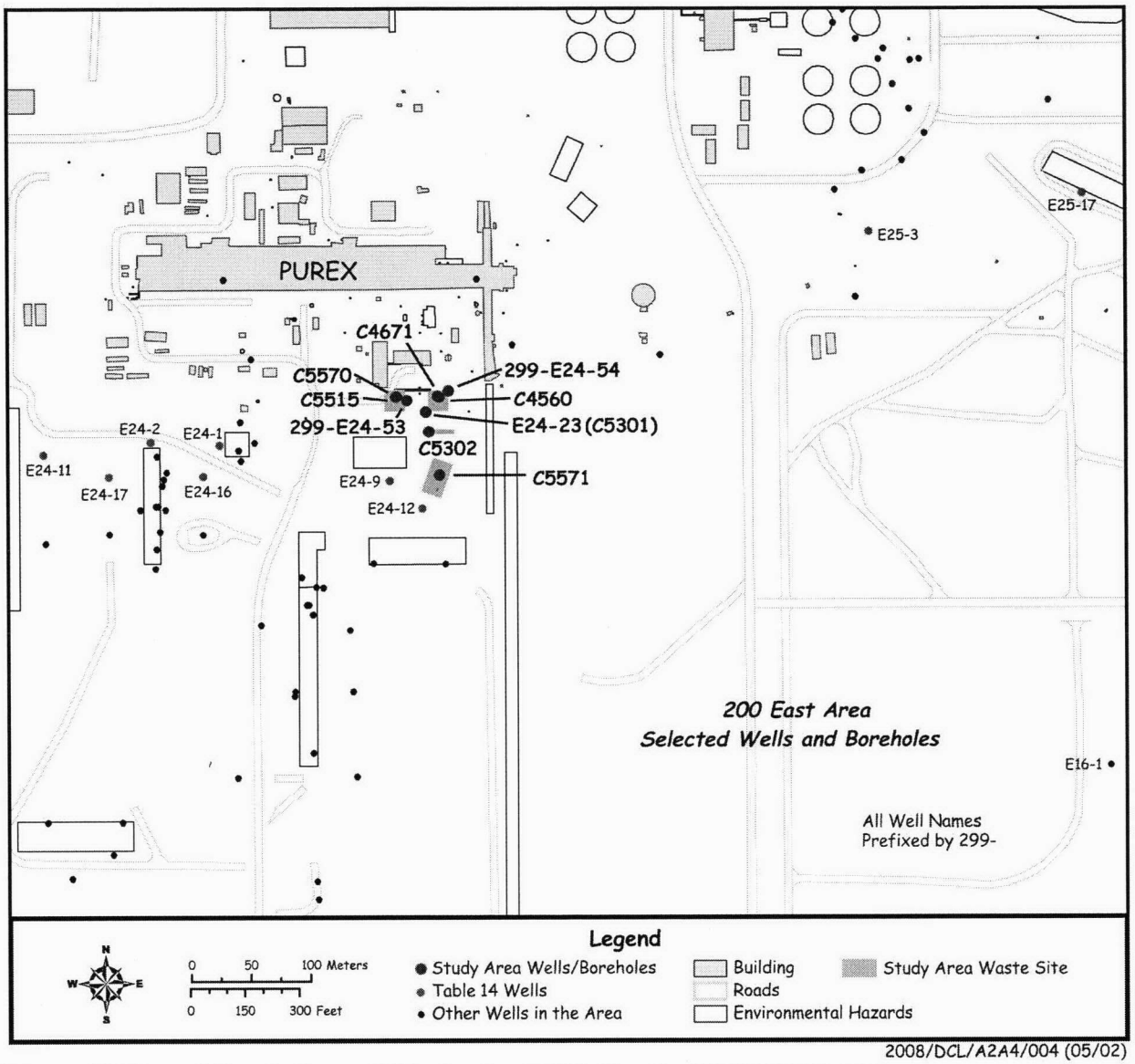

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Figure 7. Map of Boreholes and Monitoring Wells South of PUREX Building

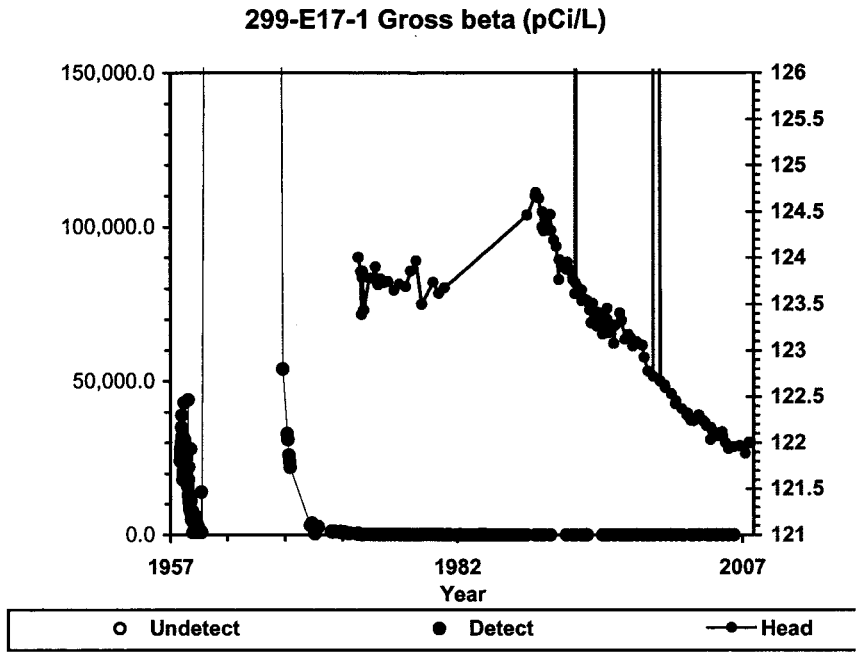

Figure 8. Water Table Elevation and Gross Beta Concentrations in Monitoring Well 299-E17-1 versus Time. Note that relatively high gross beta was observed in 1957 with a decreasing trend. No measurements of gross beta were made between 1960 and 1971.

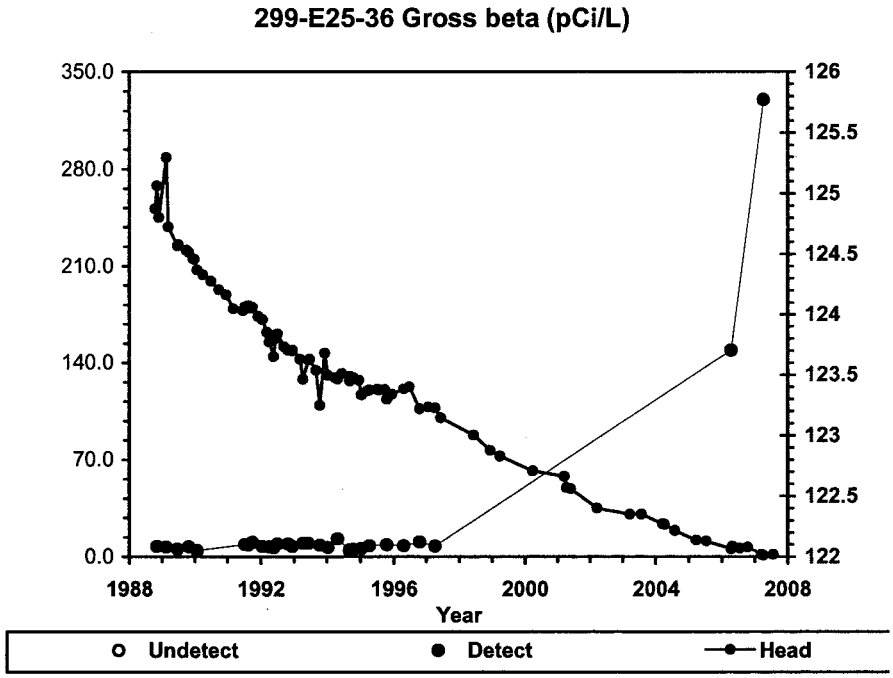

Figure 9. Water Table Elevation and Gross Beta Concentrations in Monitoring Well 299-E25-36 versus Time

Figures 10 through 17 are plots of constituents of interest as a function of depth from sediment samples in borehole C5515, which was drilled within the foot print of 216-A-2 Crib. In Figure 10, the pH of the sediment:water extracts shows slightly elevated values (8.5 to 8.7) between 24 and 31 ft bgs, but no deeper pH values exceed pH = 8. It would appear that the waste stream disposed into 216-A-2 Crib was not acidic and the poor cation-anion balance is not caused by the waste being acidic. The dilution corrected electrical conductivity of the sediment water extracts can be used to estimate pore water salinity. The sediments between 24 and 31 ft bgs exhibit slightly elevated electrical conductivity, suggesting some slightly soluble waste might have precipitated in the shallow vadose zone sediments right below the crib bottom. The slightly elevated pore water electrical conductivities deep in the profile near the silty strata at ~282 ft bgs and the shallower zone between 50 and 80 ft bgs is caused by slightly elevated nitrate, sulfate, calcium, and sodium that could be from waste liquids or natural variations in the sediments. The electrical conductivity values below 6 mS/cm are within the range of many uncontaminated Hanford Site vadose zone sediments. Figure 11 shows the water extractable calcium and sodium contents of the vadose zone sediments below the 216-A-2 Crib foot print. Shallow in the profile it is obvious that sodium from the waste has displaced native calcium (and magnesium) from the sediment cation exchange sites such that divalent cations are low and sodium is high. The zone where the sodium has displaced the native calcium in similar to the zone with elevated pH, suggesting that the waste was in fact neutralized with sodium hydroxide. In the thick fine-grained zone from ~282 to 300 ft bgs, both calcium and sodium are elevated because the fine-grained sediments have a significantly higher cation exchange capacity than the sand-dominated sediments found shallower. The water-extractable mobile anion nitrate's distribution in the vadose zone sediments is shown in Figure 12, and the somewhat mobile anion sulfate's distribution is shown in Figure 13. Figure 12 shows the PNNL data as well as data from sediment water extracts performed by analytical labs under Fluor Hanford contract. There is elevated nitrate only in the fine-grained strata from ~280 to 300 ft bgs, suggesting that the leading edge of the waste plume entered this silt zone and some or all of the nitrate has been retained. For unsaturated flow conditions, when a fine-grained strata overlies a coarser-grained strata, the coarse-grained strata can act as a capillary break that does not transmit fluids until the fine-grained zone's water content increases close to saturation levels. The contact between the overlying gravelly sand sequence and the top of the fine-grained strata (which is ~20 feet thick) is undoubtedly acting as a horizontal spreading plane for fluids disposed to the 216-A-2 Crib. Also shown in the figure is a yellow triangle showing that the groundwater below the crib has slightly elevated nitrate ~70 mg/L. Thus, the groundwater under the 216-A-2 Crib is currently contaminated with nitrate by a factor of 1.6 times (above) the drinking water standard. It is not clear if the elevated nitrate concentrations in the silt zone ~15 ft above the water table is supplying the local groundwater with nitrate. The source of the nitrate in the groundwater could also be from several upgradient sources where other inactive disposal facilities are found.

