0100253

Department of Energy
Richland Operations Office
P.O. Box 550
Richland, Washington 99352

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12-AMCP-0029

Mr. K. Niles, Assistant Director
Nuclear Safety Division
Oregon Department of Energy
625 Marion Street Northeast, Suite 1
Salem, Oregon 97301

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Dear Mr. Niles:

PROPOSED PLAN FOR THE REMEDIATION OF THE 200-CW-5, 200-PW-1, 200-PW-3, AND 200-PW-6 OPERABLE UNITS, DOE/RL-2009-117, REVISION 0

The purpose of this letter is to respond to the September 6, 2011, supplemental comments on the Proposed Plan for the Remediation of the 200-CW-5, 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units, DOE/RL-2009-117, Revision 0.

We appreciate the opportunity to respond to the Oregon Department of Energy's supplemental comments that address the potential for plutonium mobility. It is clear from your extensive literature review that this is an important concern for the State of Oregon.

As your letter indicates, the environmental chemistry of plutonium is one of the most complex and challenging topics for subsurface research in the DOE complex today. However, the literature cited in your supplemental comments does not include Hanford specific studies of waste streams, process chemistry or subsurface conditions. To draw conclusions regarding the mobility of plutonium at Hanford, it is essential to understand studies of actual Hanford waste sites and disposal practices. For example, the process chemistry of the Z-9 trench represents an extreme, perhaps "worst-case scenario," where more than 1 million gallons of plutonium-bearing waste was discharged from 1955 to 1962 in a highly acidic, high-salt and organic-rich waste stream. This practice led to the unprecedented migration of significant quantities of plutonium to depths of up to 120 feet below ground surface. Today, nearly fifty years since that disposal practice was ended, we can learn from the environmental evidence that has been assembled specific to this site and other sites at Hanford. We have attempted to capture that evidence in responding to your comments by addressing the following topics:

- 60+ year history of the 216-B-5 reverse well. From 1945 to 1947 nearly 10 million gallons of plutonium-bearing liquid waste were directly injected into the groundwater. This site provides a unique "case study" that provides important insights into the mobility of plutonium in Hanford groundwater. Based on a treatability test conducted at this site in the mid-1990s and continued groundwater monitoring, plutonium remains within this original location and is not migrating with groundwater.

- Overview of historic groundwater monitoring results for plutonium at the Hanford site. Hanford's extensive groundwater monitoring network provides an important historical record of plutonium impacts and provides another means of assessing the likelihood of plutonium reaching groundwater and its ability to migrate within Hanford groundwater. Only three wells regularly show plutonium concentrations at or near drinking water standards. All three wells are located within a few meters of the 216-B-5 reverse well. These data show that plutonium concentrations are not increasing and migration is not occurring in groundwater.

- Supplemental analyses of the Z-9 trench borehole samples (beyond those available for the 200-PW-1/3/6 Remedial Investigation report). These analyses have attempted to unravel some of the mysteries surrounding the subsurface migration at the Z-9 trench disposal site. These studies also address some of the migration mechanisms hypothesized by the literature cited in the Oregon comments. These studies show that: past subsurface mobility of plutonium is associated with highly acidic waste streams; plutonium adheres strongly to Hanford sediments under normal conditions; and plutonium does not migrate in solution as pH values approach those of typical Hanford Site groundwater (i.e., near neutral to mildly alkaline, ~ pH 8). (This material is provided by Dr. Kirk Cantrell, Senior Research Scientist at the Pacific Northwest National Laboratory, who has conducted numerous studies of plutonium mobility at Hanford.)

- Overview of Hanford-specific studies of colloidal transport. There is a growing body of work on colloidal transport of radionuclides at Hanford. These studies have not found evidence that colloid facilitated transport is a significant driver for contaminant transport in the subsurface at Hanford.

- Office of Science supported studies of plutonium mobility at Hanford. Several important studies have been and continue to be conducted using state-of-the-art methods and collaborative research efforts with the most capable scientists in this field, including some of those researchers cited in Oregon's comments. These studies will continue to explore the challenging subsurface chemistry of plutonium. (This material is provided by Dr. Andrew Felmy, Laboratory Fellow at the Pacific Northwest National Laboratory. Dr. Felmy is an internationally recognized expert in actinide chemistry; is currently engaged in several research projects on plutonium chemistry at Hanford; and was the organizer and chair of the international Migration 2009 conference held in Kennewick, Washington.)

Our responses are contained in two attachments. The first attachment is a "summary" of the more detailed information provided in the second attachment. The second attachment provides many Hanford-specific technical references and also includes a bibliography of additional relevant publications.

We welcome the opportunity for further dialogue with the Oregon Department of Energy on this topic. We also want to offer the opportunity for you and your staff to engage in topical discussions with researchers involved with ongoing Office of Science supported research on plutonium mobility. Please contact Paula Call (509) 376-2048 to arrange for follow up discussions, if desired.

Thank you again for your interest and engagement in Hanford cleanup.

If you have any questions, please contact me, or your staff may contact Briant Charboneau, of my staff, on (509) 373-6137.

Sincerely,

Jonathan Dowell

Jonathan A. Dowell, Assistant Manager
for the Central Plateau

AMCP:GLS

Attachments

cc w/attachs:
G. Bohnee, NPT
L. Buck, Wanapum
C. E. Cameron, EPA
K. J. Cantrell, PNNL
D.A. Faulk, EPA
A. R. Felmy, PNNL
S. Harris, CTUIR
J. A. Hedges, Ecology
R. Jim, YN
E. Laija, EPA
S. L. Leckband, HAB
N. M. Menard, Ecology
D. Rowland, YN
M. B. Triplett, PNNL
Administrative Record
Environmental Portal

cc w/o attachs:
L. M. Dittmer, CHPRC
D. L. Foss, CHPRC
T. W. Noland, MSA
R. E. Piippo, MSA

Attachment 1

Summary Discussion of Hanford Information Related to Plutonium Mobility in the Environment

DOE thanks the State of Oregon for providing DOE with an opportunity to respond to their concerns regarding plutonium mobility in the environment. Much is known about plutonium mobility at Hanford based on a very long (60+ years) groundwater monitoring record as well as investigations of key waste sites and DOE Office of Science-supported research. DOE agrees that there remain important questions that may warrant continued study to improve our understanding of the mechanisms that drove contaminants deep into the subsurface at certain waste sites, including the Z-9 Trench. These studies may serve to unlock the complexities of plutonium migration and help to inform remedy and disposal decisions within the DOE complex. However, much of the literature cited by Oregon is not specific to the Hanford Site or to Hanford-specific subsurface conditions and therefore should not be extrapolated to draw conclusions about plutonium mobility at Hanford.

The information provided below summarizes Hanford-specific studies beyond those included in the PW-1/3/6 Remedial Investigation Report (DOE/RL 2007). The additional material provided in Attachment 2 also summarizes groundwater monitoring results at the Hanford site and includes an evaluation of the 216-B-5 reverse well where plutonium-bearing liquid waste was injected directly into the groundwater in the late 1940s. We also summarize current DOE Office of Science supported research on plutonium at Hanford including the significant areas of inquiry and collaborations with external researchers. A bibliography of relevant studies is also provided

Our summary of Hanford-specific data, studies and research includes the following topics:

1. Summary of the 216-B-5 reverse well and the direct injection of plutonium bearing waste into Hanford groundwater in the 1940s. (What has happened to the plutonium that was discharged directly to the groundwater more than 60 years ago?)

2. Overview of historic groundwater monitoring results for plutonium. (What observed evidence is there for plutonium impact on and mobility in Hanford groundwater?)

3. Synopsis and findings from supplemental analyses conducted on the 216-Z-9 waste samples. (What is the distribution of subsurface plutonium associated with this site, what do these studies suggest about the past mobility of plutonium, and what do these studies suggest about the past, present and future mobility of plutonium?)

4. Review of Hanford-specific studies of colloid transport. (Under what conditions is colloid-facilitated transport at Hanford possible and do these conditions exist in the subsurface?)

5. Summary of on-going research supported by the DOE Office of Science related to plutonium mobility at Hanford. (What are the key unresolved questions and what studies are being conducted to address these questions?)

6. How can new information be factored into Hanford cleanup decisions?

Summary of Detailed Information Provided in Attachment 2

This section summarizes the detailed material provided in Attachment 2 and provides key points that address the principal topics raised in Oregon's comments.

1. **216-B-5 reverse well and direct injection of plutonium bearing waste into groundwater**. What has happened to the plutonium that was discharged directly to the groundwater more than 60 years ago? The 216-B-5 reverse well provides a case study of plutonium mobility in Hanford groundwater. There is probably no better location to assess the likelihood of plutonium mobility in groundwater at the Hanford Site.

    - From 1945 to 1947 nearly 10 million gallons of plutonium-bearing waste (up to 4.3 kg of plutonium) was injected directly into the groundwater at the 216-B-5 reverse well. Characterization of this site in 1979 and again in 1994 shows the plutonium remains within a few meters of the injection site. Three groundwater monitoring wells within 7 meters of the injection site routinely show plutonium detection with occasional readings slightly exceeding drinking water standards (15 pCi/L). However, continued monitoring does not show increasing concentrations or migration of plutonium. A treatability study at this site was conducted in the mid-1990s to determine if an interim remedial action would be effective. The results of the treatability test showed that only insignificant quantities of plutonium could be removed with groundwater pumping because plutonium is tightly bound to sediments and not highly soluble or mobile within groundwater. This site continues to be monitored and provides a substantial base of information for evaluating plutonium mobility in Hanford groundwater.

2. **Overview of historic site-wide groundwater monitoring results for plutonium**. What observed evidence is there for plutonium impact on Hanford groundwater? The Hanford Site has an extensive network of groundwater monitoring wells which have been monitored since operations began in the mid-1940s. To draw conclusions regarding subsurface mobility of plutonium at Hanford, it is essential to understand the relevant observations from groundwater monitoring results.

    - Hanford's groundwater monitoring data are readily available on Hanford's Environmental Dashboard Application (http://environet.hanford.gov/eda/). Only three wells regularly show plutonium concentrations at or near drinking water standards. These are the three wells referred to above that are within a few meters of the 216-B-5 reverse well. Even with the liquid discharge of more than 11,000 Ci of plutonium-239 at Hanford (mostly to about a dozen sites associated with the Plutonium Finishing Plant), there is little evidence of migration through the vadose zone to groundwater (as discussed in Attachment 2). There is no evidence of increasing concentrations of plutonium in groundwater or migration from the few locations where plutonium has been detected in groundwater.

3. **Synopsis and findings from supplemental analyses conducted on the 216-Z-9 waste samples**. What is the distribution of subsurface plutonium associated with this site, what do these studies suggest about the past mobility of plutonium, and what do these studies suggest about the past, present and future mobility of plutonium? As discussed in Attachment 2, the key conclusions from sample analyses for the Z-9 Trench include:

   - Studies with actual sediments collected beneath or near the 216-Z-9 Trench indicate that silt layers at approximately 65 and 115 feet below ground surface significantly reduced the vertical advection of plutonium, americium, and tributyl phosphate and likely resulted in horizontal spreading of the waste components along the tops of these layers during active disposal.
   - The studies also indicate that plutonium and americium can only be mobilized from the 216-Z-9 contaminated sediments by pore-waters that remain acidic (pH 4.3 to 5.4) after contact with the sediments. Because an advective driving force is no longer present to transport the plutonium and americium, further subsurface migration of plutonium and americium does not appear to be likely.
   - At waste sites within the 200-PW-1/3/6 operable unit plutonium and americium were co-disposed with large volumes of acidic high-salt wastes that contained organic complexants. This practice resulted in significant transport through to vadose zone. The significant transport of plutonium and americium through the vadose zone was the result of the combination of high advective flux of the waste along with a high solubility and low sorption potential of plutonium and americium associated with low pH solutions. Association with dissolved organic complexing agents such as dibutyl phosphate may have added to the high mobility of plutonium and americium during the disposal phase of the site. In addition, it is possible that some fraction of the plutonium that migrated through the vadose zone may have been in particulate form.
   - Under typical Hanford subsurface conditions [ground water dominated by Ca, Na, and HCO_3^- at near neutral pH (~8), and oxidizing conditions] plutonium is very insoluble and adsorbs strongly to Hanford sediments.

4. **Colloidal transport**. In some of the literature cited in the Oregon comments, colloidal transport is suggested as a mechanism that could enhance subsurface transport of plutonium and other actinides. What has been learned about the potential for colloidal transport at Hanford?

   - There is a growing body of research on colloid transport of radionuclide contaminants at Hanford (see discussion in Attachment 2 and associated bibliography of studies of colloidal transport). These studies indicate that colloidal transport of highly sorptive radionuclides is unlikely to be important at Hanford unless water contents and flow rates are locally and temporally increased by snowmelt or episodic artificial recharge. Some work has shown a significant decrease in colloid mobility at vadose zone saturation levels similar to Hanford sediments (i.e., ~6%). Additionally, both Pu(V) complexes and $Pu(IV)O_2(am)$ colloids or nanoclusters are known for their adsorption affinity for oxide and hydroxide mineral surfaces (see Attachment 2, Section 3.d). As a result, these species are not likely to remain in solution as pH values approach those of typical Hanford Site groundwater (mildly alkaline, ~pH 8).

- Dai et al (2005) investigated plutonium in groundwater at the 100-K Area of Hanford including colloid facilitated transport. Ultra-sensitive methods were used to detect very low concentrations of plutonium (e.g., 10^{-4} to 10^{-6} pCi/kg). The study concluded "there is no clear evidence for colloid facilitated transport of plutonium in groundwater at the Hanford Site, since downstream wells have both an order of magnitude lower concentration of plutonium and a lower fractional colloidal distribution."
- DOE's Office of Science is funding new work at PNNL to characterize particle distributions in Z-9 Trench sediments. The spring meeting of the American Chemical Society will include a paper on this work during a special symposium on colloid migration.

5. **On-going DOE Office of Science research related to plutonium mobility at Hanford**. (What are the key unresolved questions and what studies are being conducted to address these questions?)

   - There are currently three main research programs working on plutonium contamination issues at Hanford: The PNNL Science Focus Area (PNNL SFA) which includes collaborators at Los Alamos National Laboratory (LANL), the Transuranic Science Focus Area (TSFA) at Lawrence Livermore National Laboratory (LLNL), and project funded research at Clemson University. The plutonium research in the PNNL SFA is focused on two activities 1) determining the chemical form of plutonium in Hanford soils and sediments and 2) unraveling the fundamental mechanisms of electron transfer (i.e. oxidation/reduction) of plutonium compounds. Research in the TSFA at LLNL is focused on the environmental transport of plutonium at ultra low concentrations and is examining the role of natural organic matter, microbial interactions, and colloid interactions. The research at Clemson is focused on the development of mechanistic models of plutonium partitioning to sediments and is investigating subsurface sediments that were obtained from the Savannah River Site and from Hanford.

6. **How can new information be factored into Hanford cleanup decisions?**

   - The CERCLA process recognizes that remedy decisions are made with some degree of uncertainty. As a result, CERCLA mandates the use of 5-year reviews to periodically re-evaluate the effectiveness of remedies and whether new information has emerged that could call into question the protectiveness of the selected remedy. This process previously resulted in a determination that the uranium plume in the 300 Area was not dissipating as predicted in the 1990s and led to the current set of remedy design and evaluation studies to address that plume.
   - Office of Science supported research will continue to investigate plutonium chemistry and mobility at sites around the DOE complex. PNNL scientists will continue to be involved in collaborations with researchers from other Laboratories and universities. PNNL has retained multiple samples from Hanford plutonium sites that will be made available for future analyses as research findings warrant. We welcome the

opportunity for Oregon staff to engage with these scientists as their research continues.

DOE recognizes the inherent complexities and uncertainties of plutonium subsurface transport. Hanford includes some of the most extreme plutonium disposal practices anywhere in the DOE complex (e.g., direct injection of plutonium-bearing liquid waste into the groundwater and discharge of plutonium in acidic high-salt wastes that contained organic complexants). Several decades of monitoring and characterization activities provide a wealth of information about plutonium in the environment at Hanford. Hanford researchers will continue to collaborate with other researchers on important issues related to plutonium mobility.

References:

Cantrell KJ and RG Riley. 2008. A Review of Subsurface Behavior of Plutonium and Americium at the 200-PW-1/3/6 Operable Units. PNNL-SA-58953, Pacific Northwest National Laboratory, Richland, Washington.

Dai M, KO Buesseler, SM Pike. 2005. "Plutonium in Groundwater at the 100K-Area of the U.S. DOE Hanford Site." Journal of Contaminant Hydrology 79: 167-189.

DOE/RL. 2007. Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units. DOE/RL-2006-51, Rev. 0, prepared for the U.S. Department of Energy, Richland, Washington.

Attachment 2

Plutonium Mobility Comments and Responses to Oregon Letter and Attachment ("Discussion of research related to the movement of plutonium in the environment") September 6, 2011

This attachment provides a more in depth review of Hanford-specific literature, research and analyses that are relevant to understanding the mobility of plutonium in the subsurface of the Hanford Site. DOE's responses to Oregon's September 6th letter and attachment address the following topical areas:

1. Summary of the 216-B-5 reverse well and the direct injection of plutonium bearing waste into Hanford groundwater in the 1940s. (What has happened to the plutonium that was discharged directly to the groundwater more than 60 years ago?)

2. Overview of historic groundwater monitoring results for plutonium. (What observed evidence is there for plutonium impact on Hanford groundwater?)

3. Synopsis and findings from supplemental analyses conducted on the 216-Z-9 waste samples. (What is the distribution of subsurface plutonium associated with this site, what do these studies suggest about the past mobility of plutonium, and what do these studies suggest about the past, present and future mobility of plutonium?)

4. Discussion of Hanford-specific studies of colloidal transport. (What are the findings from studies of colloidal transport in the subsurface at Hanford?)

5. Summary of on-going research supported by the DOE Office of Science related to plutonium mobility at Hanford. (What are the key unresolved questions and what studies are being conducted to address these questions?)

Specific technical references associated with our responses are listed in each of the sections below.

References:

DOE/RL. 2007. Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units. DOE/RL-2006-51, Rev. 0, prepared for the U.S. Department of Energy, Richland, Washington.

1. Summary of the 216-B-5 reverse well and the direct injection of plutonium bearing waste into Hanford groundwater in the 1940s

The 216-B-5 reverse well provides a 60+ year "case study" in plutonium mobility in Hanford groundwater. While the chemistry of the discharge stream differs from that at the PW-1/3/6 waste sites, the experience from this site is relevant to the general concerns raised in the Oregon letter regarding plutonium mobility in Hanford groundwater, i.e., "plutonium would be most mobile in high pH carbonate-rich ground waters (like Hanford)." During a 2-year period from 1945 to 1947, approximately 3.2×10^7 L of liquid waste from the Bismuth-Phosphate operations at B Plant was discharged to the 241-B-361 settling tank (DOE/RL 1996). The over flow was disposed of to the 216-B-5 reverse well. The settling tank was designed to remove waste solids before water disposal to the reverse well. The well penetrated approximately 3.7 m below the water table, and waste was introduced into the aquifer at this level. The liquid discharge was estimated to contain 4.3 kilograms of plutonium.

Eleven wells were drilled adjacent to the reverse well from 1947 to 1948 to characterize groundwater contamination from this discharge. Results are summarized in Brown and Ruppert (1950). Three additional groundwater wells were drilled in 1979 to 1980 to further characterize radionuclide distributions around the reverse well. In 1980, DOE completed a characterization study of the 216-B-5 Reverse Well (Smith 1980). The characterization study suggests approximately 50 percent of the plutonium inventory remained in the settling tank and was not discharged to the reverse well. Plutonium exceeding 10 nanocuries/gram of soil was limited to within 6 meters of the reverse well in 1979 (when the study was performed). Plutonium concentrations exceeding 100 nanocuries/gram were limited to a narrow 1 meter layer, located at the position of the 1948 water table. Figure 1-1 shows the estimated distribution of plutonium resulting from that characterization effort.

In 1995, DOE implemented a treatability test plan for certain portions of the 200-BP-5 groundwater operable unit that had been identified as candidates for accelerated remedial action. One location included the 216-B-5 reverse well with key groundwater contaminants including cesium-137, strontium-90, and plutonium-239/240. The treatability test was performed to determine whether the contaminated groundwater at this site would be amenable to remediation by extraction of the groundwater. The results of the test, including groundwater extraction, analytical studies and risk assessment modeling, are described in DOE/RL (1996). Plutonium concentrations in extracted groundwater are shown in Figure 1-2 below. The conclusion of the treatability test regarding the 216-B-5 reverse well (DOE/RL 1996, p. 7-3) was "that the B-5 Reverse Well plumes will not produce an unacceptable risk to offsite groundwater users. Therefore, it is recommended that the plumes be removed from the accelerated IRM (interim remedial measure) pathway and that the future course of action include only groundwater monitoring to track plume movement and verify modeling results." Today, groundwater monitoring indicates that plutonium in groundwater remains in this original region and concentrations in groundwater are generally in the range of 1-40 pCi/L.

Section 2.0 describes the groundwater monitoring results for plutonium in the region near this disposal site.