Figure 13 shows the water-extractable sulfate distribution in the vadose zone sediments under the 216-A-2 Crib. The highest sulfate concentrations are found between 80 and 150 ft bgs perhaps from sulfate in disposed liquid waste being slightly retarded compared

to nitrate in its percolation from the crib. The smaller elevated sulfate concentration in the fine-grained sediment strata between 280 and 300 ft bgs may be either natural or a

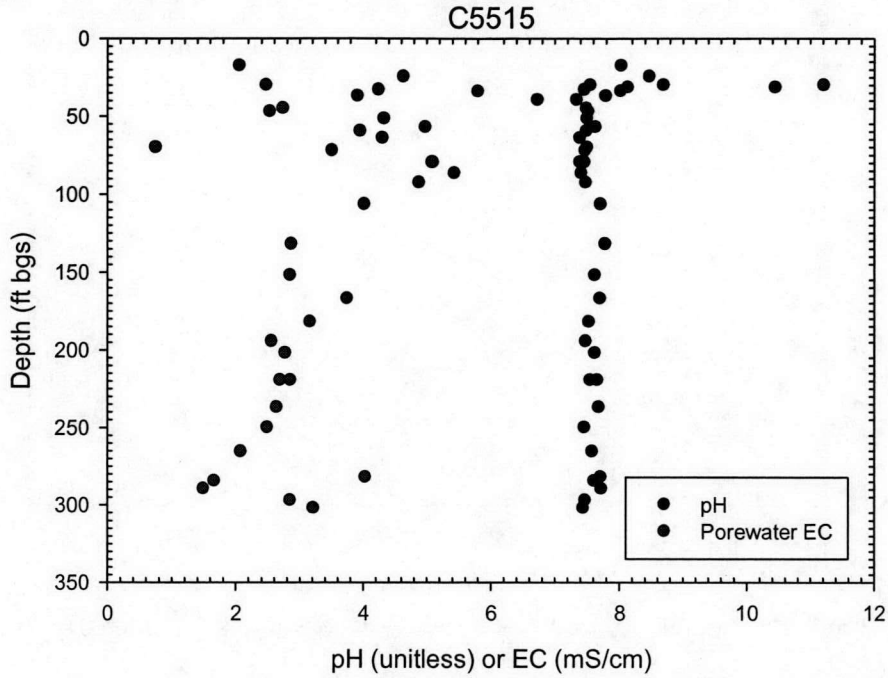

Figure 10. Sediment:water Extract pH and Dilution-Corrected (Pore Water) Electrical Conductivity for Vadose Zone Sediments Inside 216-A-2 Crib

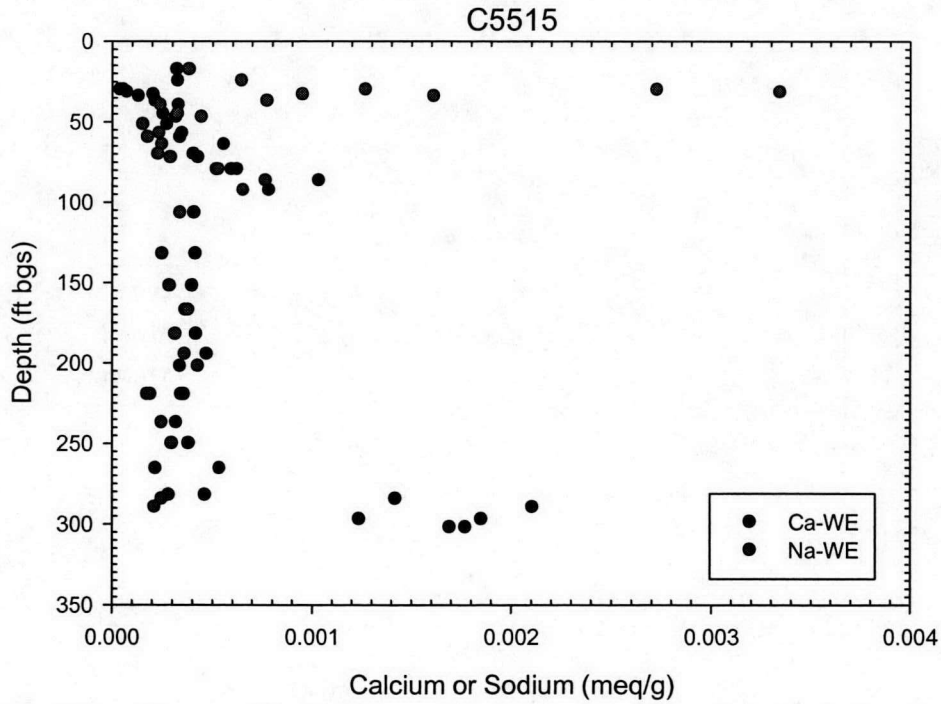

Figure 11. Water-Extractable Sodium and Calcium Concentrations in Vadose Zone Sediments Inside 216-A-2 Crib

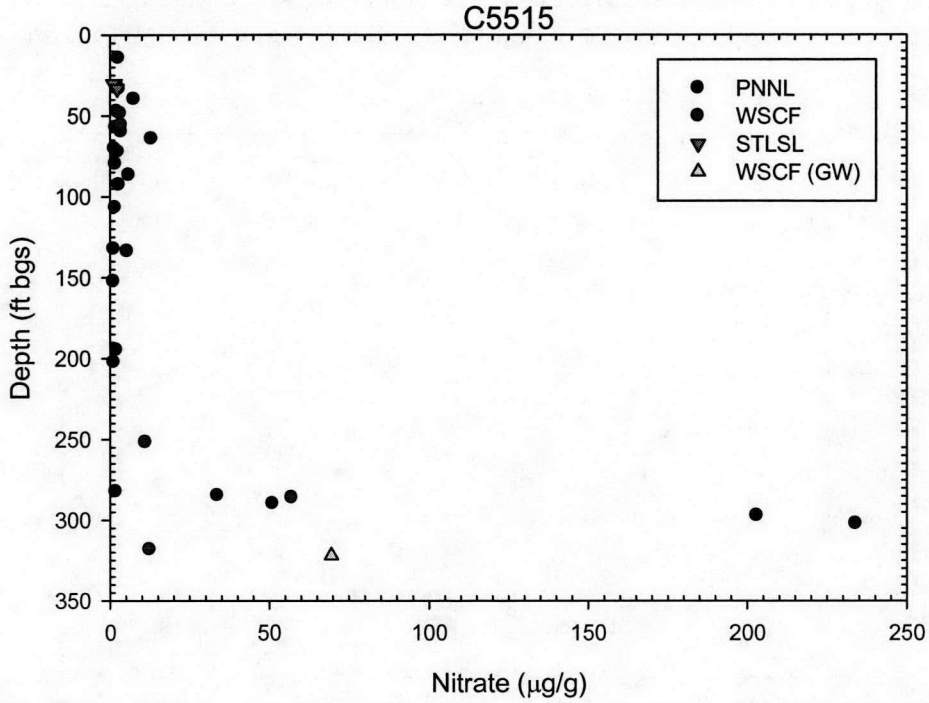

Figure 12. Water-Extractable Nitrate in Vadose Zone Sediments Inside 216-A-2 Crib

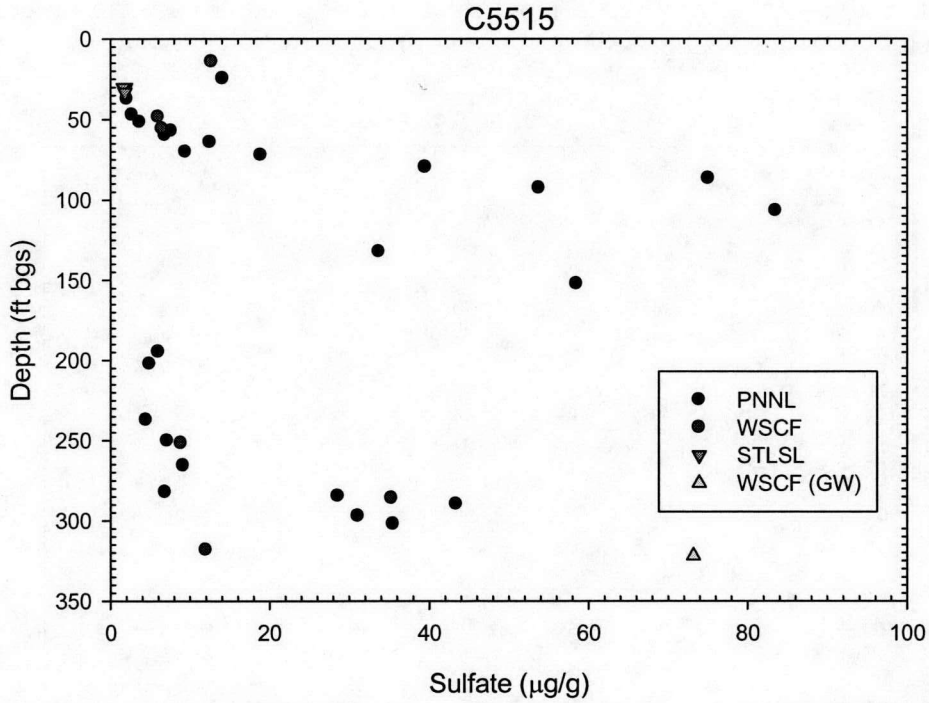

Figure 13. Water-Extractable Sulfate in Vadose Zone Sediments Inside 216-A-2 Crib

slight indication of wastes from the A cribs that has reached this horizontal spreading layer. The groundwater sulfate concentration in C5515 is 73.2 mg/L, which is within the normal range of uncontaminated groundwaters at the Hanford site.

Figure 14 shows the distribution of Cs-137 measured directly in the sediments from borehole C5515, which was emplaced within the foot print of 216-A-2 Crib. Cs-137 was found essentially from the bottom of the crib down just a few tens of feet. Below 48 ft bgs none of the analytical labs found Cs-137 present above 10 pCi/g compared to a value near 10,000 pCi/g at 30 ft bgs.

Figure 15 shows the distribution of Sr-90 in the sediments from borehole C5515 measured on strong hot acid extracts. Similar to Cs-137, the Sr-90 is retained in the sediments at the bottom of the crib and sediments a few tens of feet deeper into the vadose zone. Figure 16 shows the distribution of acid-extractable U in the sediments from borehole C5515. In a similar fashion to the Cs-137 and Sr-90, uranium is strongly bound to the sediments at the bottom of the crib and the sediments a few tens of feet deeper contain only minor concentrations of uranium.

In contrast, the mobile contaminant tritium, see Figure 17, is found mainly in the fine-grained sediments between 280 and 300 ft bgs. It is not clear whether the tritium travelled vertically down through the predominately sandy sediments below the foot print of the 216-A-2 Crib, or whether the tritium migrated horizontally on top of the silty unit, (slowly migrating vertically into the fine grained unit) from upgradient of the crib. The groundwater below the 216-A-2 crib currently contains 600,000 pCi/L tritium. The PNNL gross beta measurement on water extracts of the deep sediments have similar values as the tritium measurements performed by the other Fluor contract analytical labs, suggesting that tritium dominates the beta emitters in sediments deeper than about 20 feet below the crib bottom.