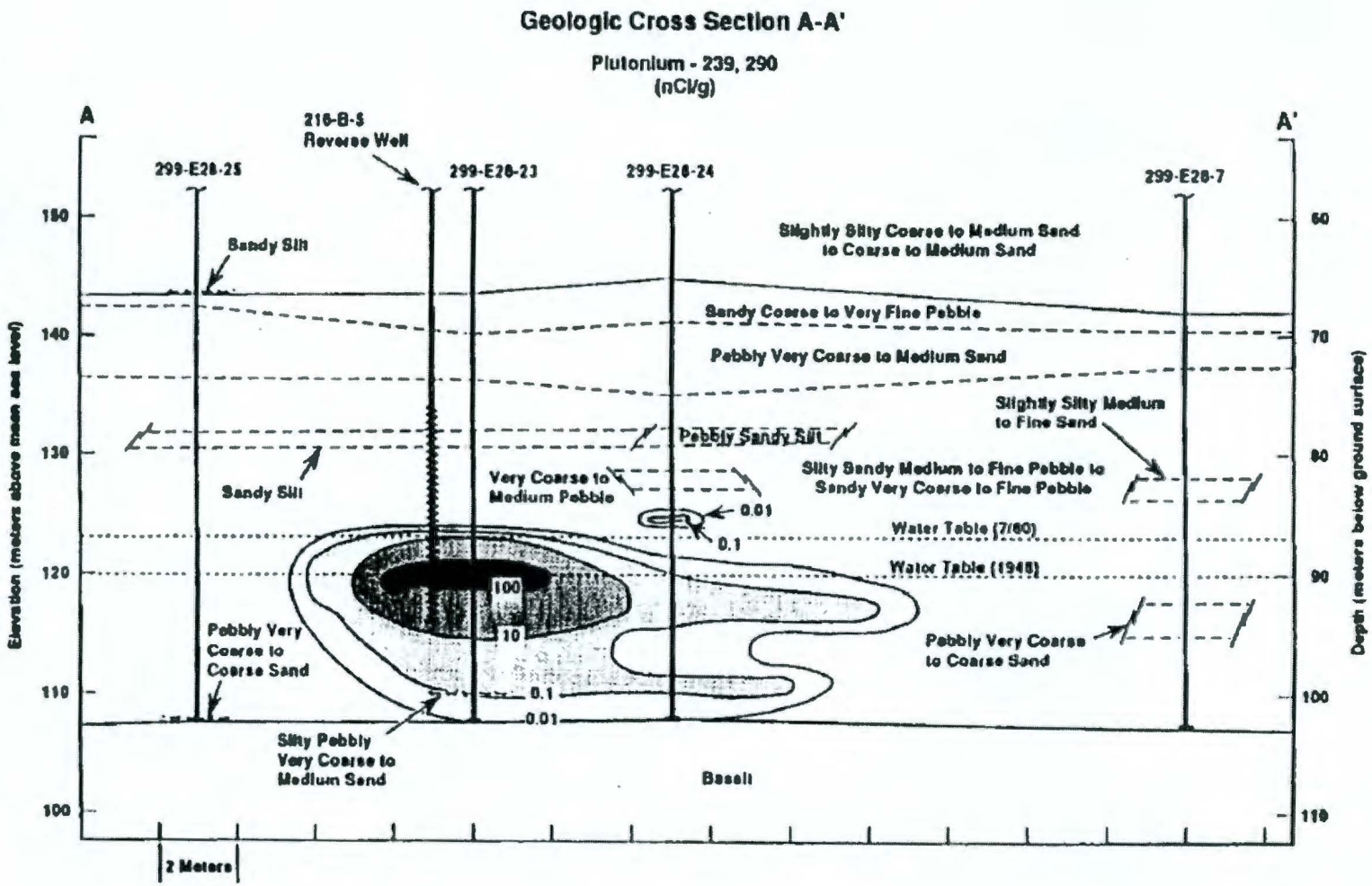

Figure 1-1. Cross-Section of Plutonium 239/240 Distribution in the vicinity of the 216-B-5 Reverse (Source: DOE/RL (1996), Figure F-4)

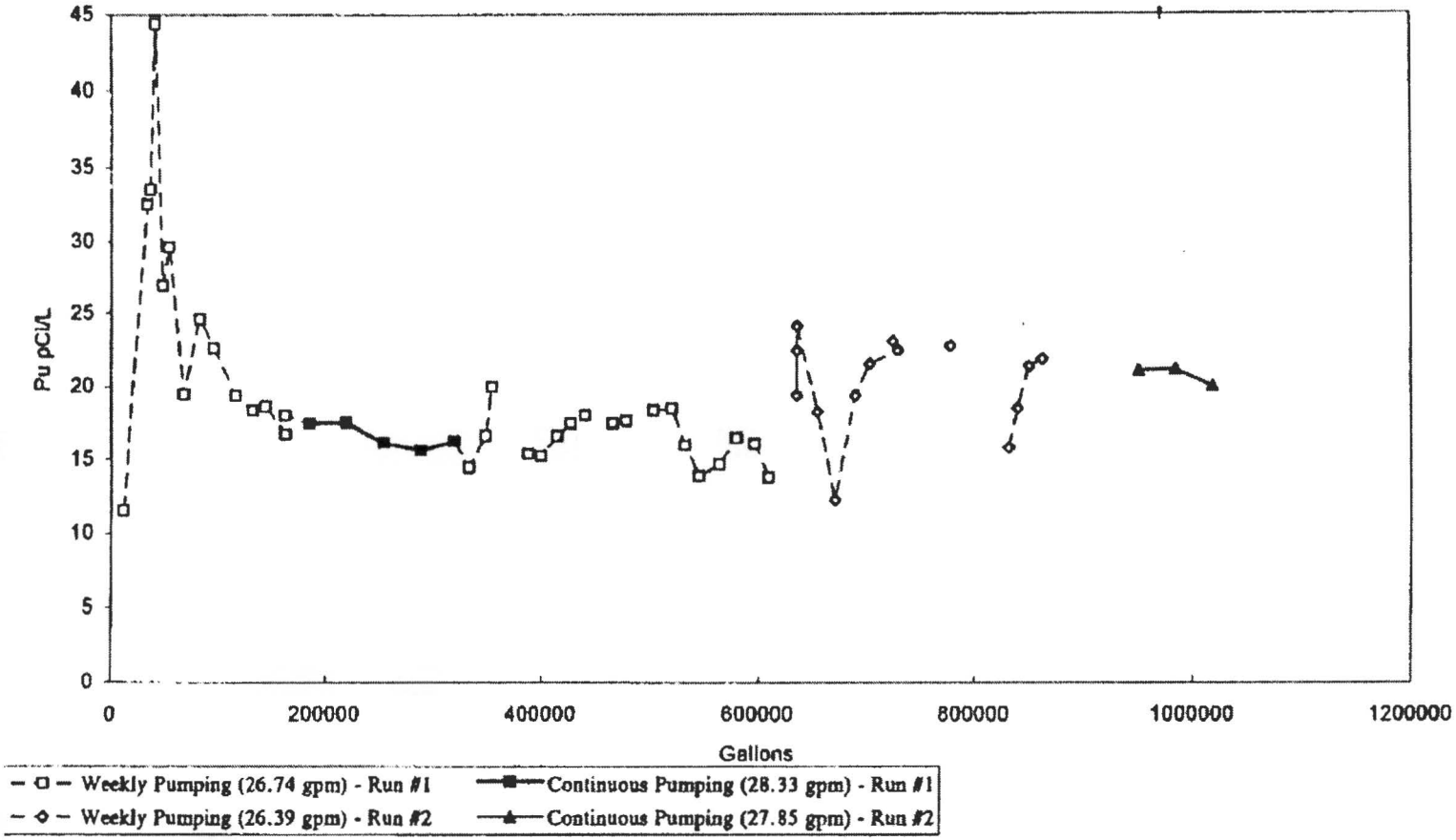

Figure 1-2. Plutonium 239/240 Extracted from 216-B-5 Reverse Well During Treatability Testing (Source: DOE/RL (1996), Figure 4-4)

References:

Brown, R.E. and H.G. Ruppert. 1950. The Underground Disposal of Liquid Wastes at the Hanford Works, Washington. HW-17088, General Electric Company, Hanford Atomic Products Operation, Richland, Washington.

DOE/RL. 1996. 200-BP-5 Operable Unit Treatability Test Report. DOE/RL-95-98 Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Smith, R.M. 1980. 216-B-5 Reverse Well Characterization Study. RHO-ST-37, Rockwell Hanford Operations, Richland, Washington.

2. Overview of historic groundwater monitoring results for plutonium

To support the response to the Oregon comments on plutonium mobility, DOE conducted a review of actual groundwater monitoring results for plutonium. Because of the very long history of operation, some extreme disposal practices and the very long history of groundwater monitoring, understanding actual field observations of groundwater concentrations provides the most direct insight into plutonium's mobility at Hanford. This section summarizes the key observations from DOE's re-look at this extensive base of data and observations.

It is estimated that more than 11,800 Ci of plutonium-239 have been disposed as liquid waste to the near surface environment at the Hanford Site (Cantrell 2009). Despite this quantity of plutonium-bearing waste disposed to the vadose zone at Hanford, only minuscule amounts have entered the groundwater. The Hanford Site maintains an extensive network of groundwater monitoring wells. These wells are routinely sampled for key contaminants of concern. For the reporting period covered by the Groundwater Monitoring Report for 2009 (DOE/RL 2010), "workers sampled 922 monitoring wells and 326 shoreline aquifer tubes to determine the distribution and movement of contaminants. Many of the wells and aquifer tubes were sampled multiple times during the reporting period. A total of 18,899 samples were analyzed for the reporting period" (October 1, 2008 – December 31, 2009). Groundwater monitoring has been a routine practice since the earliest days of Hanford operations and has continually been expanded and refined. Today, this enormous base of historical information provides a direct means of observing plutonium impacts on and mobility within Hanford groundwater.

A search of the Hanford Environmental Dashboard Application (http://environet.hanford.gov/eda/) for Pu-239/240 measurements in groundwater since 1984[1] showed 52 laboratory validated detections above 15 pCi/L. All of these measurements came from three wells located within a few meters of the 216-B-5 reverse well. The full set of measurements for these wells is shown below in Figure 2-1. Only one other well on site has historical measurements above 1 pCi/L (well 299-W15-8). This well is in the vicinity of the Z-9 trench and is also discussed below. This extensive body of data provides an essential resource for evaluating questions regarding plutonium mobility in the subsurface and groundwater at the Hanford Site.

[1] Prior to 1984 a variety of less sensitive analytical methods were used. Also, there was not consistency in looking for specific isotopes of plutonium versus total plutonium so comparison with earlier data is very difficult.

Early 1990s Groundwater Sampling Results for Plutonium

Because of concerns in the early 1990s about the potential for plutonium mobility in Hanford groundwater, an intensive survey of plutonium in groundwater was conducted. More than 3,600 groundwater samples from 475 different wells were analyzed for plutonium from 1990 -1994. Only 27 samples were found with concentrations above 1 pCi/L. Of these, 25 samples were from three wells in close proximity to the 216-B-5 reverse well and 2 samples were from one well in close proximity to the Z-9 Trench. (Source: http://environet.hanford.gov/eda/, laboratory validated detections).

The following statements are extracted from the 1991 annual groundwater monitoring report (PNL 1992) and are representative of the findings from this time period.

- From pp. 2.43 – 2.44: "A survey of plutonium in ground water was continued during 1991. The survey covered 132 wells including most of the usable wells in the 200 Areas and a few selected 600 Area wells. Concentrations of plutonium-239/240 were below the detection limit in all wells, except for one well located near the 216-B-5 Injection Well and one well in the 200-West Area near the 216-Z-9 Trench."
- From p. 2.46: "Plutonium-239/240 was detected for the first time in May 1990 in a well located in the 200-West Area (299-W15-8). That well monitors the 216-Z-9 Trench, which received a large burden of plutonium and americium from Z Plant liquid effluent streams....The well was resampled on November 14, 1991. Unfiltered, acidified samples were collected in the normal manner for transuranic analysis. In addition, a filtered acidified sample was collected for plutonium assay. The unfiltered samples confirmed the presence of plutonium-239/240 (1.9 pCi/L), plutonium-238 (0.03 pCi/L), and americium-241 (5.9 pCi/L). No plutonium was found in the filtered samples confirming that the transuranic fraction is associated with particulate material."

200-BP-5 Groundwater Operable Unit

The Groundwater Monitoring Report for 2009 (DOE/RL 2010, p. 4.0-17) states:

> "Only the three wells near the 216-B-5 injection well have continuously detected plutonium-239/240 over the years. The activities during this reporting period ranged between 0.64 and 42 pCi/L. Well 299-E28-23, located ~1 meter from the 216-B-5 injection well, had the highest concentration (42 pCi/L). Plutonium-239/240 is nearly immobile in the subsurface, as reflected by the stable low results in wells 299-E28-24 and 299-E28-25 (located ~5 to 7 meters from the 216-B-5 injection well)."

Figure 2-1 shows trend plots for Pu-239/240 concentrations for the three monitoring wells closest to the reverse well. While there have been a handful of measurements above 100 pCi/L in the early 1990s, more recent values have been fairly stable ranging from somewhat above the EPA maximum contaminant level (MCL), 15 pCi/L, to well below this level. Comparable plutonium measurements do not exist in wells beyond this immediate location as is shown in Figure 2-2.