As mentioned earlier, 216-A-2 was the only crib in this study that received organic solvents [NPH] and tri-butyl phosphate. Their total inventories were NPH (63,920 kg) and TBP (149,200 kg) as shown in Table 1. Interestingly, about a dozen sediment samples from the entire profile of borehole C5515 were analyzed for tri-butyl phosphate and total petroleum hydrocarbons. If one assumes that the latter analysis would capture normal paraffin hydrocarbons, then none of the measured samples contained measureable TBP or hydrocarbons. It is known from other characterization work that TBP can be degraded all the way to inorganic phosphate with time. Eleven sediment samples covering the depth range 28 to 50 ft bgs had water-extractable phosphate present at concentrations ranging from 313 mg/kg in the shallowest sample to 6 mg/kg in the deepest sample. For all sediments analyzed below 50 feet bgs the water extractable phosphate was below the detection limit, which varied from ~2 to 6 mg/kg dependent on sediment water content. The water extractable phosphate concentration averaged about 50 mg/kg throughout the depth range 30 to 40 ft bgs. The SIM, Rev. 1 estimate for inorganic phosphate disposed to 216-A-2 was 0 kg. Thus the observed phosphate in the relatively shallow depths is likely an indication of degraded tri-butyl phosphate. Either normal paraffin hydrocarbons are not measured in the total petroleum hydrocarbon

analysis procedure or they are either quickly degraded to species that are not readily quantified by GC-MS or they migrated and dispersed quickly after disposal. The latter fate is not as likely.

Figures 18 through 24 are plots of constituents of interest as a function of depth from sediment samples in well 299-E24-23 (C5301), which was emplaced 2.5 m outside the south-west corner of the 216-A-4 Crib. The data for well 299-E24-23 (C5301) generated by both the WSCF laboratory and PNNL are plotted when available. When applicable, each plot contains data generated for the C4560 borehole that was drilled within the 216-A-4 Crib foot print and analyzed by WSCF and its subcontractor analytical laboratories. With the exception of sediment pH results shown in Figure 18, the C5301data generated by WSCF correlate well with the data generated by PNNL (see Figures 20, 21, 22 and 24).

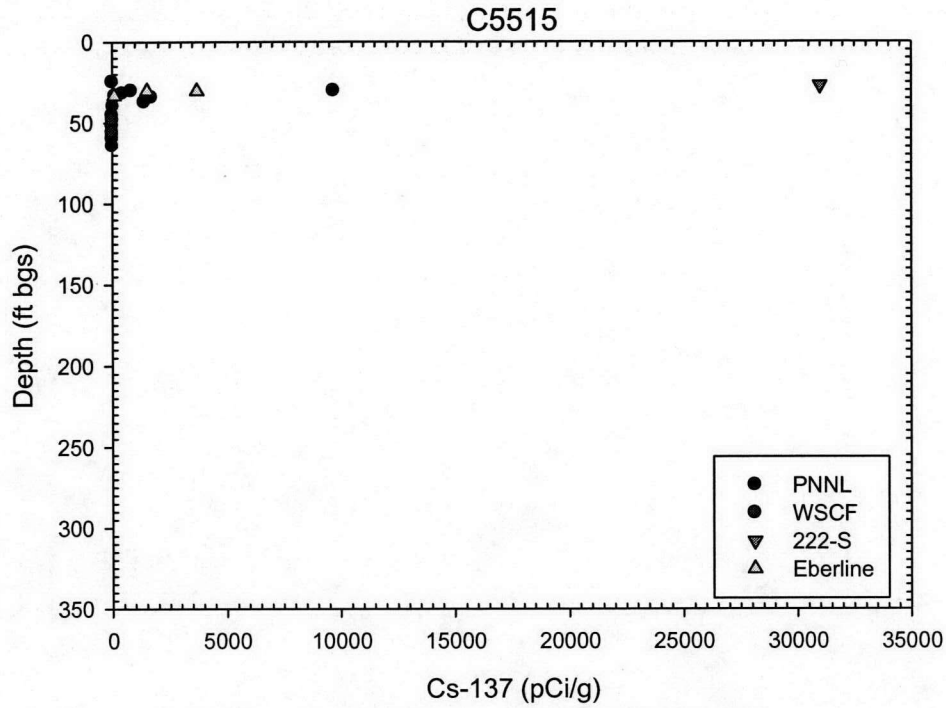

Figure 14. Cs-137 in Vadose Zone Sediments Inside 216-A-2 Crib

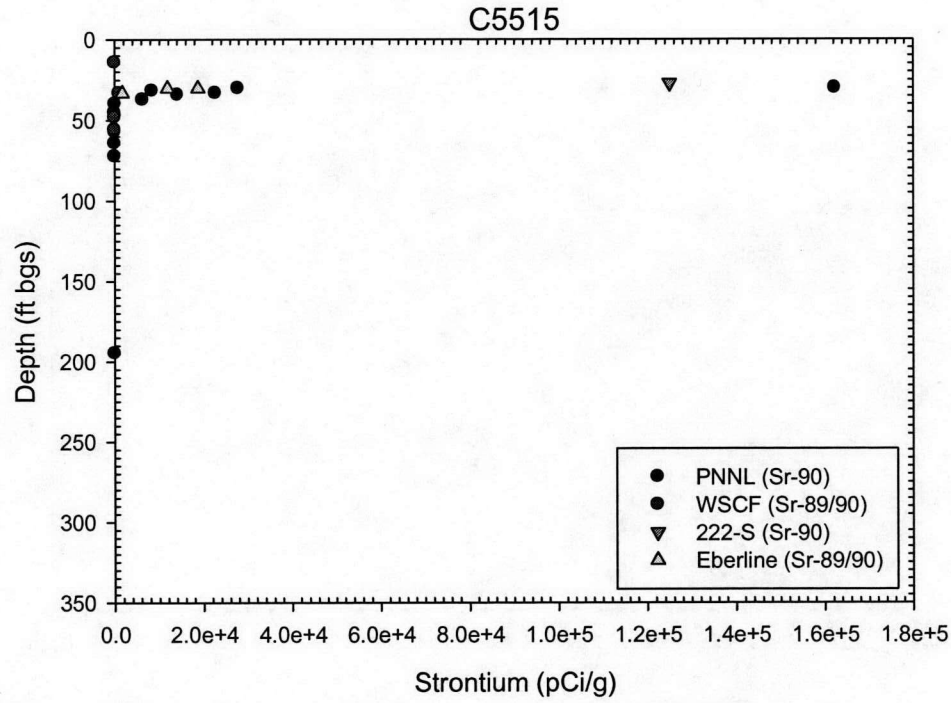

Figure 15. Sr-90 in Vadose Zone Sediments Inside 216-A-2 Crib

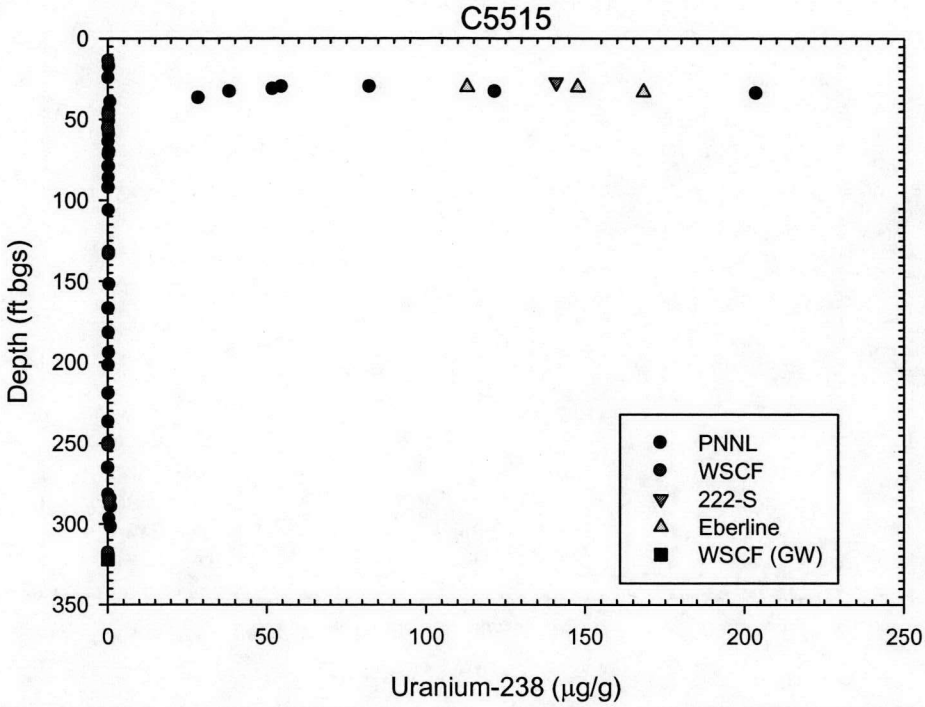

Figure 16. Acid-Extractable U in Vadose Zone Sediments Inside 216-A-2 Crib

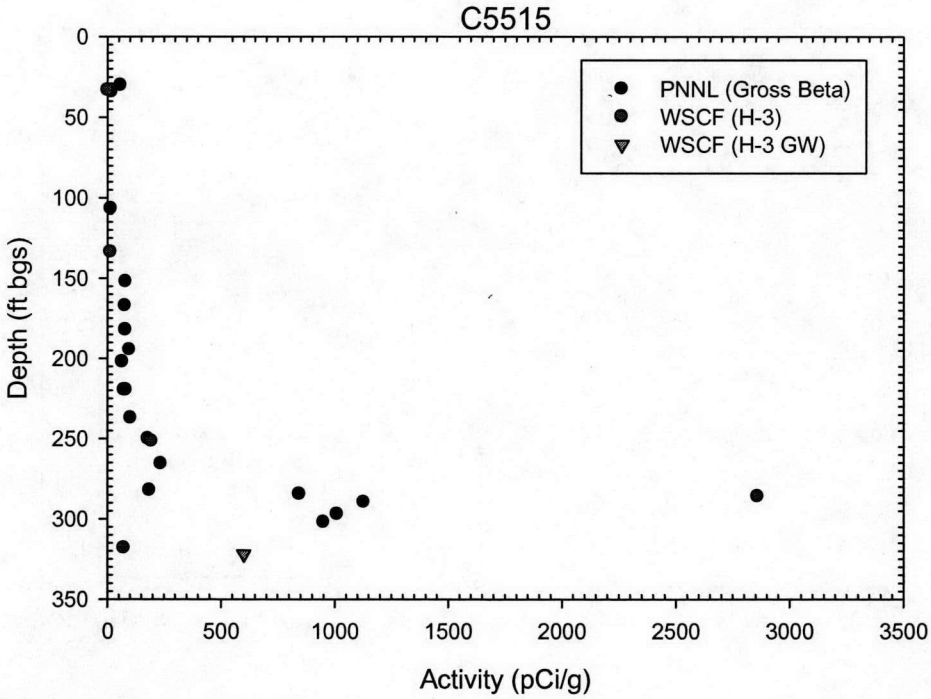

Figure 17. Gross Beta and Tritium Contents in Vadose Zone Sediments Inside 216-A-2 Crib

Figure 18 shows the water extract pH for sediments from both borehole C4560 (emplaced within the 216-A-4 crib foot print) and well 299-E24-23 (C5301) (emplaced 2.5 m outside the southwest corner of the crib). It is obvious from the figure for C5301 sediments that the two analytical labs are using different water extract procedures and perhaps methods to measure pH. Regardless, the fact that shallow sediments from inside the crib show pH values ranging from 9.2 to 9.5 indicates that the wastes disposed were slightly caustic and have interacted with the sediments right below the crib bottom. The zone of caustic attack is rather limited, compared to regions below leaking single-shell tanks, which was more than likely caused by the dilute nature of the wastes disposed to the PUREX A cribs. Many metal-like contaminants exhibit pH-dependent solubility and adsorption properties. In most cases, the metal-like contaminants (Cs-137, Sr-90, U, actinides, and RCRA metals) bind more strongly to sediments when the pH conditions are slightly caustic.