200-ZP-1 Groundwater Operable Unit

Detectable plutonium concentrations in the 200-ZP-1 groundwater operable unit are much sparser than for 200-BP-5. Despite discharge of ~1.5 pore volumes of plutonium-containing liquid waste to the 216-Z-9 crib in the form of a highly acidic waste stream, detection of plutonium in the groundwater is limited to two observations in the 1990s that were well below the MCL – both occurred in well 299-W15-8, 8.27 pCi/L (5/7/1990) and 1.9 pCi/L (11/13/1991). Discharges to the Z-9 Trench took place over 7 years and the post-operational period of observation has now lasted for ~50 years. It is known that because of the high-discharge volumes to 216-Z-9, that plutonium migrated to the top of the Cold Creek Unit.

PNL (1994) discusses the observed low levels of plutonium detected in well 299-W15-8:

> "The origin of the TRU contaminants in the well is unclear. They may be associated with poor quality well completion and thus vary localized. The plutonium was associated only with unfiltered samples and was thus found to be in a relatively immobile form." (PNL 1994, p. 5.15)

The primary reason that disposal of plutonium-bearing waste has not resulted in widespread groundwater contamination is that under the typical oxidizing and neutral to slightly alkaline pH conditions of the Hanford vadose zone, transuranic radionuclides (plutonium and americium in particular) have a very low solubility and high affinity for surface adsorption to mineral surfaces common within the Hanford vadose zone (Cantrell 2009). In addition, the vadose zone is typically very thick (hundreds of feet in the central portion of the Hanford Site), and the recharge rate is very low due to the desert climate.

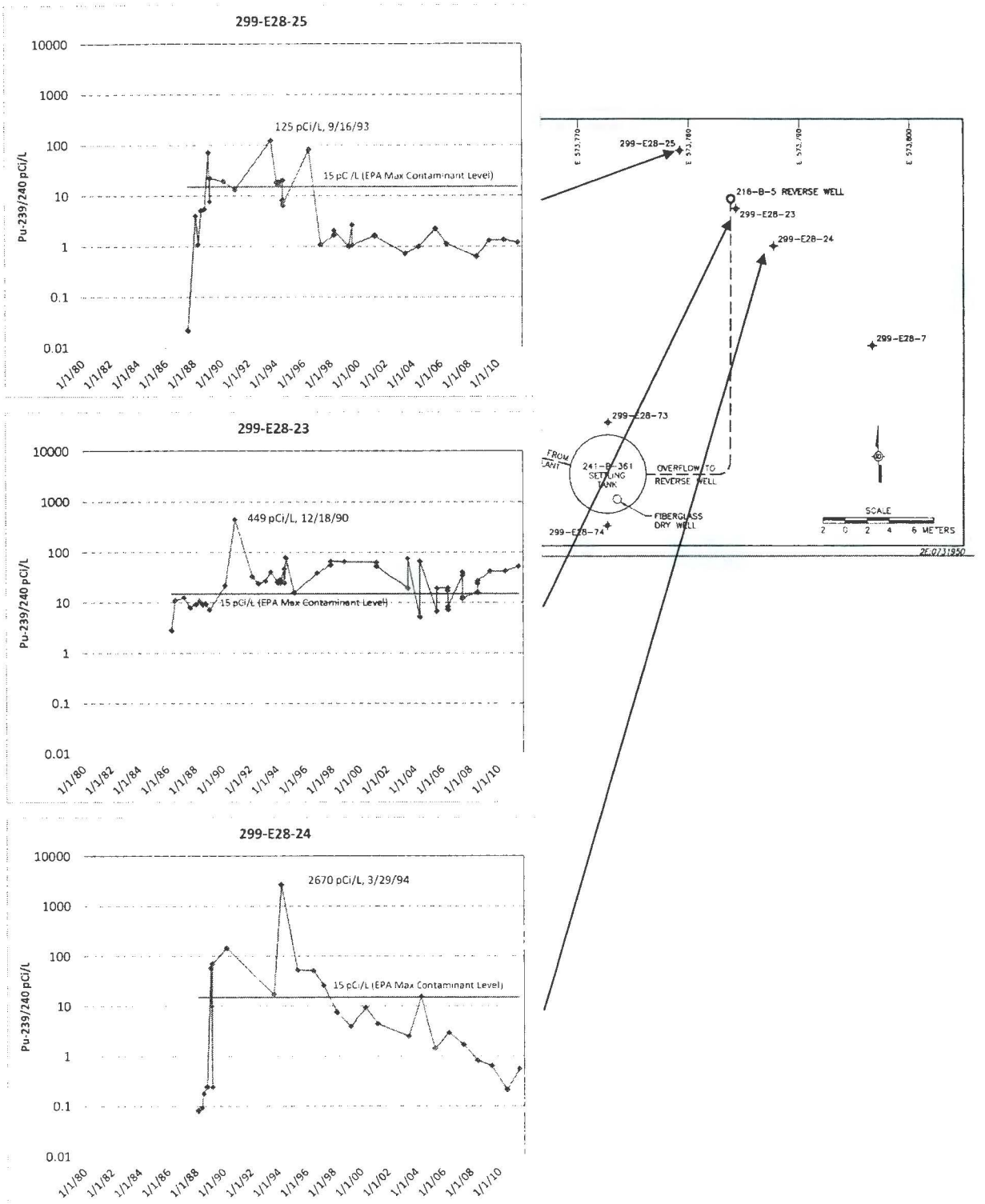

Figure 2-1. Trends in Plutonium Groundwater Concentrations near the 216-B-5 Reverse Well Injection Site, includes filtered and unfiltered samples (Source: Hanford Environmental Information System [HEIS] query, October 13, 2011)

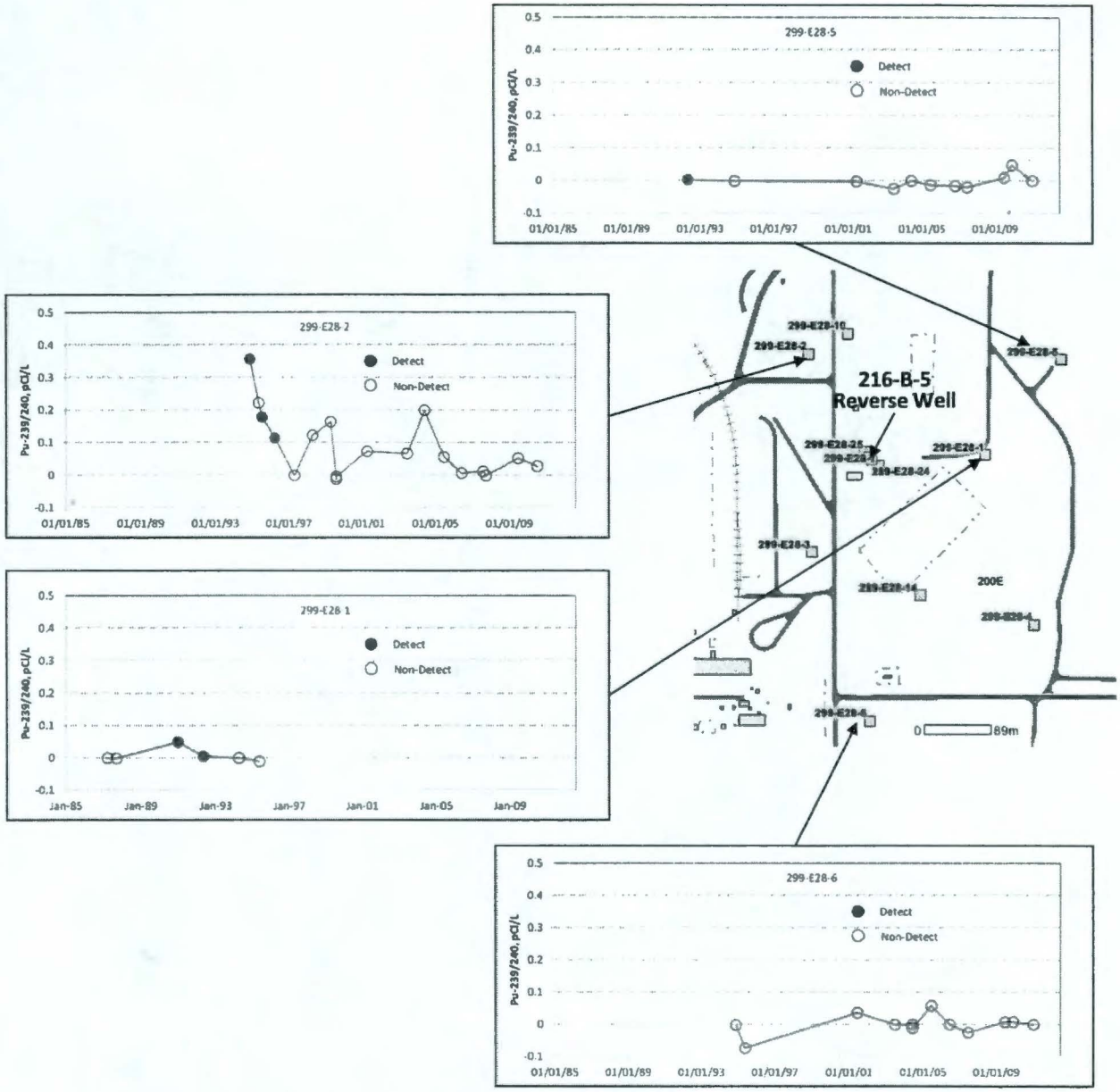

Figure 2-2. Trends in Plutonium Groundwater Concentrations in wells within ~200 meters of the 216-B-5 Reverse Well , includes filtered and unfiltered samples (Source: Hanford Environmental Information System [HEIS] query, October 13, 2011)

References:

Cantrell, KJ. 2009. Transuranic Contamination in Sediment and Groundwater at the U.S. DOE Hanford Site. PNNL-18640, Pacific Northwest National Laboratory, Richland, Washington.

DOE/RL. 2010. Hanford Site Groundwater Monitoring Report for 2009. DOE/RL-2010-11, Rev 1, U.S. Department of Energy, Richland, Washington.

PNL 1992. Hanford Site Ground-Water Monitoring for 1991. PNL-8284, Pacific Northwest Laboratory, Richland, Washington.

PNL. 1994. Hanford Site Ground-Water Monitoring for 1993. PNL-10082, Pacific Northwest Laboratory, Richland, Washington.

3. Synopsis and findings from supplemental analyses conducted on the 216-Z-9 waste samples

This section summarizes work from two PNNL reports: PNNL-SA-58953 (Cantrell and Riley 2008) and PNNL-17839 (Cantrell et al 2008). These documents augment the 200-PW-1/3/6 Remedial Investigation report (DOE/RL 2007). Cantrell and Riley (2008) provides: 1) a summary of the characterization data and studies of the Z-9 Trench, among other sites; conceptual models for plutonium transport at Z-9 for both the operational period and the post-operational period (about 45 years); and 2) a summary of data gaps and information needs that would improve our understanding of the past movement and current distribution of plutonium at this site. Cantrell et al (2008) describes the results of subsequent analytical tests that expand our understanding of this waste site. Summaries of the key observations and findings from these reports are provided below.

Under typical Hanford subsurface conditions, plutonium is observed to be highly immobile. This behavior is based on plutonium's very low solubility and tendency to sorp strongly to Hanford sediment under typical Hanford groundwater chemistry conditions. In contrast, remedial investigations conducted within the Hanford Site 200-PW-1/3/6 operable units have determined that, in one case (216-Z-9 Trench), significant Pu and Am have moved to depths of up to 120 ft below ground surface. To address this issue Cantrell and Riley (2008) conducted a review of the subsurface behavior of Pu and Am at the Hanford Site 200-PW-1/3/6 operable units. The 216-Z-9 Trench received a large inventory of Pu [1,880 Ci Pu-239, 3,273 Ci Pu (all isotopes)] and a high volume of carbon tetrachloride containing effluent (Cantrell 2009). A summary of what is known regarding the history, characterization work performed, and current distribution of contaminants at the 216-Z-9 Trench is provided below.

a. Background: 200-PW-1/3/6 Operable Units

The Plutonium/Organic-Rich Group Operable Unit (OU) waste sites are in the 200 East and 200 West Areas near the center of the Hanford Site. The Plutonium/Organic-Rich Group OU includes three OUs where liquid wastes were disposed of into cribs, French drains, trenches, an injection/reverse well, settling tanks, drain/tile fields, and at an unplanned release site. The three OUs are the 200-PW-1 OU, the 200-PW-3 OU, and the 200-PW-6 OU. The 200-PW-1 OU waste sites primarily received Pu- and organic-rich wastes (mostly carbon tetrachloride, tributyl phosphate [TBP], and lard oil) from processes within the Z Plant Complex (now referred to as

the Plutonium Finishing Plant [PFP] complex). The 200-PW-3 OU waste sites received organic-rich wastes (primarily refined kerosene [normal paraffin hydrocarbon (NPH)], TBP, and butanol) from the A Plant (Plutonium-Uranium Extraction [PUREX] process). The 200-PW-6 OU waste sites received Pu-rich wastes from the PFP complex but did not receive organic-rich wastes from that complex. Both the 200-PW-1 and 200-PW-6 OU waste sites are in the 200 West Area. The 200-PW-3 OU waste sites are n the 200 East Area.

Based upon analysis of the various sites within the 200-PW-1/3/6 OUs, it has been determined that the waste sites can be classified into two major categories based primarily upon the type of wastes that were received by the waste site. The first waste site category received low-salt near-neutral wastes. Plutonium and Am solubility in this type of waste is expected to be low and adsorption is expected to be high (Cantrell et al. 2003). Characterization results are consistent with these expectations (DOE/RL 2007). The second waste site group is categorized as acidic high-salt waste with organic complexants. Plutonium and americium solubility in this type of waste is expected to be relatively high, and adsorption is expected to be relatively low (Cantrell et al. 2003).

b. Plutonium and Americium Contamination at 216-Z-9 Trench

The 216-Z-9 Trench is located in the 200 West Area and consists of a 6 m (20-ft)-deep excavation with a 37- by 27-m (120- by 90-ft) concrete cover. The walls of the trench slope inward and downward to the 18- by 9-m (60- by 30-ft) floor space, which had a slight slope to the south. The underside of the concrete cover was paved with acid-resistant brick/tiles. The cover of the trench is supported by six concrete columns.

From July 1955 through June 1962, the 216-Z-9 Trench received solvent and aqueous wastes from the Recovery of Uranium and Plutonium by Extraction (RECUPLEX) process that operated in the 234-5Z Building (i.e., Z Plant). The two major liquid streams used in the RECUPLEX process were an aqueous stream composed of nitric and hydrofluoric acids to produce soluble plutonium as plutonium nitrate and an organic phase solvent extraction stream composed of carbon tetrachloride and TBP (85:15 ratio) or carbon tetrachloride and DBBP (50:50 ratio) to recover the plutonium or plutonium and americium from the aqueous streams. The process was used to recover plutonium from many different types of scrap or wastes, such as ingot and casing skulls (ingoting dross), slag, and crucible button line supernates. With exposure to ionizing radiation and nitric acid, the TBP in the solvent extraction stream gradually would degrade to dibutyl phosphate. Dibutyl phosphate DBP has a much greater affinity for plutonium than TBP and would not work in the process because of its poor stripping properties. The degraded solvent was periodically discharged batch-wise and replaced with fresh solvent. The DBBP solution was discharged after each use. The RECUPLEX waste solutions consisted of aluminum, magnesium, calcium, and other metal nitrate salt wastes; used solvents (15% TBP (i.e., a mixture of TBP and DBP) or 50% dibutybutyl phosphonate (DBBP) in CCl_4; other organic wastes such as solvent washings, fabrication oil (a mixture of lard oil and carbon tetrachloride (CCl_4) used as a cutting

oil during the machining of plutonium) (Ridgway et al., 1971), and other deteriorated materials from hood and equipment flushes.

The 216-Z-9 Trench received approximately 4.1 million L (1.1 Mgal) of high-salt, acidic, aqueous, and organic liquid waste from the RECUPLEX process. Material discharged to the trench reportedly included 50 to 140 kg Pu [3,600 to 11,000 Ci $^{239/240}$Pu (assuming 6% by wt. ^{240}Pu, DOE/DP 1996)], 8,580 Ci of ^{241}Am, 130,000 to 480,000 kg (286,600 to 1,058,219 lb) of carbon tetrachloride, 9,300 L lard oil, and 500,000 kg (1,102,310 lb) of nitrate (DOE/RL 1992).

In 1976 and 1977, and plutonium was removed from the upper 0.3 m (1 ft) of soil from the floor of the 216-Z-9 Trench. The mining operation removed an estimated 58 kg (128 lb) of plutonium, leaving an estimated 48 kg (106 lb) of plutonium in the trench (RHO 1978).

c. Historical Data

Samples were collected through the roof of the trench to a maximum depth of 3 m (9 ft) below the trench floor during 1959, 1961, and 1963 and analyzed for the presence of plutonium. Concern over the potential for the accumulation of a critical mass of plutonium on the floor of the trench prompted additional sampling through the trench roof during 1973. Both plutonium and americium were detected at relatively high concentrations across the 3 m profile. Samples from the bottom of the trench to 15 cm (6 in.) below the floor yielded ^{239}Pu concentrations of up to 1.2×10^{12} pCi/L (sediment) and americium-241 concentrations of up to 1.4×10^{11} pCi/L (sediment) were found within 15 cm (6 in.) of the trench bottom. At a depth of 3 m (9 ft), ^{239}Pu and ^{241}Am concentrations were 2.0×10^{9} pCi/L (sediment) and 1.4×10^{8} pCi/L (sediment), respectively. Soil pH was 4.1 at a depth of 2.4 m (8 ft) and generally acidic through the 3 m (9 ft) soil profile (ARH 1973). Based on these data, the uppermost 30 cm (12 in.) of the trench floor was excavated in 1976 (RHO 1978). See DOE/RL (2007, Section 2.1.3) for a discussion of results of the characterization performed during excavation.

Sediment core samples collected from within the 216-Z-9 Trench were examined by autoradiography and electron microprobe analysis (Price and Ames 1975). The results of these analyses indicated the presence of both particulate and dissolved plutonium. The particulate plutonium had a composition consisting of greater than 70% (wt %) PuO_2. This material was shown to be filtered out within the first meter underlying the trench profile, and accounting for the high concentrations of Pu in this area of the sediment profile. Dissolved Pu (disposed originally as dissolved Pu IV and less than 0.5 wt % PuO_2) penetrated deeper within the sediment profile and was deposited in association with acid induced silicate hydrolysis of the sediment minerals.

Between 1954 and 1967, nine wells were drilled around the 216-Z-9 Trench. Scintillation probe profiles were completed on each of the borings at least once between 1963 and 1970, and at least once more between 1973 and 1976. Radiological contamination was detected in two borings (wells 299-W15-8 and 299-W15-86) at a depth from 15.2 to 38.1 m (49.5 to 125 ft) bgs (see ARH 1977 for profiles).

Geophysical logging of well 299-W15-8 revealed ^{239}Pu from 15.1 to 32.3 m (50 to 106 ft) bgs. Maximum activity of 300,000 pCi/g was detected at 15.5 m [51 ft] bgs (WHC 1993). Low levels of Pu and Am were detected in groundwater from well 299-W15-8 on May 7, 1990, and November 13, 1991, before the groundwater table declined below the elevation of the bottom of the well and the well went dry.

d. 2004-2006 Characterization Studies: Wells 299-W15-46 (Borehole C3426) and 299-W15-48 (Borehole C3427)

In 2004-2006, well 299-W15-46 (Borehole C3426) and well 299-W15-48 (Borehole C3427) were drilled to better characterize the extent of contamination originating from 216-Z-9 Trench. Geophysical logging using the Spectral Gamma Logging System (SGLS) was performed during these drilling activities. The geophysical log data reports are included in Appendix E of WMP 2005 and Appendix D of WMP 2007. Sediment samples collected during the drilling of wells 299-W15-46 and 299-W15-48 at 216-Z-9 Trench were also analyzed for a variety of contaminants. Results of the analyses are tabulated in Appendix B of the RI report (DOE/RL 2007). Key findings are summarized below.

Logging Results Well 299-W15-46

^{239}Pu and ^{241}Am were detected in borehole well 299-W15-46 but not below 36.6 m (120 ft). Plutonium-239 was detected between 14.3 and 15.5 m (47 and 51 ft), with a maximum concentration of approximately 284,000 pCi/g at 14.6 m (48 ft). Plutonium-239 was detected almost continuously between 16.8 and 26.2 m (55 and 86 ft) at concentrations ranging from approximately 27,000 to 221,000 pCi/g; the maximum concentration was measured at 19.8 m (65 ft). Plutonium-239 also was detected at 33.5 and 35.4 m (110 and 116 ft) at concentrations of 41,000 and 58,000 pCi/g, respectively.

Americium-241 was detected from 14 to 18.6 m (46 to 61 ft), at concentrations ranging from 56,000 to 145,000 pCi/g. It also was detected almost continuously from 19.2 to 36 m (63 to 118 ft) at concentrations ranging from just above the minimum detectable level to approximately 20,000 to 400,000 pCi/g; the maximum concentration was measured at 35.4 m (116 ft).

The passive neutron detector indicated elevated count rates between 14 and 36 m (46 and 118 ft). The highest count rates (4 to 5 counts per second) were detected at approximately 14.6, 33.5, and 35.4 m (48, 110, and 116 ft). At these depths, ^{239}Pu and ^{241}Am also were detected.

Logging Results Well 299-W15-48

^{239}Pu and americium-241 were detected in well 299-W15-48. Plutonium-239 was generally detected between 15.5 and 37.2 m (51 and 122 ft) downhole (13.2 to 31.5 m or 43.3 to 103.5 ft vertical). The dominant interval was between 18.9 and 26.5 m (62 and 87 ft) downhole (16 to 22.5 m or 52.6 to 73.8 ft vertical) with a maximum concentration of approximately 657,000

pCi/g at 22 m (72 ft) downhole (18.6 m or 61.1 ft vertical). The maximum ^{240}Pu activity in this borehole was estimated to be ~40,000 pCi/g.

Americium-241 was detected from 15.5 to 37.2 m (51 to 122 ft) downhole (13.2 to 31.5 m or 43.3 to 103.5 ft vertical) at concentrations ranging from 40,000 to 245,000 pCi/g; the maximum concentration was measured at 36.9 m (121 ft) downhole (31.3 m or 102.6 ft vertical). Low energy gamma rays attributed to ^{241}Am were detected that normally would be severely attenuated by the 17/32-in.-thick steel and 1/4-in.-thick polyvinyl chloride casings in the borehole during the logging and by the borehole geophysical tool housing itself. The fact that these gamma rays consistently were detected indicated that the source most likely originates inside the steel casing as a result of internal contamination from the drilling/sampling process. The internal contamination extends at least from approximately 9.8 m (32 ft) downhole to the bottom of the borehole at 43.9 m (144 ft) downhole (8.3 to 37.2 m or 27.1 to 122.1 ft vertical). The effect of this internal contamination is to cause a slight overestimation of radionuclide concentrations.