Figure 19 shows that the sodium in the 216-A-4 waste has displaced the native calcium (and magnesium; not plotted) from the sediment exchange sites down to a depth of about 40 ft bgs, a distance slightly greater than at the 216-A-2 Crib. This artifact was more than likely caused by the higher volume of wastes disposed in the 216-A-4 Crib (~6 million liters vs. 0.23 million liters at the 216-A-2 Crib). As found in borehole C5515 (A-2 Crib), the water-extractable sodium and calcium in the fine-grained sediments from ~280 to 300 ft bgs are higher than in the shallower sands. This is caused by the higher cation-exchange capacity of the silts. The distribution of water-extractable cations in the silt is similar to natural conditions wherein the calcium is significantly larger than the sodium. Thus, the impacts of the sodium-dominated liquid waste are found only a few tens of feet below and horizontally outside the 216-A-4 Crib foot print.

Figure 20 shows the water-extractable nitrate concentration in sediments from both the crib foot print (C4560) and just outside the foot print (C5301). Despite the fact that the wastes disposed in the 216-A-4 Crib contained almost 100,000 kg of nitrate, there is only about 15 mg/kg nitrate in the shallow sediments in the crib foot print. This is likely an indication that nitrate remained soluble and migrated deeper into the vadose zone. Slightly higher water-extractable nitrate was found in sediments outside the crib foot print in the zone 90 to 110 ft bgs, and then elevated values start at about 200 ft bgs, reaching peak values > 200 mg/kg in the fine-grained silt zone. As found below the foot print of the 216-A-2 Crib, there is residual nitrate in the fine-grained silt. It can not be stated whether this residual nitrate is from the liquid waste disposal from the two immediate cribs or whether the nitrate is a remnant of the regional horizontal spreading of liquid wastes along the top of the silt strata (that subsequently saturated the silt strata) from the entire PUREX A crib waste site region. The 216-A-2 and 216-A-4 Cribs received thousands to almost a hundred thousand kg nitrate, respectively. However, there is little difference in the concentrations of nitrate in the silt zone below the two cribs and further, the groundwater samples obtained from the two new boreholes were also similar: 69.5 and 62.9 mg/L at C5515 and C5301, respectively. Thus, we do not see any significant differences despite the mass of nitrate disposed to the two cribs differing by almost a factor of 50.

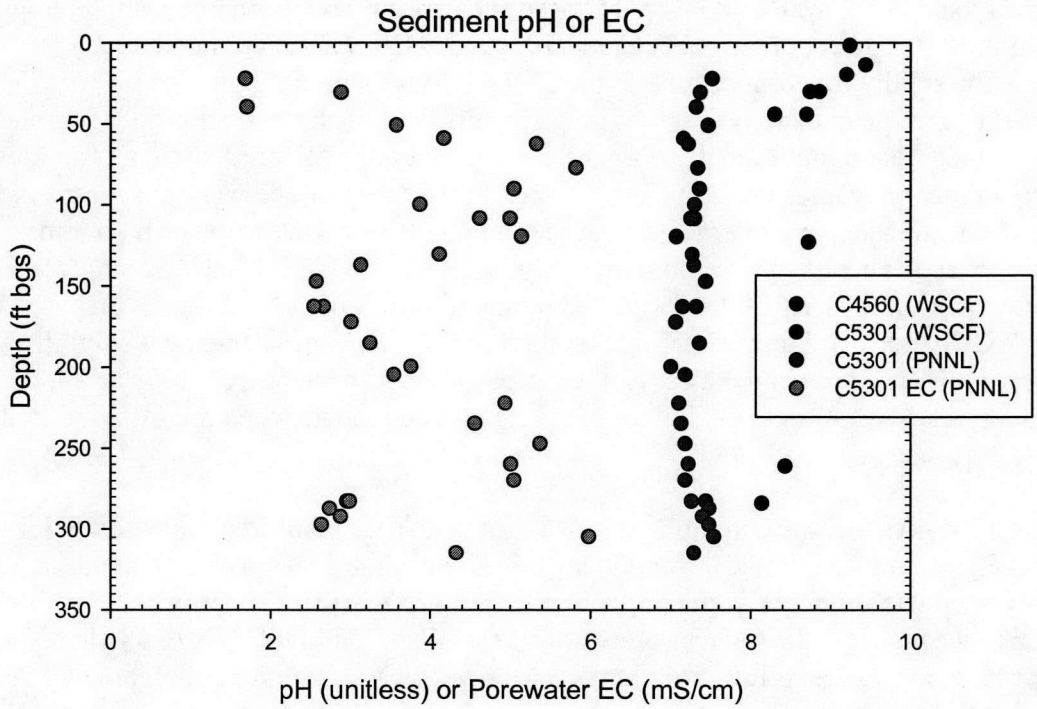

Figure 18. Sediment pH as a Function of Depth at the 216-A-4 Crib.

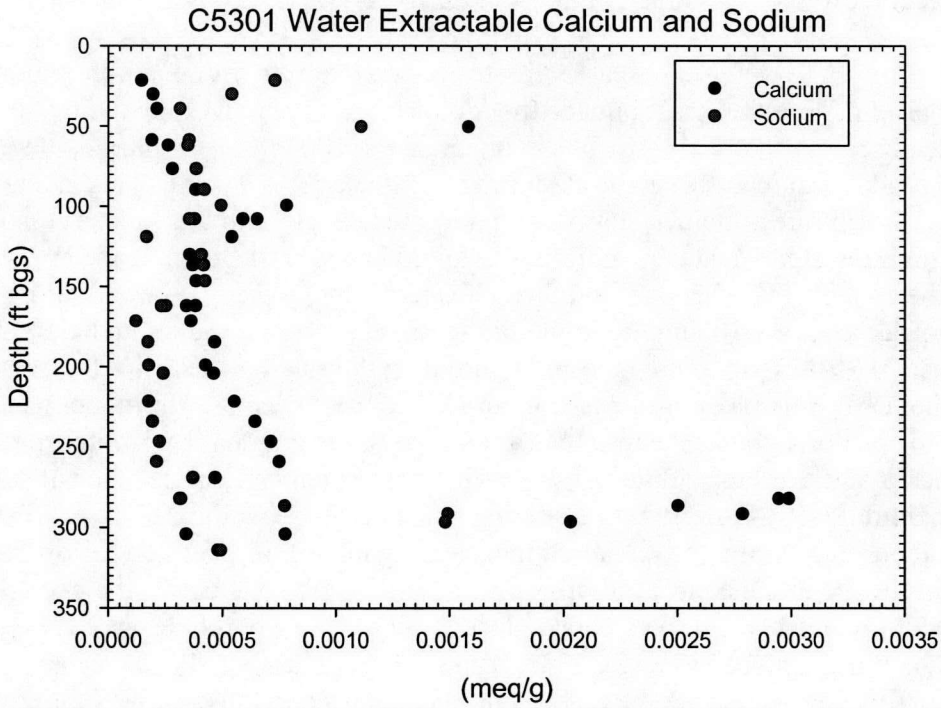

Figure 19. Water-Extractable Ca and Na for C5301 Borehole Vadose Zone Sediments

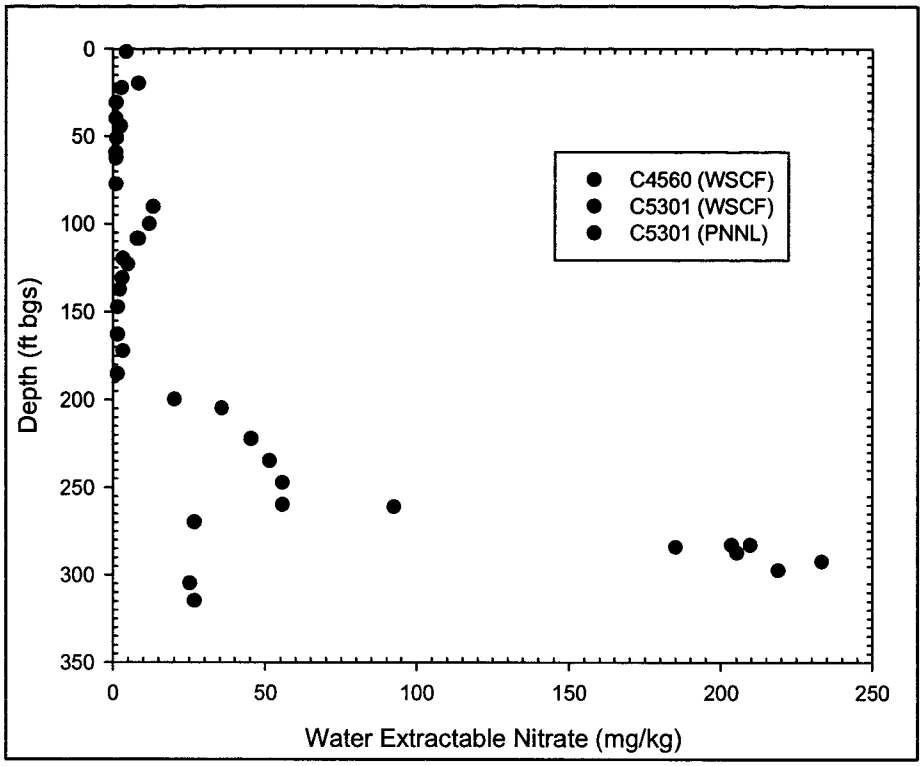

Figure 20. Water-Extractable Nitrate in Various Borehole Sediments Within and Near the 216-A-4 Crib

Figure 21 shows the distribution of Cs-137 in sediments within and proximate to the 216-A-4 Crib foot print. The Cs-137 concentration within the crib foot print shows a very thin, very high concentration right near the facility bottom. Relatively low Cs-137 concentrations were found just outside (2.5 m to the southwest) the crib foot print (in borehole C5301 sediments) at comparable depths, and no detectable Cs-137 was found below 50 ft bgs. As expected Cs-137 is strongly bound to the sediments and should decay in place before it can migrate down to the water table.

Figure 22 shows the distribution of uranium inside the foot print and just outside the 216-A4 Crib. The distribution of uranium within the crib foot print is similar to Cs-137, in that high concentrations were found right below the crib bottom and much lower concentrations were found at comparable depths right outside the crib foot print. There is slightly more uranium migration into the sediments below the crib bottom and one slightly elevated acid-extractable value at 50 ft bgs in the borehole C5301. This slightly more "diffuse" distribution in both the vertical and horizontal direction for uranium when compared to Cs-137 is expected based on sorption tendencies. However, the uranium in these two A cribs is still readily sequestered to the sediments close to the facility. There is no indication of mobile uranium in the silt zone below either crib. However, the groundwater sample obtained from borehole C5301 did contain 79.5 μg/L dissolved U whereas the groundwater below C5515 contained only 11μg/L dissolved U. Interestingly, the uranium disposed to the 216-A-4 Crib (see Table 2) was 5390 kg and

that disposed to the 216-A-2 Crib was only 228 kg. Thus, if there was some uranium moving through the vadose zone to the groundwater, one might expect some contribution from the 216-A-4 Crib compared to the 216-A-2 Crib as the two groundwater samples show.