The passive neutron detector indicated elevated count rates between 14.3 and 37.5 m (47 and 123 ft) downhole (12.2 to 31.8 m or 39.9 to 104.3 ft vertical). The highest count rates (4 counts per second) were detected where the highest ^{239}Pu concentrations are measured at approximately 19.2 m (63 ft) downhole (16.3 m or 53.4 ft vertical) and 21.3 m (70 ft) downhole (18.1 m or 59.4 ft vertical); at these depths, ^{241}Am also was detected. This count rate is considerably lower (4 vs. 2,600 counts per second) than observed in other PFP waste disposal sites such as the 216-Z-1A Tile Field and the 216-Z-12 Crib. This suggests that the plutonium compounds in the 216-Z-9 Trench are in the form of complexes with nitrates or oxides rather than fluorides, as postulated for the other PFP waste disposal sites. Fluorine has a cross section for capturing alpha particles that is 100 times greater than that for the other light elements.

Well 299-W15-46 Sediment Sample Characterization Results

Maximum concentration results for Pu, Am, and TBP and the lowest pH value, along with the depth interval for soil samples collected during the drilling of Well 299-W15-46 are presented in Table 4-1. It is notable that the highest $^{239/240}$Pu result is coincident with both the highest TBP result and the lowest pH value measured. This suggests that $^{239/240}$Pu may have migrated through the vadose zone to the observed depth relatively unimpeded along with the organic and/or acidic high salt aqueous waste streams.

Table 4-1. Maximum Concentration, and Depth Interval for $^{239/240}$Pu, ^{241}Am, TBP; and Lowest pH Value and Depth Interval, Well 299-W15-46 (Source: Cantrell and Riley [2008], Table A.1.)

Constituent or Parameter	Maximum Concentration	Depth Interval (ft bgs)	
		Top	Bottom
Plutonium-239/240	115,000 pCi/g	63.5	66
Americium-241	324,000 pCi/g	47.5	50

TBP	2,100 mg/kg	63.5	66
pH	3.9	63.5	66

Pu, Am, and TBP concentration data are plotted as a function of average core depth bgs in Figure 3-1. The bottom of a silt layer that occurs at about 65 feet bgs is indicated as well as the bottom of the Cold Creek unit at about 120 ft bgs. High concentrations of Pu, Am, and TBP occur at one location above the bottom of the silt layer indicating that Pu migrated with co-contaminants during the operational period. It also appears that this upper silt layer has prevented significant vertical migration of TBP, Pu and Am below this layer (i.e., the concentration of TBP, Pu and Am just below the silt layer are significantly lower than concentrations observed within the silt layer). The same argument would appear to hold for Am in the Cold Creek unit in the absence of Am concentration data below the Cold Creek unit. These results suggest that at this location, the silt layer and Cold Creek units are barriers to further vertical migration of Pu and Am.

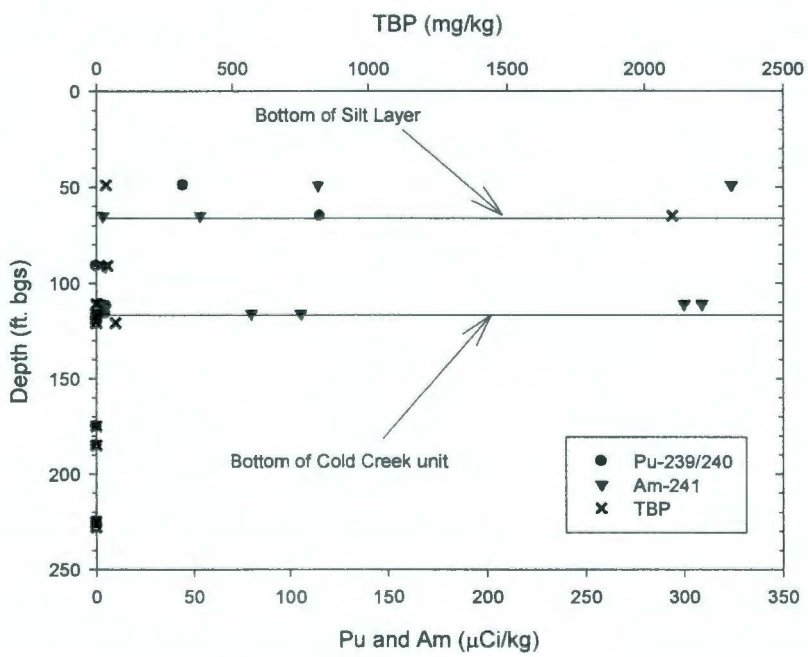

Figure 3-1. Pu, Am, and TBP Concentrations as a Function of Depth Measured in Soil Samples from Well 299-W15-46 (Source: Cantrell and Riley [2008], Figure A.2)

Pu, Am, and pH data as a function of average core depth bgs are shown in Figure 3-2. A number of low values of pH are indicated on this graph. A sample collected from the average core depth of 65 ft bgs has a particularly low pH value of 3.9. Other low values of 6.0 and 6.6 are located at average core depths of 111 ft bgs, and 49 ft bgs, respectively. These results suggest that significant impacts (e.g., loss of buffering capacity of the sediment) have occurred to sediment (e.g. the Hanford sands and gravels) underlying the 216-Z-9 Trench as a result of acidic high salt aqueous wastes. Impacts to the silt layer and Cold Creek unit have also occurred but apparently not sufficient to prevent attenuation of Pu and Am to occur in these layers. High concentrations

of Am occur above both the silt layer and the Cold Creek unit and at locations where values of pH are below neutral.

Nitrate data for Well 299-W15-46 as a function of average core depth bgs is shown in Figure 3-3. These data indicate that the acidic high salt wastes disposed to the Z-9 Trench traveled vertically down to the Cold Creek unit, where they encountered the calcium carbonate in the lower "caliche" layer. This layer appears to buffer the acidic waste and prevent significant further downward migration of the waste below the Cold Creek unit.

Well 299-W15-48 Sediment Sample Characterization Results

Maximum concentration results for Pu, Am, and TBP, along with the depth interval, for soil samples collected during the drilling of Well 299-W15-48 are presented in Table 4-2. No pH values are available for the Well 299-W15-48 soil samples. As was the case for Well 299-W15-46, data for Well 299-W15-48 indicate that the highest concentrations of Pu and TBP occur at the same depth indicating that Pu migrated with co-contaminants during the operational period.

Pu, Am, and TBP concentration data for Well 299-W15-48 as a function of average core depth below ground surface are shown in Figure 3-4. These data are consistent with that of Well 299-W15-46, indicating that vertical migration of TBP and associated Pu appears to have been slowed significantly (i.e., highly attenuated) within the silt layer located at about 65 feet bgs. Attenuation of some of the Am occurred in this layer. The acidic high salt component of the aqueous waste stream was able to breach this layer and continue its downward migration to the Cold Creek unit carrying with it Am and a small amount of the Pu in the waste. Am and a small amount of Pu showed attenuation within and at the bottom of the Cold Creek unit. Vertical migration of Pu and Am appears to have been stopped below the Cold Creek unit where Pu and Am concentration are low. This layer appears to have been effective at buffering the acidic waste (see Figure 3-2) coming into contact with this layer and preventing significant further downward migration of the waste below the Cold Creek unit. It is assumed that lateral spreading of the acidic waste occurred above the silt layer and the Cold Creek unit at this location.

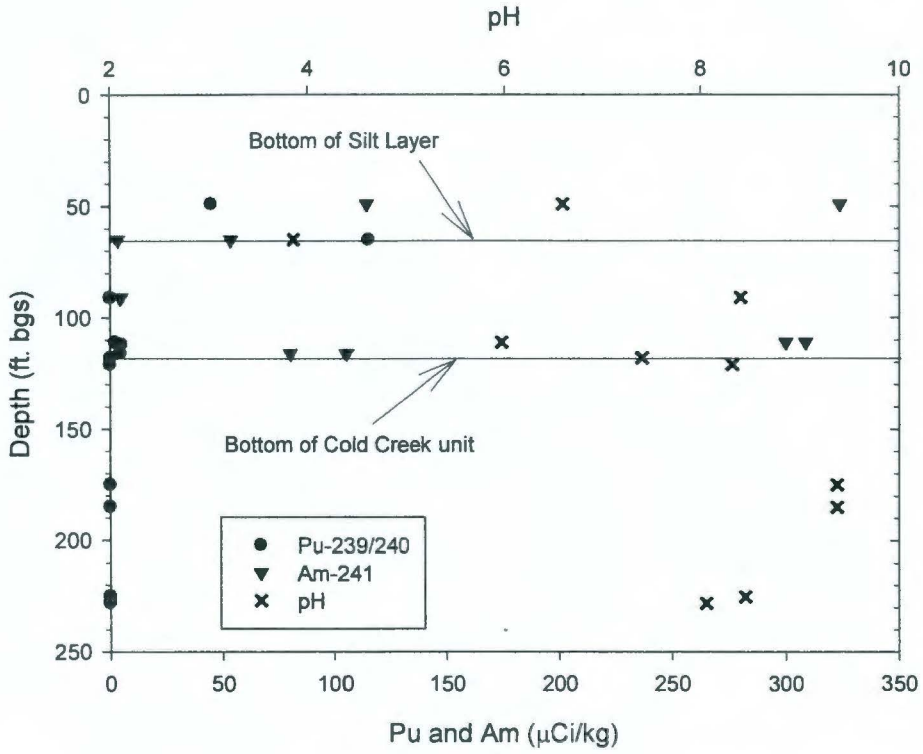

Figure 3-2. Pu, Am, and pH as a Function of Depth Measured in Soil Samples from Well 299-W15-46 (Source: Cantrell and Riley [2008], Figure A.3)

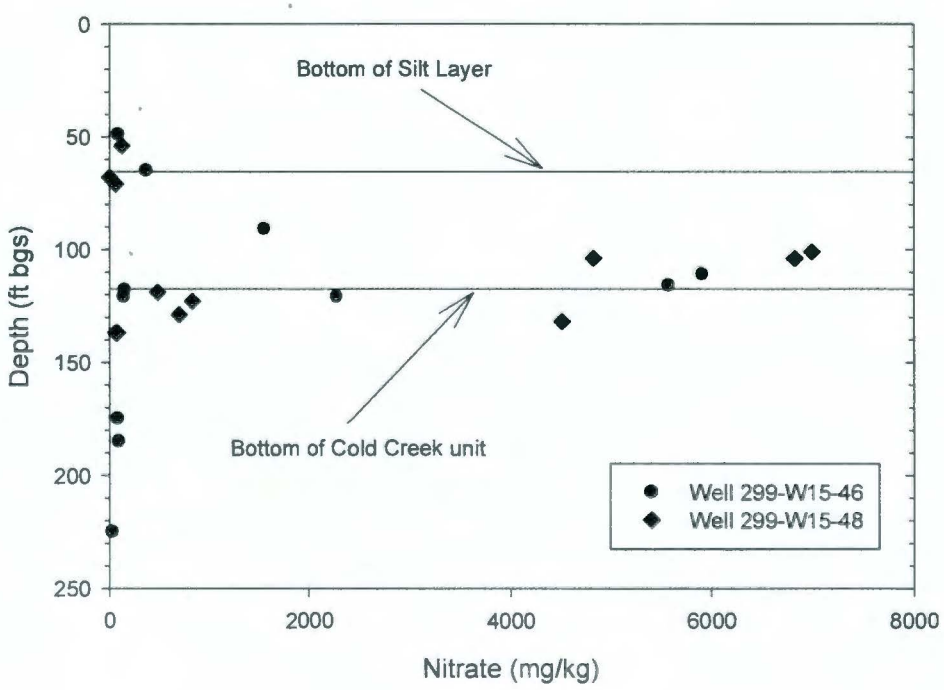

Figure 3-3. Nitrate Concentrations as a Function of Depth Measured in Soil Samples from Wells 299-W15-46 and 299-W15-48 (Source: Cantrell and Riley [2008], Figure A.4)

Table 4-2. Maximum Concentration, and Depth Interval for $^{239/240}Pu$, ^{241}Am, and TBP, Well 299-W15-48. (Source: Cantrell and Riley [2008], Table A.2)

Radionuclide Contaminant of Potential Concern	Maximum Concentration	Depth Interval (ft bgs)	
		Top	Bottom
Plutonium-239/240	254,000 pCi/g	70	72
Americium-241	131,000 pCi/g	118.5	120.5
TBP	3,000 mg/kg	70	72

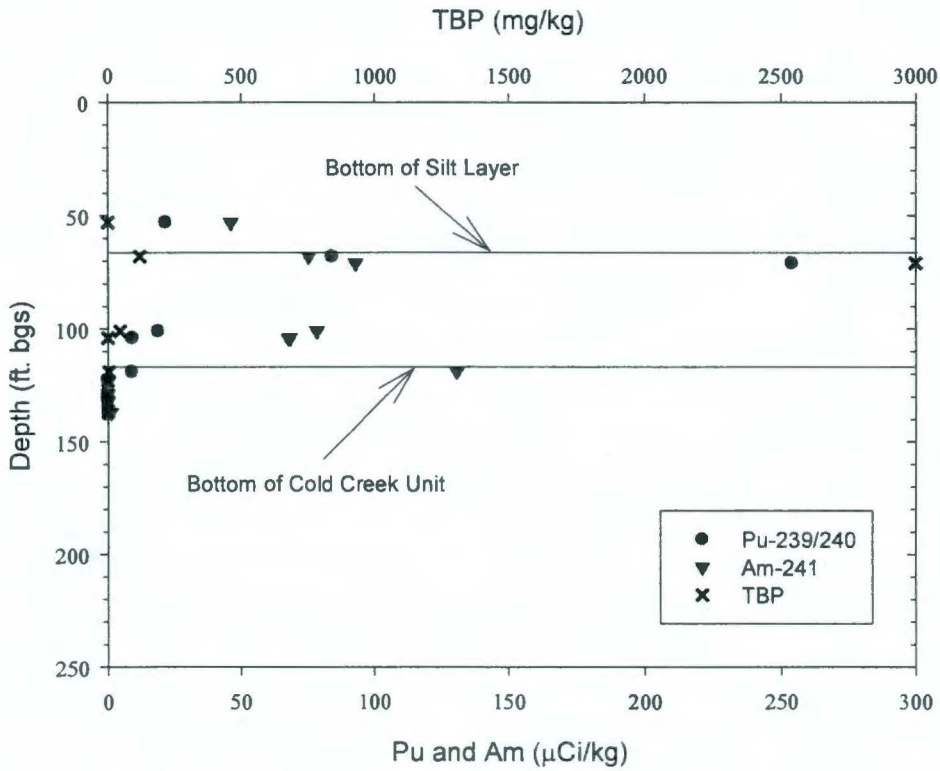

Figure 3-4. Pu, Am, and TBP Concentrations as a Function of Depth Measured in Soil Samples from Well 299-W15-48 (Source: Cantrell and Riley [2008], Figure A.5)

d. Summary of more recent plutonium mobility studies with 216-Z-9 trench samples

In 2008 a study was conducted on selected sediment samples collected from two wells (299-W15-46 and 299-W15-48) drilled near the 216-Z-9 Trench to elucidate the form and potential for plutonium and americium to be mobilized under present conditions, and in future

remediation scenarios (Cantrell et al. 2008). Analyses included moisture content, determination of the less than sand-size fraction (silt plus clay), carbon analysis, scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) analysis, microwave-assisted acid digestions for total element analysis, and extraction tests using Hanford Site groundwater as the leachate. The major findings of this study are indicated below.

- The highest concentrations of plutonium and americium were associated with sediments of low silt/clay content located above silt/clay rich layers within the sediment profile.

- Plutonium and americium were relatively enriched in the silt/clay portion of these samples

- SEM/EDS analysis indicated the plutonium and americium in these sediments does not occur as discrete micron-size particles.

- Release of plutonium and americium from the sediments correlates most significantly with the acidity of the water and not the initial concentrations of plutonium and americium in the sediments.

- Only extracts that were acidic after contact with the sediments (pH 4.3 to 5.4) contained detectable concentrations of extractable plutonium and americium.

- Water extracts from samples containing high concentrations of tributyl phosphate (TBP) indicate that if the TBP degradation products dibutyl phosphate (DBP) and monobutyl phosphate (MBP) are available in these sediments, they do not significantly increase the extractability of plutonium or americium.

- Geochemical modeling results indicate the americium concentrations in water in contact with these sediments is highly undersaturated with respect to $Am(OH)_3(c)$. It is likely that desorption of americium adsorbed to the sediments during the period of active waste water disposal is what controls americium concentrations in solutions in contact with these sediments.

- Sediment extracts that had measureable concentrations of americium only occurred in samples that were fairly acidic (pH 4.3 to 4.6), indicating that americium will remain effectively sequestered to sediments when pH conditions approach those of normal Hanford Site groundwater (mildly alkaline, ~ pH 8).

- The results of Neck et al. (2007a, 2007b) indicate that plutonium concentrations in solutions in contact with the 216-Z-9 Trench sediment samples might be controlled by a mixed valent solid phase $[(Pu^{V})_{2x}(Pu^{IV})_{1-2x}O_{2+x}(am)]$ with various dissolved Pu(V) complexes and $Pu(IV)O_2(am)$ colloids or nanoclusters being the dominant species in solution for typical Hanford Site groundwater conditions. Adsorption is likely to have a major impact on the potential for these species to be removed from solution. Recent TEM studies of upper sediments from the Z-9 Trench (personal communication, Andy Felmy to Kirk Cantrell, 10/18/2011) indicates the presence of Pu(IV) phosphates which could potentially control the solubility of Pu in water contacting these sediments.

- Both Pu(V) complexes and $Pu(IV)O_2(am)$ colloids or nanoclusters are well known for their high adsorption affinity for oxide and hydroxide mineral surfaces (Neck et al. 2007a, 2007b; Clark et al. 2006; Kaplan et al. 2006; Powell et al. 2005). As a result, these species are not likely to remain in solution as pH values approach those of typical Hanford Site groundwater (mildly alkaline, ~ pH 8).

e. Conclusions Regarding Pu Transport in the Subsurface at Hanford Based on Current State of Knowledge

Based upon the current state of knowledge of Pu transport in the subsurface environment at Hanford the following conclusions can be made. Under typical Hanford subsurface conditions [ground water dominated by Ca, Na, and HCO_3^-, at near neutral pH (~8), and oxidizing conditions] Pu is very insoluble and adsorbs strongly to Hanford sediments. At some waste sites at Hanford (200-PW-1/3/6 operable units) Pu and Am were co-disposed with large volumes of acidic high-salt wastes that contained organic complexants which resulted in significant transport through to vadose zone (up to 120 feet below ground surface). The significant transport of Pu and Am through the vadose zone was the result of the combination of high advective flux of the waste along with a high solubility and low sorption potential of Pu and Am associated with low pH solutions. Association with dissolved organic complexing agents such as DBP may have added to the high mobility of Pu and Am during the disposal phase of the site. In addition, it is possible that some fraction of the Pu that migrated through the vadose zone may have been in particulate form.

The limited studies that have been conducted to date with actual sediments collected beneath or near the 216-Z-9 Trench indicates that silt layers that occur at approximately 65 and 115 feet below ground surface significantly reduced the vertical advection of Pu, Am, and TBP and likely resulted in horizontal spreading of the waste components along the tops of these layers during active disposal. The studies also indicate that Pu and Am can only be mobilized from the 216-Z-9 contaminated sediments by pore-waters that remain acidic (pH 4.3 to 5.4) after contact with the sediments. Because an advective driving force is no longer present to transport the Pu and Am, further subsurface migration of Pu and Am does not appear to be likely.

Much speculation has occurred with regard to the role of nanoparticulate forms of Pu at Hanford. Although previous studies at Hanford have not specifically addressed this issue, the empirical experimental work conducted to date suggest that mobility of Pu will be limited to conditions which are relatively acidic, regardless of whether Pu occurs in the dissolved form or as nanoparticles.

References:

ARH. 1973. Nuclear Reactivity Evaluations of 216-Z-9 Enclosed Trench. ARH-2915, Atlantic Richfield Hanford Company, Richland, Washington.

ARH. 1977. Evaluation of Scintillation Probe Profiles from 200 Area Crib Monitoring Wells. ARH-ST-156, Atlantic Richfield Hanford Company, Richland, Washington.

Cantrell KJ, RJ Serne, and GV Last. 2003. Hanford Contaminant Distribution Coefficient Database and Users Guide. PNNL-13895, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

Cantrell KJ and RG Riley. 2008. A Review of Subsurface Behavior of Plutonium and Americium at the 200-PW-1/3/6 Operable Units. PNNL-SA-58953, Pacific Northwest National Laboratory, Richland, Washington.

Cantrell, KJ, KN Geiszler, and BW Arey. 2008. Plutonium Mobility Studies: 216-Z-9 Trench Sample Analysis Results. PNNL-17839, Pacific Northwest National Laboratory, Richland, Washington.

Clark DL, SS Hecker, GD Jarvinen and MP Neu. 2006. "Plutonium." Chapter 7 in The Chemistry of the Actinide and Transactinide Elements, 3rd ed., pp. 813-1264, eds LR Morss, NM Edelstein, J Fuger, and JJ Katz, Springer, Netherlands.

DOE/DP. 1996. Plutonium: The First 50 Years. DOE/DP-0137, U.S. Department of Energy, Washington D.C.

DOE/RL. 1992. Z Plant Source Aggregate Area Management Study Report. DOE/RL-91-58, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

DOE/RL. 2007. Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units. DOE/RL-2006-51, Rev. 0, prepared for the U.S. Department of Energy, Richland, Washington.

Kaplan DI, BA Powell, L Gumapas, JT Coates, RA Fjeld, and DP Diprete. 2006. "Influence of pH on Plutonium Desorption/Solubilization from Sediment." Environmental Science & Technology 40:5937-5942.

Neck V, M Altmaier, A Seibert, JI Yun, CM Marquardt and T Fanghänel. 2007a. "Solubility and Redox Reactions of Pu(IV) Hydrous Oxides: Evidence for the Formation of PuO2+x(s,hyd)." Radiochimica Acta 95:193-207.

Neck V, M Altmaier, and T Fanghänel. 2007b. "Solubility of Plutonium Hydroxides/Hydrous Oxides Under Reducing Conditions and in the Presence of Oxygen." Comptes rendus Chimie 10:959-977.

Price SM and LL Ames. 1975. "Characterization of Acinide-Bearing Sediments Underlying Liquid Waste Disposal Facilities at Hanford." ARH-SA-232, Atlantic Richfield Hanford Company, Richland, Washington.

Powell BA, RA Fjeld, DI Kaplan, JT Coates, and SM Serkiz. 2005. "Pu(V)O2+ Adsorption and Reduction by Synthetic Hematite and Goethite." Environmental Science & Technology 39:2107-2114.

RHO. 1978. Report on Plutonium Mining Activities at *216 Z 9 Enclosed Trench.* RHO-ST-21, Rockwell Hanford Operations, Richland, Washington.

Ridgway KR, MD Veatch and DT Crawley. 1971. 216-Z-9 Crib History and Safety Analysis. ARH- 2207, Atlantic Richfield Hanford Company, Richland, Washington.

WHC. 1993. Results of Spectral Gamma Ray Logging of Select Boreholes for the 200 Aggregate Area Management Study. WHC-SD-EN-TI-021, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

WMP. 2005. Borehole Summary Report for Well 299-W15-46 (C3426) Drilled at the 216-Z-9 Trench. WMP-26264, Rev. 0, Fluor Hanford, Inc., Richland, Washington.