Figure 23 shows the distribution of gross beta (PNNL) and tritium (WSCF) in sediments from borehole C5301, emplaced right outside the foot print of the 216-A-4 Crib. We are fairly confident that the PNNL gross beta measurement is responding almost entirely to tritium, such that the two data sets can be merged to reflect the tritium distribution. The data suggest that there is tritium in the vadose zone sediments from about 120 ft bgs down to the water table, with a significant amount of tritium found in the deep fine-grained silt strata. The values of tritium residing in the silt strata at both boreholes below the 216-A-2 and 216-A-4 Cribs were similar [800 to 1120 pCi/g with one value at 2850 pCi/g below 216-A-2], despite the fact that the 216-A-4 Crib received much more tritium inventory because much more liquid was disposed to the 216-A-4 Crib than the 216-A-2 Crib. Further, the concentration of tritium in the waste streams disposed to the 216-A-2 and 216-A-4 Cribs also varied by more than 3 orders of magnitude (see Tables 1 and 2). Given the fact that tritium is considered to be non-reactive with Hanford sediments, any residual tritium in pore water should reflect the original concentration in disposed liquids as opposed to reflecting total inventories released. Thus, one might expect there to be more difference in the observed tritium concentrations in the vadose zone sediments below these two cribs. Other possibilities, include deep mixing of the tritium waste liquids from the A-2 and A-4 Cribs, rendering them indistinguishable from each other, or perhaps the residual tritium in the silt strata today is not related to the disposals from the 216-A-2 and 216-A-4 Cribs, but is more indicative of some other source that migrating beneath the area on this somewhat continuous horizontal spreading plane.

The tritium concentrations per gram of dry sediment can be converted to pore water concentrations in units of pCi/L by multiplying by the the reciprocal of the average gravimetric moisture content {as a fraction} of the sediments in the fine-grain silt zone. The average moisture content of this stratum is 21% wt so the dilution factor is 4.76; finally to convert to tritium per liter multiply by 1000. This conversion leads to the tritium in the vadose fine-grained sediments equating to ~ 4 to 5 x 10^{+6} pCi/L. The tritium concentrations in the two groundwater samples collected from the two new boreholes are also similar, with C5515 (below the 216-A-2 Crib) having 6.0 x 10^5 pCi/L and C5301 (near the 216-A-4 Crib) having 4.2 x 10^5 pCi/L. These groundwater concentrations are about a factor of ten lower than the calculated vadose zone pore water concentrations. It is quite common to find estimated deep vadose zone pore water concentrations to exceed actual groundwater concentrations by a factor of ten or more. The tritium results for the vadose zone sediments in comparison with the underlying groundwater do not readily differentiate between a conceptual model where each localized vadose zone region is supplying the groundwater below. However, the large differences in estimated tritium concentrations disposed to 216-A-2 and 216-A-4 suggest a regional plume or a total commingling of the two adjacent cribs vadose zone plumes as opposed to separate localized inputs from the vadose zone right above the water table.

Figure 24 shows the acid-extractable chromium in sediments from within the 216-A-4 Crib foot print (C4560) and right outside the foot print (C5301). Within the crib foot print, directly beneath the crib bottom, there is no indication of significantly elevated concentrations of chromium; based on the low inventory (see Table 2) of chromium disposed to the 216-A-4 Crib, this is not surprising. The distribution of acid-extractable chromium values over the entire C5301 profile falls within the range of background Hanford sediments. The more elevated chromium values in the fine-grained silt strata are consistent with the fact that fine-grained sediments generally contain higher concentrations of trace metals. The water extraction of sediments throughout the C5301 profile shows no detectable chromium concentrations, suggesting no "contaminant" chromium is present. We do not believe that this observed elevated acid-extractable chromium data in the deep fine-grained strata is indicative of any chromium contamination having reached this depth.

One obvious conclusion can be drawn from a quick glance at all of the plots of vadose zone sediment constituent distributions; it would be very difficult if not impossible to generate a constituent profile based on the sparse data set generated using the samples analyzed solely by WSCF. The WSCF data set does not contain enough samples to adequately capture the peak water-extractable nitrate or gross beta/tritium in the C5301 (or C5515) borehole samples. It is also clear that there are elevated concentrations of some mobile contaminants in the fine-grained sediments between ~280 and 300 ft bgs. Although we can not rule out very localized mounding during the period of active disposal to the 216-A-4 Crib having saturated this strata, the sparse regional water level data available suggest that this strata might never have been saturated. The strata, which still need to be mapped to determine the lateral extent, would then represent a somewhat continuous perching horizon or horizontal spreading zone in which waste liquids would spread across the region from the various local disposals to the cribs. At some places, either there was localized mounding such that the silt layer became saturated and thus transmitted waste fluids down to the water table or at some locations this ~20 ft silt layer does not exist and waste fluids did percolate to the water table. The regional- and local-scale water table elevation with time is not available and not readily developed because of inadequate well coverage, especially in the early time period (1950s-mid 1960s) when the PUREX A cribs were most active.

The degree to which lateral spreading of mobile contaminants occurred below the 216-A-2 and 216-A-4 Cribs is still not well understood; however, it does appear that the 2-ft thick fine-grained layer of sediment centered at approximately 51 ft bgs in borehole C5301 did not prohibit the vertical migration of mobile contaminants in the vadose zone, but the thicker ~20 ft silt strata between 280 and 300 ft bgs likely did force much of the fluids disposed to the cribs to spread horizontally.

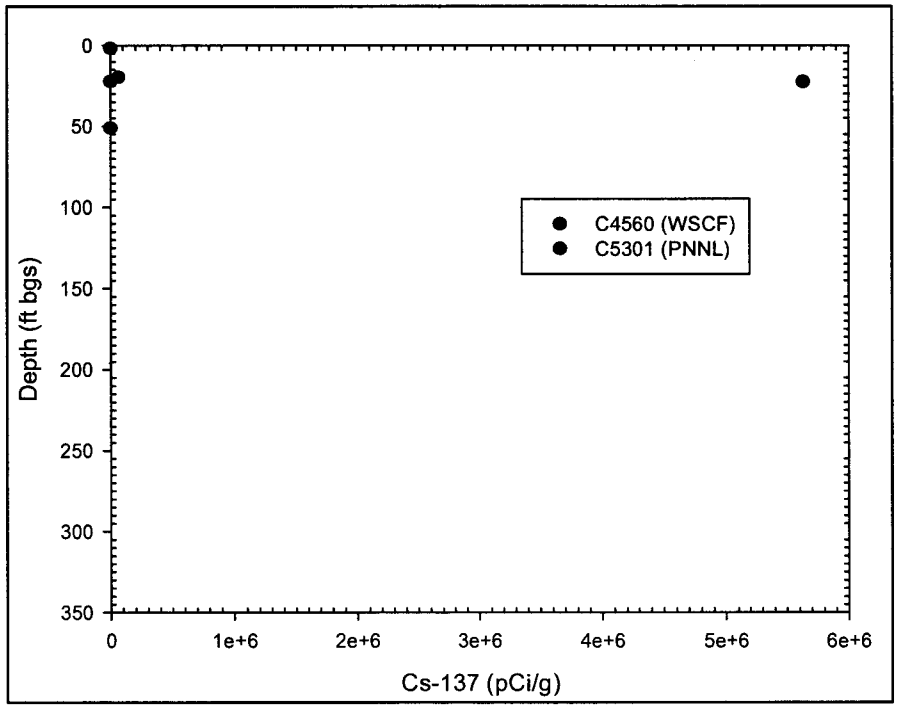

Figure 21. Cs-137 Activity of Sediments collected within and near the 216-A-4 Crib.

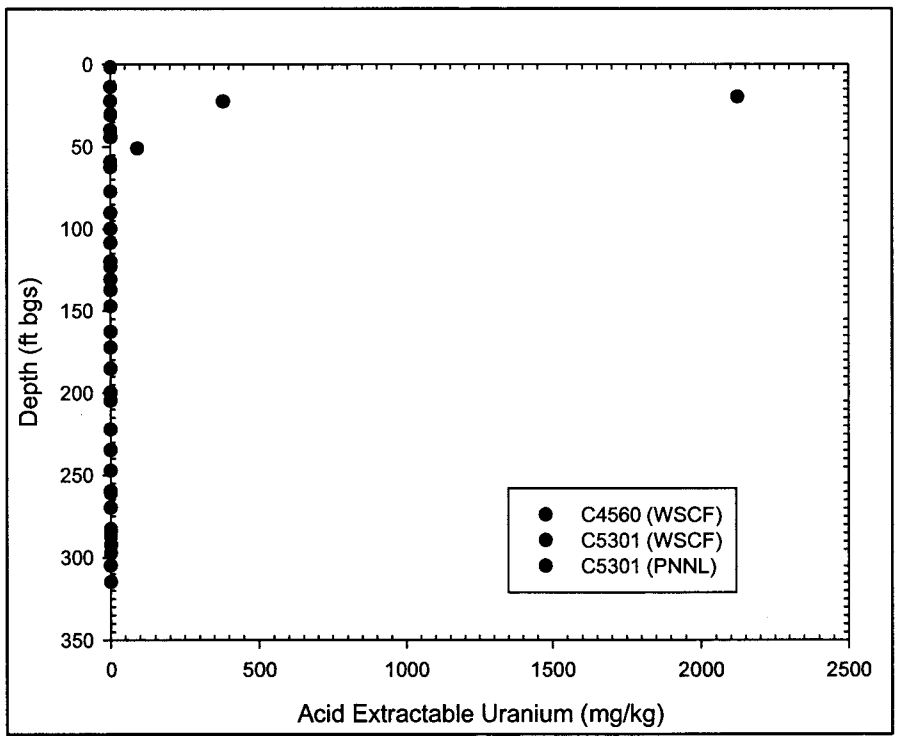

Figure 22. Acid-Extractable Uranium in Sediments collected within and Near the 216-A-4 Crib.

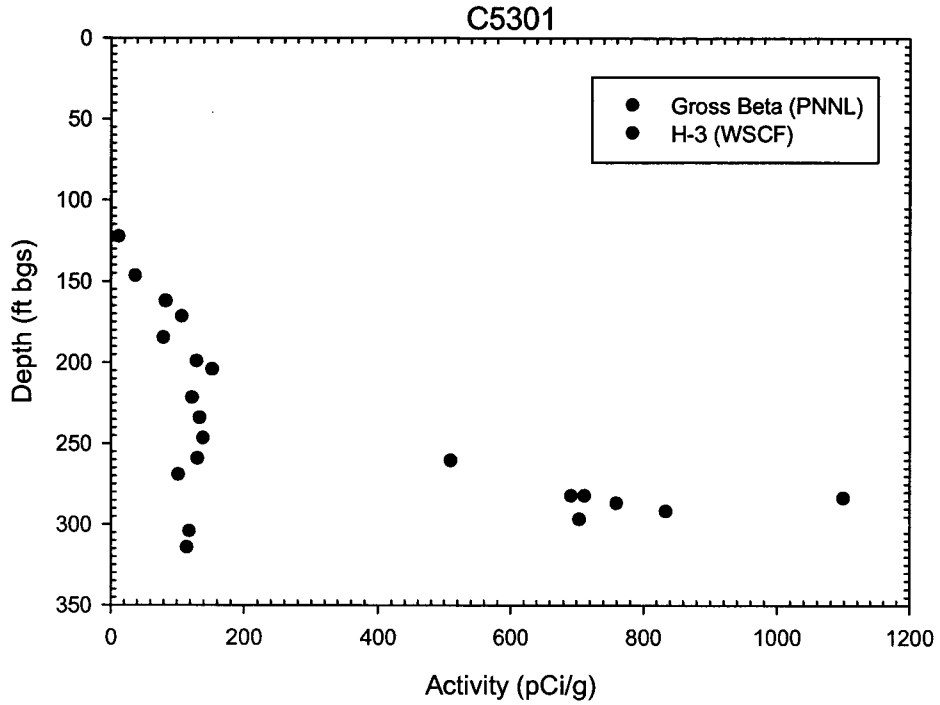

Figure 23. Gross Beta and Tritium in Sediments Collected neat the Foot print of the 216-A-4 Crib (borehole C5301).