WMP. 2007. Borehole Summary Report for Well 299-W15-48 (C3427) Drilled at the 216-Z-9 Trench. WMP-30566, Fluor Hanford, Inc., Richland, Washington.

4. Overview of Colloidal Transport Studies at the Hanford Site

Several recent studies of colloidal transport of radionuclide have been conducted (Cantrell and Riley 2008, p. 8, provides a listing of these sources). Most of these studies focus on colloidal transport of Cs-137. These studies indicate that colloidal transport of highly sorptive radionuclides is unlikely to be important at Hanford unless water contents and flow rates are locally and temporally increased by snowmelt or episodic artificial recharge. Some work has shown a significant decrease in colloid mobility at vadose zone saturation levels similar to Hanford sediments (i.e., ~6%). Additionally, both Pu(V) complexes and Pu(IV)O_2(am) colloids or nanoclusters are known for their adsorption affinity for oxide and hydroxide mineral surfaces. As a result, these species are not likely to remain in solution as pH values approach those of typical Hanford Site groundwater (mildly alkaline, ~pH 8).

One study has specifically addressed colloidal transport of plutonium in Hanford groundwater -- Dai et al (2005). A synopsis of this study is provided below. This work was supported by a grant from the DOE Environmental Management Science Program to Woods Hole Oceanographic Institution.

In addition to the published literature, there is an ongoing research effort supported by the Office of Science at PNNL that is examining the particle size distribution in upper and lower sediments associated with the Z-9 Trench. The spring meeting of the American Chemical Society will include a paper on this new work during a special symposium on colloid migration.

This publication is an essential reference for this discussion because it specifically investigates colloid-enhanced plutonium transport in Hanford groundwater. This study was undertaken in response to some of the literature cited in the Oregon comments that suggest colloids could facilitate subsurface transport of actinides. The following is a synopsis of this paper and its findings.

Dai et al (2005) examined the concentration, size distribution, redox state and isotopic composition of plutonium in groundwater at the 100-K Area. This area was chosen for study because of a significant leak event occurring from the KE spent fuel storage basin in the mid-1970s. Samples were collected from one upgradient and two downgradient wells. An ultra-sensitive sampling and analysis system was used that included cross flow ultrafiltration, redox speciation, and thermal ionization mass spectrometry techniques. These methods were able to detect concentrations of plutonium isotopes as low as 10^{-6} pCi/kg, substantially lower than more traditional alpha spectroscopy methods. The highest plutonium-239 concentration found was 0.0001 pCi/kg, more than ~10,000 times lower than the EPA drinking water standard (15 pCi/L).

For purposes of this study colloids were operationally defined as particles between 1 kDa – 0.2 μm in size. Analyses of samples from the two down-gradient wells suggest that 7 – 29% of the plutonium was associated with colloids. Plutonium in the colloid fraction was found to be "exclusively in the more reduced Pu(III/IV) form, consistent with the higher affinity of Pu in the lower oxidation states for particle surfaces." In comparing analytical results between the two down-gradient wells the researchers found more than an order of magnitude reduction in plutonium in the downstream well and a decrease in the colloid fraction from 13-19% near the source to 7-10% downstream. The authors conclude:

- "The results suggest that transport of Pu in association with groundwater colloids is not a substantial process."
- "There is no clear evidence for colloid facilitated transport of Pu in groundwater at the Hanford Site, since downstream wells have both an order of magnitude lower concentration of Pu and a lower fractional colloidal distribution."

References:

Cantrell KJ and RG Riley. 2008. A Review of Subsurface Behavior of Plutonium and Americium at the 200-PW-1/3/6 Operable Units. PNNL-SA-58953, Pacific Northwest National Laboratory, Richland, Washington.

Dai M, KO Buesseler, SM Pike. 2005. "Plutonium in Groundwater at the 100K-Area of the U.S. DOE Hanford Site." Journal of Contaminant Hydrology 79: 167-189.

5. Summary of on-going research related to plutonium mobility at Hanford supported by the DOE Office of Science

Recent studies of the chemical form of Pu in Hanford soils and sediments shows that the chemical form of Pu in Hanford sediments is more variable than just the expected PuO_{2+x}. The chemical form can vary from site to site depending upon the types of waste disposed and the chemical form can differ between surface sediments and deep subsurface sediments at the same site. The issue then is to understand how this type of variability in speciation is associated with possible subsurface transport. Further identification of the distribution of the chemical forms of Pu in the sediments will yield invaluable information on the possible subsurface transport mechanisms of Pu in the Hanford 200 West area.

Key scientific questions that still remain unresolved include:

- Current information indicates that the solid phase Pu in the subsurface is present as insoluble Pu(IV) compounds. Can possible changes in redox conditions alter these compounds to more soluble Pu(III) or Pu(V)?
- What is the role of nanoparticles or colloids in subsurface transport? How would the changing pH and other geochemical conditions impact their possible subsurface transport?
- What is the possible role of organic solvents in subsurface transport? Could nanoparticles or colloids be transported with the organic phase as well as in the aqueous phase?
- What is the impact of complexants on the transport of the transuranics? Are accurate thermodynamic data available to predict these effects?

Answers to these questions would go a long way to explaining the past transport of transuranics and greatly assist in predicting any future possible subsurface movement or transport.

In order to address these issues the DOE Office of Science is supporting research activities at multiple National Laboratories and Universities to help gain fundamental insight into these key issues in Pu chemistry. These activities are summarized below.

There are currently three main research programs working on Pu contamination issues at Hanford: The PNNL Science Focus Area (PNNL SFA) which includes collaborators at Los Alamos National Laboratory (LANL), the Transuranic Science Focus Area (TSFA) at Lawrence Livermore National Laboratory (LLNL), and project funded research at Clemson University. All three of these research programs are funded by the Office of Biological and Environmental Research (BER).

The Pu research in the PNNL SFA is focused on two activities 1) determining the chemical form of Pu in Hanford soils and sediments and 2) unraveling the fundamental mechanisms of electron transfer (i.e. oxidation/reduction) of Pu compounds. Determining the chemical form of Pu in the Hanford sediments is important in this research program since it provides information on the relevant Pu phases to study in the electron transfer research. Currently the chemical characterization studies are focused on sediments from the Z-9 site and to a lesser extent the Z-12 site. The electron transfer research is focused on the mechanism of reduction of PuO_{2+x} to Pu(III) by Fe(II). However, plans call for extending this research to other Pu containing phases identified in the Pu characterization studies.

Research in the TSFA at LLNL is focused on the environmental transport of Pu at ultra low concentrations which takes advantage of LLNL's highly accurate analytical instrumentation for detection and identifying transuranic species. The TSFA has several research objectives including examination of the role of natural organic matter, microbial interactions, and colloid interactions. One aspect of this program is studying field samples at Tomsk Russia, the Nevada Test Site and Hanford. The Hanford sediments were supplied by the PNNL SFA. LLNL has been able to find the Pu containing particles in the deep Hanford sediments (~64 feet and 77

feet) and completed an initial characterization. These detailed characterization studies of the Pu particles are on-going.

The research at Clemson is focused on the development of mechanistic models of Pu partitioning to sediments. The project is examining both model mineral systems (pure phases such as hematite) and subsurface sediments. The subsurface sediments have been obtained from the Savannah River site and from Hanford. The Hanford sediments were uncontaminated sediments from the 200 West area at the same depth as the silt layer that accumulates Pu at the Z-9 site. The Hanford sediments were supplied by the PNNL SFA. In developing their partitioning model the Clemson researchers (in collaboration with the University of Michigan and SRNL) are focusing on the more oxidized forms of Pu (i.e. Pu(IV) and Pu(V)).

Bibliography of Additional Hanford-Specific Publications

Colloid Transport Studies Specific to the Hanford Site

Chen G and M Flury. 2005. "Retention of mineral colloids in unsaturated porous media as related to their surface properties." Colloids Surface A: Physicochem. Eng. Aspects 256:207-216.

Chen G, M Flury, and JB Harsh. 2005. "Colloid-facilitated transport of cesium in variably saturated Hanford sediments." Environmental Science and Technology 39:3435-3442.

Cherrey KD, M Flury, and JB Harsh. 2003. "Nitrate and colloid transport through coarse Hanford sediments under steady state, variably saturated flow." Water Resources Research 39(6):1165-1174.

Czigany S., M Flury, and JB Harsh. 2005. "Colloid stability in vadose zone Hanford sediments." Environmental Science and Technology 39:1506-1512.

Dai M, KO Buesseler, and SM Pike. 2005. "Plutonium in groundwater at the 100K-Area of the U.S. DOE Hanford Site. Journal of Contaminant Hydrology *76:167-189.*

McGraw MA and DI Kaplan. 1997. Colloid Suspension Stability and Transport Through Unsaturated Porous Media. PNNL-11565, Pacific Northwest National Laboratory, Richland, Washington.

Zhuang J, M Flury, and Y Jin. 2003. "Colloid-facilitated Cs transport through water-saturated Hanford sediment and Ottawa sand." Environmental Science and Technology 37:4905-4911.

Zhuang, J., Y. Jin, and M. Flury. 2004. "Comparison of Hanford colloids and kaolinite transport in porous media." Vadose Zone Journal 3:395-402.

Recent Publications on Plutonium Chemistry

Felmy A. R., Moore D. A., Rosso K. M., Qafoku O., Rai D., Buck E. C., and Ilton E. S. (2011) Heterogeneous Reduction of PuO_2 with Fe(II): Importance of the Fe(III) Reaction Product. Environmental Science & Technology 45, 3952-3958.

Felmy AR, KJ Cantrell, and SD Conradson. 2010. "Plutonium Contamination Issues in Hanford Soils and Sediments: Discharges from the Z-Plant (PFP) Complex." Physics and Chemistry of the Earth 35(6-8):292-297.

Rai D, DA Moore, AR Felmy, KM Rosso, and H Bolton, Jr. 2010. "$PuPO_4$(cr, hyd.) Solubility Product and Pu^{3+} Complexes With Phosphate and Ethylenediaminetetraacetic Acid." Journal of Solution Chemistry 39(6):778-807.

Rai D, DA Moore, KM Rosso, AR Felmy, and H Bolton, Jr. 2008. "Environmental Mobility of Pu(IV) in the presence of ethylenediaminetetraacetic acid: Myth or Reality." Journal of Solution Chemistry 37(7):957-986.

Studies of Plutonium at Hanford

Cantrell KJ and RG Riley. 2008. A Review of Subsurface Behavior of Plutonium and Americium at the 200-PW-1/3/6 Operable Units. PNNL-SA-58953, Pacific Northwest National Laboratory, Richland, Washington.

Cantrell KJ and RG Riley. 2008. Subsurface Behavior of Plutonium and Americium at non-Hanford Sites and Relevance to Hanford. PNNL-17386, Pacific Northwest National Laboratory, Richland, Washington.

Cantrell, KJ, KN Geiszler, and BW Arey. 2008. Plutonium Mobility Studies: 216-Z-9 Trench Sample Analysis Results. PNNL-17839, Pacific Northwest National Laboratory, Richland, Washington.

Cantrell, KJ. 2009. Transuranic Contamination in Sediment and Groundwater at the U.S. DOE Hanford Site. PNNL-18640, Pacific Northwest National Laboratory, Richland, Washington.

DOE/RL. 1996. 200-BP-5 Operable Unit Treatability Test Report. DOE/RL-95-98 Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

DOE/RL. 2007. Remedial Investigation Report for the Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit: Includes the 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units. DOE/RL-2006-51, Rev. 0, prepared for the U.S. Department of Energy, Richland, Washington.