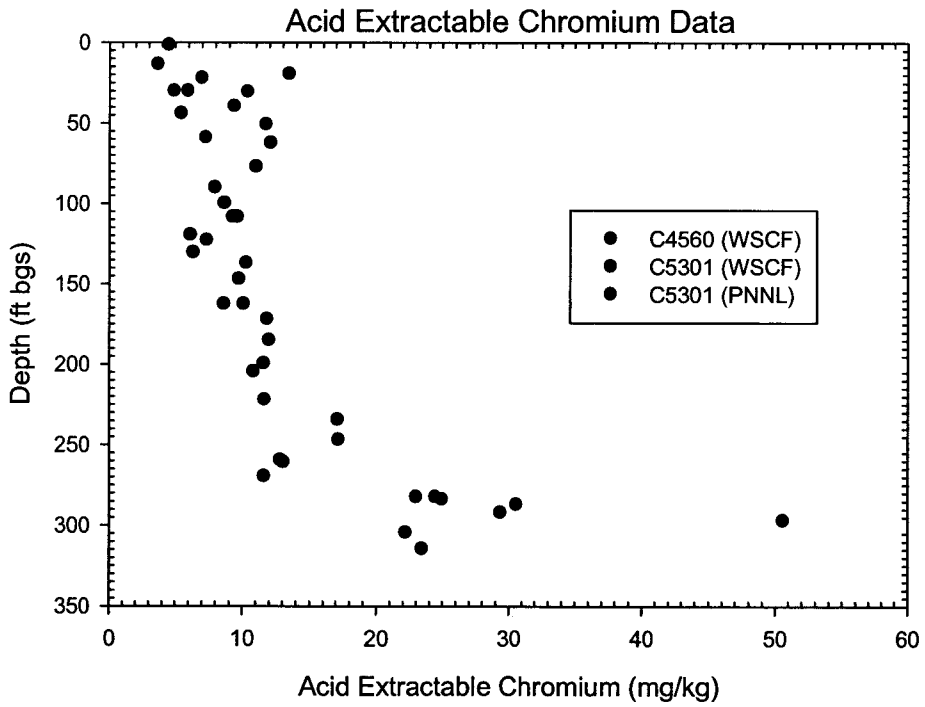

Figure 24. Acid-Extractable Chromium in Sediments Collected within and near the 216-A-4 Crib.

8.0 Comparison of Current Vadose Zone Constituent Concentrations as a Function of Depth and Lateral Spread with Historical Groundwater Observations

The time period of active disposal to the PUREX A cribs, especially the three for which recent boreholes have been emplaced (216-A-2, 216-A-4, and 216-A-21), was about five decades ago. Additionally, the volume of liquid disposed to the 216-A-4 and 216-A-21 Cribs exceeded the volume of vadose zone sediment directly below the facility foot prints by considerable margins. As a result of these activities, waste fluids discharged to the 216-A-4 and 216-A-21 Cribs might have reached the groundwater a long time ago and mobile constituents could have migrated and dispersed down gradient within the aquifer essentially leaving little current traces. Therefore, we reviewed historical groundwater data in the region south of the PUREX building to determine the feasibility of this scenario. The HEIS database was queried to find groundwater data for all the wells/boreholes shown in Figures 1 and 7. We requested data from the time period 1945 to 1995. The data retrieved showed information for 27 wells, but only four wells located just south of the PUREX building along an east west transect have data for the period prior to 1965, the latest date that liquids were disposed to any of the three cribs of interest [216-A-2, 216-A-4, and 216-A-21]. The four wells are 299-E17-2, 299-E24-1, 299-E24-2, and 299-E25-3. We originally assumed that the regional groundwater flow direction just south of the PUREX building has not changed from the general west to east flow direction since before the Hanford Site was built so the wells shown in Table 14 were expected to intercept a local plume from the PUREX A cribs region. However, a recent groundwater data package that focused on tank farms, Horton (2007), concluded that the groundwater flow direction below the A-AX Tank Farm Waste Management Area (WMA), about 600 m to the north of the PUREX A cribs area of interest, could not be determined before 1990 because of a lack of adequate well coverage. Since 1992, flow direction below the A-AX WMA is towards the south to southeast [see Figure 3.10 in Horton (2007)]. This differs from our assumption that the regional groundwater flow at the PUREX A cribs is from west to east. It would be useful to have groundwater experts revisit the data that we present below (and other historical groundwater data that we amassed but did not place in Table 14) to assess whether it is possible to determine what direction groundwater flowed below the PUREX A cribs during the period of active liquid waste disposal and whether there have been flow direction changes between the mid 1950s and present.

It has also been brought to our attention [personal communication D. G. Horton (Fluor Hanford Company in April 2008] that the HEIS database is not very complete and that historical groundwater monitoring data exist in old Hanford General Electric (HW-xxxx) reports that would improve our understanding of groundwater flow and contamination below the PUREX A cribs site over the time period of the 1950s to the mid 1990s when most information started to be documented in a readily retrievable format within the HEIS database. Table 14 shows a listing of wells close to an east-west transect through the 216-A-2/216-A-4 Cribs area. More data was retrieved for wells labeled E17-xx that are even farther to the south. These data should also be reviewed critically should it be shown that the groundwater flow direction south of the PUREX building was in fact to the south or southeast. The 299-E17 series of wells are to southwest of the three cribs of

interest (see Figure 7). There are very few wells to the south east of the three cribs of interest, so capturing the time progression of localized and even regional contaminant plumes south and east of the PUREX A cribs over the time period of interest will be challenging if not impossible.

At present, based on Table 14 results, we can only make some general comments on what mobile waste constituents were present in the groundwater over specific time periods. We tabulated the data in Table 14 under the assumption that groundwater was flowing from west to east, so that wells to the west are shown first and subsequent wells are located sequentially farther to the east. A few succinct observations are that the groundwater below the PUREX A cribs site has been "regionally" contaminated by several constituents since at least the 1958 [we found no data that pre-dates 1958 but most contaminant trends show high concentrations were present in 1958 that generally trended lower with time] through at least the mid 1990s. The fact that we cut off our data query in 1995 makes it possible that the plumes still exist; in fact the groundwater samples taken from the two new boreholes do show residual contamination today. Tritium, nitrate, Ru-106, Co-60, and gross beta (most likely dominated by Ru-106) were the "most elevated in concentration" contaminants. In smaller more localized regions at low but measurable amounts, Tc-99 and I-129 were reported in some groundwater wells during this 30 to 40 year time period. In fact, I-129 was found at concentrations between 5 and 6 pCi/L in the two new wells associated with boreholes C5515 and C5301 in 2007. Tc-99 at 290 pCi/L (below the drinking water standard of 900 pCi/L) was also found in the groundwater from C5301. Groundwater from both boreholes also contain tritium in the mid 10^{+5} pCi/L range and nitrate at 65 to 70 mg/L, both slightly above drinking water standards. The regional tritium and nitrate groundwater plumes reached concentrations as high as 10^{+8} pCi/L and 900 mg/L, respectively, during and shortly after the period of active waste disposal to the PUREX A cribs. Thus, liquid disposal to the PUREX A cribs undoubtedly impacted groundwater over a large region and concentrations of a few mobile contaminants still slightly exceed the drinking water standards today.

The data in Table 14 show increases in tritium, gross beta, and nitrate at particular time periods, such as 1963 and 1985 in wells 299-E24-2 and E24-1, both of which are located to the west of the 216-A-21 Crib. It is likely that a detailed analysis of disposal histories at other PUREX facilities located closer to these wells might yield the source disposal unit. It is also evident that a large region of groundwater south and west of the three cribs studied herein was, and still is, contaminated with mobile contaminants. Further, the vadose zone silt strata below the 216-A-2 and 216-A-4 Cribs contains some additional tritium and nitrate that might slowly percolate to the groundwater in the future.

Some bounding calculations for the mass of tritium and nitrate remaining in the deep vadose zone below the 216-A-2 and 216-A-4 Cribs could be made using their known concentrations and an assumed range of lateral extent if the areal extent of the deep vadose zone silt strata could be delineated. This could then be compared with the current regional groundwater plume mass to see if the residual mass in the vadose zone would significantly increase the mass currently in the groundwater. At first glance, unless there is a large area of the silt strata containing the residual tritium and nitrate, the existing

Table 14. Groundwater Data for Wells South of the PUREX Building with Data Between 1945 and 1995

Well #	Earliest Data	Tritium	Conc. (pCi/L)	Nitrate	Conc. (mg/L)	Gross Beta/Ru-106	Conc. (pCi/L)	Co-60	Conc. (pCi/L)	Comments
E24-11	Jan-71	Mar-87	7 to 10 E+07	Mar-87	230 to 470	Jan-71	400 to 700	Jan-71	90	
		1988	2 to 8 E+06	1988	115 to 235	1971-1972	200 to 1400	gap	no data	
		1989	3 to 4 E+06	1989	100 to 130	1973	100 to 150	1987	<dl	
		1991-1995	2 E+06	1991-1995	60 to 90	1974-1976	75			
						gap	no data			
						1987-1989	10 to 35			
E24-17	Nov-88	Feb-89	2.50E+06	Nov-88	122	Nov-88	65	1991	<dl	
		1989-1990	2 to 3 E+06	1989	97 to 110	1990-1991	15 to 30			
		1993 to 1995	8 E+05	1991	85					
				1992	60					
				1993-1995	40 to 50					
E24-2	Oct-57	Feb-63	500	Oct-57	50	Nov-57	28000 to 38000	Aug-62	1200	
		5/1/1963 to Jan-67	3 to 4 E+07	1958	16 to 180	1958	8000 to 35000	1963	1200	sign of two tritium influxes May 1963 and Jun 1985
		gap	no data	gap	no data	1959	3500 to 16000	1967	120	sign of nitrate influx between 1958 and 1961; missing data
		Nov-72	6 E+06	1961	550 to 890	gap	no data	1971	40 to 150	another slight influx of nitrate mid 1985
		gap	no data	gap	no data	1963	5 to 8 E+06	1972	30 to 50	sign of gross beta influx in 1963; agrees with tritium
		Oct-74 to Jan-76	4 to 6 E+06	1963	250 to 480	gap	no data	1973-1979	20 to <dl	
		Feb-76 to Mar-79	1 to 3 E+06	gap	no data	1967	30000 to 81000	1980 to 1983	5 to 10; many dl	
		Mar-79 to May-85	2 to 6 E+05	1967-1974	120 to 400	gap	no data	1984 to 1994	<5 (dl)	
		Jun-85 to Mar-91	1.5 to 5 E+06	gap	no data	1969	5000 to 7000			
		gap	no data	1983-mid 85	10 to 45	gap	no data			

Well #	Earliest Data	Tritium	Conc. (pCi/L)	Nitrate	Conc. (mg/L)	Gross Beta/Ru-106	Conc. (pCi/L)	Co-60	Conc. (pCi/L)	Comments
		Mar-92 to 1995	5 to 7 E+05	mid 85 to 1988	150 to 300	1971	800 to 2000			Ru-106 confirms it represents most of gross beta
				mid 88 to 1994	30 to 100	1972	500 to 800			
						1973	200 to 500			
						1974-1976	<dl to 100			
						1974-1994	10 to 40			
E24-16	Nov-88	Feb-89 to 1990	3 E+06	Nov-88	100	Nov-88	70	1991-1994	< dl	well too recent to see rapidly decaying Co-60 & Ru-106
		1991-1993	1 to 1.5 E+06	gap	no data	1989-1995	15 to 40			Tritium similar to E24-2 for time period measured
		1994-1995	8 E+05	1995	57					
E24-1	Oct-57	Jan-62 to Jan-63	0.5 to 2 E+07	Oct-57	1600	Nov-57	30000 to 40000	Feb-63 to 1964	1200	Co-60 questionable likely all <1200
		Jan-63 to Jan-64	<dl to 4 E+07	Dec-57 to Oct-58	100 to 400	1958	10000 to 50000	gap	no data	report Cs-137 between 1957 and 1965 but questionable likely < high dl value
		gap	no data	1959-1963	50 to 100	1959	8000 to 25000	Mar-83 to 1985	5 to 10	reports high I-129 from 1987 to end of query in 1995
		Oct-74 to Mar-78	1 to 6 E+06	gap	no data	gap	no data			
		Jun-78 to Jan-83	2 to 6 E+05	1982-1984	10 to 35	1974-1980	<75 (dl)			influx of nitrate in 1985 same as E24-2
		Feb-83 to Nov-84	1.1 to 2 E+05	1985-1988	150 to 500	1981 to 1995	20 to 60			2 influxes of tritium same time as E24-2
		Jan-85 to Jun-88	0.1 to 1 E+07	1989-1995	80 to 150					
		Jul-88 to May-91	1.5 to 3 E+06							
		gap	no data							
		Jul-93 to Jan-95	0.7 to 1.5 E+06							

Well #	Earliest Data	Tritium	Conc. (pCi/L)	Nitrate	Conc. (mg/L)	Gross Beta/Ru-106	Conc. (pCi/L)	Co-60	Conc. (pCi/L)	Comments
E24-9	May-66	Oct-66	2.6 E+07	Jul-63	190	May-66	42,000			not enough time series data in this well to say much; certainly was highly contaminated in mid 60s
		gap	no data	gap	no data	Jun-67	55,000			
				Oct-66	290	1969	1500 to 9800			
				gap	no data	gap	no data			
				1971 to 1973	190 to 310	1971	800 to 1600			
						1972	770 to 1200			
						1973	170 to 560			
						1974-1977	90 to 200			
E24-12	Apr-71	Feb-89 to 1990	3 E+06			Apr-71	700 to 1300			this well is directly south of E24-9 and if GW flow is to south it would be a good check
		1991 to 1995	0.8 to 1 E+06			1972 to 1975	50 to 100			however neither E24-9 or E24-12 have adequate data to track southward moving plume
						1975 to 1995	<20 to 100			
E25-3	1957	Jan-62 to 1966	1 E+06	1957 to 1962	<10	1957	data suspect	1987	<dl	Co-60 measurements too recent to be useful
		gap	no data	Jul-62 to Jul-67	20 to 70	1959-1961	1500 to 7000			faint sign of gross beta and nitrate early 1960s
		1987 to 1995	4 E+03	gap	no data	gap	no data			too many time gaps in data to be real useful
				1988 to 1995	<10	1969 to 1995	< dl			

Well #	Earliest Data	Tritium	Conc. (pCi/L)	Nitrate	Conc. (mg/L)	Gross Beta/Ru-106	Conc. (pCi/L)	Co-60	Conc. (pCi/L)	Comments
E25-17	1980	1980	1 E+05	Mar-83	<10	1980	<dl			
		1982 to 1984	decreases to 4 E+04	1985	10 to 25	gap	no data			tritium plume passed by between 1984 and 1990
		Jun-84 to 1990	increases to 6 E+05	1989-1990	25 to 45	1995	<dl			
		1992-1995	decreases to 4 E+04							

Values in red type are high, reflecting an influx of contaminants at this location and time. Values in blue type are lower, reflecting plume dispersion and dissipation at this location and time. Yellow shading represents highly variable data values over the time period denoted such that definitive trends can not be assessed.

groundwater plume has a larger mass. Also, no data are available to assess whether there is a significant variation in the concentration of contaminants in the groundwater as a function of depth. To our knowledge, none of the monitoring wells in the vicinity of the PUREX A cribs are sampled for depth-discrete analysis. Therefore, the volume of contaminated groundwater that exists today below the PUREX A crib sites is not available. This makes it difficult to predict the total mass of contaminants in the groundwater plume. However, assuming that the groundwater samples taken are well mixed over the entire length of the screened interval, which is commonly 15 to 30 ft, the area of the groundwater plume is much larger than the area of the silt zone in the vadose zone below the three cribs studied in this letter report. Thus, the existing groundwater plume below the PUREX A crib site undoubtedly contains more mass of tritium and nitrate than the mass still residing in the vadose zone.

9.0 Summary and Conclusions

Although all three disposal cribs were active over the same general time period (216-A-2: 1956-1960; 216-A-4: 1955-1958; and 216-A-21: 1957-1965), they received substantially different waste streams. The 216-A-2 Crib received waste characterized as PUREX P1 organic waste; of the three disposal cribs, it was the only one to receive a significant amount of organic waste (149,000 kg of TBP and 64,000 kg of NPH). Conversely, the 216-A-4 Crib received PUREX UNH waste, while the 216-A-21 Crib received PASF (P2) waste.

In addition to different waste streams, the three disposal cribs received significantly different volumes of waste. The 216-A-2 Crib received the lowest volume of waste, at 0.230 mega liters. The 216-A-4 Crib received approximately 27 times more waste, at 6.21 mega liters. However, the discharges to both of these cribs were dwarfed by the volume of waste sent to the 216-A-21 Crib, which received more than 77 mega liters total. These statistics are particularly important to highlight since all three cribs were meant to be operated as specific retention cribs. The fundamental idea behind specific retention disposal facilities is that waste will be added at low enough volumes such that it does not promote the vertical migration of contaminants (i.e., capillary pressure would facilitate the retention of the pore fluids in the vadose zone). This was supposed to be controlled by ensuring that the volume of waste disposed was kept at no greater than 10% of the volume of the facility's cross section multiplied by the depth to the water table. Surprisingly, the only crib that seemed to follow this practice (disposed low volumes of waste that would not overcome the capillary pressure in the vadose zone sediment) was the 216-A-2 Crib. For the other two cribs, the volume of waste disposed exceeded the retention capacity of the facility by 19 times (216-A-4 Crib) and 93 times (216-A-21 Crib). In essence, disposal of liquid effluents to the 216-A-4 and 216-A-21 Cribs likely caused rapid migration of mobile contaminants (such as tritium and nitrate) deep into the vadose zone and subsequently, into the aquifer.

Attempting to use the "continuous" distribution of Cs-137 obtained from spectral gamma logging information tempered with the direct measurement of Cs-137 in a handful of

depth-discrete samples led to large over-estimations of sorbed Cs-137 inventories for 216-A-2 and 216-A-4 but proved a very good comparison for 216-A-21 when only data for the facility foot prints were considered. When the apparent contribution from sediments outside the 216-A-2 crib (which showed more lateral spreading than 216-A-4 crib) was included the estimated inventory was even more unrealistic. We conclude that Cs-137, because of its high sorptive tendencies is very difficult to accurately measure the highly irregular distribution within the cribs' foot print. Dependent on the nature of the sediments (and any fine-grained sludge/precipitates physically filtered out) and the juxtaposition of the boreholes to the disposal pipes, highly irregular concentration profiles of Cs-137 are formed. If the boreholes/probe holes placed through the crib foot prints at 216-A-2 and 216-A-4 happened to capture uniquely high concentration zones, our using this biased data to average throughout the foot print cross section at the given depth intervals could explain the gross over-estimation of disposed Cs-137 inventory. For 216-A-2, lateral spreading of Cs-137 was observed in sediments collected from well 299-E24-53. The spectral gamma log for this well shows Cs-137 a ~10 ft thick zone of Cs-137 with concentrations peaking at 4500 pCi/g. Given the short distance from the crib foot print, this plume seems reasonable. At 216-A-4 there are spectral gamma logs available right outside the crib foot print at two locations on opposite sides of the crib that show maximum concentrations of only 15 to 55 pCi/g and the distances from the crib foot print is only 0.5 and 2.5 m. The main take home message out of these "box model" calculations of Cs-137 inventory in the shallow vadose zone based on the observed spectral gamma logs and discrete sediment measurements of Cs-137 is that this immobile contaminant binds to sediments within a few tens of feet to maybe 50 ft below and only a few to ten ft laterally from the facility foot prints. Cs-137 will not migrate any significant distance if the driving force is natural recharge or potable water for pipe-line leaks near the inactive facilities should such active pipe-lines exist today.

This analysis does corroborate the fact that observed Cs-137 activities near the 216-A-4 Crib bottom are surprisingly higher than expected based on historical records of the types of waste disposed. Further, the SIM, Rev. 1 predicted waste composition of the concentrated miscellaneous UNH (P1) waste stream is dominated by potassium at ~0.35 M. If this was the case, the Cs-137 K_d for sediments in the 216-A-4 crib foot print would be relatively low [<10 mL/g] and the distribution of sorbed Cs-137 should be rather diffuse [a thick zone] compared to the sharp, thin, intensely concentrated plume observed in the push holes placed into 216-A-4 Crib. The borehole geophysical spectral gamma log for borehole C4671 within the foot print of the 216-A-4 Crib shows a distinctly sharp vertical distribution, and the two boreholes outside the crib foot print [C5301 and A5911 (299-E24-54)] show little evidence of lateral spreading of Cs-137, despite the disposal of 6.21 million liters of waste. The water and acid extracts of the sediments throughout the vertical extent of well 299-E24-23 (C5301) also do not show any elevated potassium concentrations above natural background amounts. The total estimated inventory of potassium disposed to the 216-A-4 Crib was ~76,000 kg, yet no anomalously high potassium concentrations were found outside the crib foot print. No potassium data was collected on sediments within the crib foot print. We thus question whether the correct waste stream composition was assigned to the 216-A-4 Crib by the SIM, Rev. 1 staff or

alternately, the chemical algorithm used to assign chemical compositions might be erroneous.

Regarding the use of boreholes to characterize contaminated sediments within and around inactive CERCLA facilities, in our opinion, it is equally important to measure and define the geochemical environment in the vadose zone sediment-pore water system as it is to measure total concentrations of selected regulated chemicals and radionuclides (i.e., contaminants of concern). Knowledge of the geochemical environment present in the subsurface, (obtained from direct measurement of the major chemical species in the pore water or calculating the pore water composition and pH from water extracts of sediment samples as well as determining some of the properties of the sediments (including calcium carbonate content, moisture content, particle size, bulk sediment and clay size fraction mineralogy, cation exchange capacity, and hydrous ferric oxide content) allows geochemists to understand the major processes that control sediment-pore water interactions. The major soil chemical constituent's interactions with pore water in general dominate and control the interactions of the trace quantities of contaminants present in contaminated systems. If one only measures the total concentrations of contaminants, it is difficult to predict their fate over future times. Further, the recommended characterization scheme is iterative and somewhat unique for each borehole as opposed to being locked in based on *a priori* assumptions, historical information about the site, and generic Hanford expert opinion.

One of the key parameters to measure on vadose zone sediments is moisture content. A combination of field neutron moisture logging and discrete sediment sample (properly kept moisture proof in transit from the field) measurement of gravimetric moisture content is needed. We have found from numerous vadose zone characterization studies that elevated moisture contents correlate strongly with the presence of fine-grained sediments and that thin fine-grained lens can act as horizontal perching and spreading planes. As can be seen in Figure 6, there are two depths in the boreholes, which were recently completed using our recommended characterization strategy, where there are significantly elevated moisture zones. The shallow elevated moisture zone in C5515 (in the 216-A-2 Crib foot print) occurs at ~70 ft bgs and is no thicker than 6 ft; however, this single data point was not confirmed via neutron moisture logging of the borehole and we do not have more sample coverage in this region to provide confirmation via laboratory analysis. At C5301, which was emplaced right outside the southwest corner of the 216-A-4 Crib, a thin (<2 ft thick) zone of elevated moisture was found at 51 ft bgs and is composed of 25% very fine sand with 75% fine to medium sand. This shallow zone contains about ~13 to 16 wt% water, and could be acting as a horizontal spreading plane. A much thicker zone (20 to 22 ft thick) of elevated moisture (averaging ~21 %wt) is found in both boreholes between the depths of ~280 to ~305 ft bgs. This deeper zone, which is located approximately 15 ft above the current water table, is most likely an efficient perching and horizontal spreading plane for fluids that were disposed to the cribs. This deep and relatively thick zone of fine-grained sediment contains elevated concentrations of several mobile contaminants at this time.

Using water extract measurements of the common cations sodium, calcium, magnesium and potassium and pH, we can assess the interaction zone within the sediments caused by the liquid waste disposal. At both boreholes with adequate characterization, it is obvious that sodium from the waste has displaced native calcium (and magnesium) from the sediment cation exchange sites such that divalent cations are low and sodium is high does not penetrate more than tens of feet below the crib bottoms. Figure 19 shows that the sodium in the 216-A-4 waste has displaced the native calcium (and magnesium; not plotted) from the sediment exchange sites down to a depth of about 40 ft bgs, a distance slightly greater than at the 216-A-2 Crib. This observation was more than likely caused by the higher volume of wastes disposed in the 216-A-4 Crib (~6.2 million liters vs. 0.23 million liters at the 216-A-2 Crib). The zone where the sodium has displaced the native calcium in similar to the zone with elevated pH in 216-A-4's foot print, suggesting that the more significant sediment-waste interactions occurred above 40 ft bgs, roughly within 20 feet of the crib bottom. The zone of caustic attack is rather limited, compared to regions below leaking single-shell tanks, which was more than likely caused by the dilute nature of the wastes disposed to the PUREX A cribs. Many metal-like contaminants exhibit pH-dependent solubility and adsorption properties. In most cases, the metal-like contaminants (Cs-137, Sr-90, U, actinides, and RCRA metals) bind more strongly to sediments when the pH conditions are slightly caustic.

Regarding mobile contaminants, elevated nitrate is found only in the fine-grained strata from ~280 to 300 ft bgs in both boreholes, suggesting that the leading edge of the waste plume entered this silt zone and has been retained. The 216-A-2 and 216-A-4 Cribs received thousands to almost a hundred thousand kg nitrate, respectively. However, there is little difference in the concentrations of nitrate in the silt zone below the two cribs and further, the groundwater samples obtained from the two new boreholes were also similar: 69.5 and 62.9 mg/L at C5515 and C5301, respectively. Thus, we do not see any significant differences despite the mass of nitrate disposed to the two cribs differing by almost a factor of 50.

The slightly more "diffuse" distribution in both the vertical and horizontal direction for uranium [see Figures 16 and 22] when compared to Cs-137 is expected based on sorption tendencies. However, the uranium in these two A cribs is still readily sequestered to the sediments close to the facilities' bottoms. There is no indication of mobile uranium in the silt zone below either crib. However, the groundwater sample obtained from borehole C5301 did contain 79.5 μg/L dissolved U whereas the groundwater below C5515 contained only 11μg/L dissolved U. Interestingly, the uranium disposed to the 216-A-4 Crib (see Table 2) was 5390 kg and the uranium disposed to the 216-A-2 Crib was only 228 kg. Thus, if there was some uranium moving through the vadose zone, at low concentrations not readily discernable from the ubiquitous natural uranium background, to the groundwater, one might expect more contribution from the 216-A-4 Crib compared to the 216-A-2 Crib as evidenced in the two groundwater measurements.

The values of tritium residing in the deep silt strata at both boreholes below the 216-A-2 and 216-A-4 Cribs were similar [800 to 1120 pCi/g of sediment with one value at 2850 pCi/g below 216-A-2], despite the fact that the 216-A-4 Crib received much more tritium

inventory because much more liquid was disposed to the 216-A-4 Crib than the 216-A-2 Crib. Further, the concentration of tritium in the waste streams disposed to the 216-A-2 and 216-A-4 Cribs also varied by more than 3 orders of magnitude (see Tables 1 and 2). Given the fact that tritium is considered to be non-reactive with Hanford sediments any residual tritium in pore water should reflect the original concentration in disposed liquids as opposed to reflecting total inventories released. Thus, one might expect there to be more difference in the observed tritium concentrations in the vadose zone sediments below these two cribs. The tritium results for the vadose zone sediments in comparison with the underlying groundwater do not readily differentiate between a conceptual model where each localized vadose zone region is supplying the groundwater below. However, the large differences in estimated tritium concentrations disposed to 216-A-2 and 216-A-4, which are not manifested in the data for the two boreholes, suggest that a much larger region (horizontal spreading plane) of tritium may have been present in the vadose zone mixing on top of the silt strata or that there has been a localized commingling of the two adjacent crib's vadose tritium plumes as opposed to separate localized inputs from the vadose zone right above the water table. Perhaps the residual tritium in the silt strata today is not related to the disposals to the 216-A-2 and 216-A-4 Cribs, but is more indicative of some other nearby source(s) that have moved laterally along the silt strata, now residing at least beneath the A cribs.

Comparison of the data sets generated by the various analytical laboratories leads to two general conclusions. First of all, there is relatively good agreement between the four laboratories when similar extraction/analytical techniques are used to measure the samples. The second conclusion is that it would be very difficult if not impossible to generate a constituent profile based on the sparse data set that is typically generated during characterization campaigns (i.e., those samples solely analyzed by WSCF or Eberline). In all cases, the data sets generated by these two laboratories failed to capture either the total vertical extent or peak concentration of the contaminants of concern such as the peak water-extractable nitrate or gross beta/tritium in the C5301 (or C5515) borehole samples. It is also clear that there are elevated concentrations of some mobile contaminants in the fine-grained sediments between ~280 and 300 ft bgs. Clearly, a more comprehensive and rigorous sediment sample collection and analysis protocol is necessary if the ultimate goal is to understand the true nature and extent of contamination at each waste site.

Finally, there is no substitute for site-specific data. The three cribs studied as part of this campaign received different waste streams and significantly different waste volumes. In several cases, the observed data did not correlate with historical disposal records. Therefore, it would not be possible, or prudent, to attempt to use a borehole emplaced through one waste site as a surrogate for another waste site.

The lateral spread of historically mobile contaminants, such as tritium and nitrate, at the three cribs can not be quantitatively determined at this time. Relatively thin zones of fine-grained material exist in the vadose zone directly below the 216-A-2 and 216-A-4 Cribs that could have served to promote both perching and lateral spreading of contaminants. The shallower lens of finer-grained material could have promoted lateral

migration of the more mobile contaminants as long as the thin lens did not become fully water saturated during the active disposal episodes. More importantly, the deeper approximately 20-foot thick silt lens occurred from approximately 280 to 300 ft bgs at both waste sites and would certainly have led to significant perching and lateral spreading of mobile contaminants and could conceivably have inhibited further vertical migration of the contaminants. It is highly unlikely that the flux rate of water during the active disposal episodes could have forced this thick zone of fine-grained sediment to become water saturated, which would then reduce its horizontal spreading capability. Also, the sediment above the silt interval is composed of much coarser grained sand and gravel and thus assumed to be much higher in hydraulic conductivity, which would promote lateral spreading on top of the silt zone. Nitrate and tritium, both of which were major constituents in PUREX waste streams, were first observed as groundwater contaminants while the cribs were still in operation. Therefore, given the excessive amount of water discharged to some of the PUREX cribs (such as 216-A-4 and 216-A-21), coupled with observed historical contamination in the groundwater, it is obvious that at least some of the contamination disposed to the cribs has reached the water table regardless of the presence of a 20-foot thick silt lens deep in the vadose zone.

It would be useful to have groundwater experts revisit the historical groundwater data to assess whether it is possible to determine what direction groundwater flowed below the PUREX A cribs during the period of active liquid waste disposal and whether there have been flow direction changes between the mid 1950s and present.

Tritium, nitrate, Ru-106, Co-60, and gross beta (most likely dominated by Ru-106) were the "most elevated in concentration" contaminants found in the groundwater. In smaller more localized regions at low but measurable amounts, Tc-99 and I-129 were reported in some groundwater wells during this 30 to 40 year time period. The regional tritium and nitrate groundwater plumes reached concentrations as high as 10^{+8} pCi/L and 900 mg/L, respectively, during and shortly after the period of active waste disposal to the PUREX A cribs. Thus, liquid disposal to the PUREX A cribs undoubtedly impacted groundwater over a large region and concentrations of a few mobile contaminants still slightly exceed the drinking water standards today.

The historical groundwater data show increases in tritium, gross beta, and nitrate at particular time periods, such as 1963 and 1985 in wells 299-E24-2 and E24-1, both of which are located to the west of the 216-A-21 Crib. It is possible that a detailed analysis of disposal histories at other PUREX facilities located closer to these wells might identify the source disposal unit(s) that caused the episodic high groundwater concentrations at the cited wells. It is also evident that a large region of groundwater south and west of the three cribs studied herein was, and still is, contaminated with mobile contaminants. Further, the vadose zone silt strata below the 216-A-2 and 216-A-4 Cribs contains some additional tritium and nitrate that might slowly percolate to the groundwater in the future.

Some bounding calculations for the mass of tritium and nitrate remaining in the deep vadose zone below the 216-A-2 and 216-A-4 Cribs could be made using their known concentrations and an assumed range of lateral extent if the areal extent of the deep

vadose zone silt strata could be delineated from critical review of all regional geologic data obtained during drilling of boreholes and groundwater monitoring wells. This could then be compared with the current regional groundwater plume mass to see if the residual mass in the vadose zone would significantly increase the mass currently in the groundwater.

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