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Hexavalent Chromium Density Stratification Study, 100-D Area, Hanford Site, Washington

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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K. A. Ivarson
North Wind, Inc.

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Contents

1 Purpose **1**

2 Background **1**

3 Methodology **3**

3.1 Sampler Deployment, Retrieval and Analysis 5

3.2 Pump and Treat System Effects 6

4 Summary of Results **6**

5 References **10**

Figures

Figure 1. Kabis® depth-discrete sampler 2

Figure 2. Solinst Model 425 Discrete Groundwater Sampler 2

Figure 3. RPP Porous Polyethylene Cylinder 3

Figure 4. RPP Sampler with Polyethylene Mesh Tubing 3

Figure 5. RPP Passive Sampler deployment and Retrieval 4

Figure 6. Sample Deployment RPP Monitoring Well Locations at 100-D 5

Figure 7. Vertical Distribution Profiles of Cr(VI) in Well 199-D5-99. 8

Figure 8. Hexavalent Chromium and Groundwater Elevation Time Series in Well 199-D5-99 9

Tables

Table 1. Summary of Vertical Cr(VI) Distribution Results for Selected Wells at 100-D Area 7

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1 Purpose

Prior to the startup of the 100-DX pump and treat system, hexavalent chromium [Cr(VI)] was present at 100-D in the unconfined aquifer at concentrations up to 69,700 µg/L (DOE/RL-2011-118). While these concentrations have decreased since the startup of the 100-DX system, they remain the highest concentrations of Cr(VI) in groundwater (27,900 µg/L in February 2011) at the Hanford Site (DOE/RL-2011-118). The nature, extent, and sources of Cr(VI) contamination at 100-D are detailed in the *Remedial Investigation/Feasibility Study For The 100-DR-1, 100-DR-2, 100-HR-1, 100-HR-2, And l00-HR-3 Operable Units*, DOE/RL-2010-95, Draft A. The area of high-concentration Cr(VI) contamination in groundwater at 100-D is related to the handling of large volumes of highly-concentrated sodium dichromate solutions used as a corrosion inhibitor in reactor cooling water (DOE/RL-2010-95, Draft A).

The geology of the area and depressions observed in the surface of the Ringold Formation upper mud (RUM), which forms the bottom of the unconfined aquifer, supported a hypothesis that concentrated solutions of sodium dichromate (i.e., a dense brine) spilled in the soil column may have stratified in the groundwater after reaching the aquifer. This hypothesis suggested a dense phase brine containing very high concentration Cr(VI) may lie at the bottom of the aquifer acting as a secondary source for the southern 100-D "hot spot." To test this hypothesis, a series of vertical distribution samples were collected from selected wells at 100-D Area and analyzed for Cr(VI). This included evaluation of groundwater grab samples collected during drilling and vertical profile samples of groundwater collected using two methods of collecting discrete vertical samples from existing wells.

This document summarizes the sampling and analysis effort in 2010 and 2011 and presents the conclusion that conditions observed do not indicate the presence of a dense sodium dichromate source located deep within the shallow unconfined aquifer. The conditions are, instead, consistent with continuing releases of Cr(VI) from secondary sources within the overlying vadose zone and periodically-rewetted zone at historical release points (DOE/RL-2010-95, Draft A) and some geologic heterogeneity within the aquifer.

2 Background

In April 2007, March 2008, and June 2008 investigations were conducted at 100-D to evaluate the vertical stratification of Cr(VI) contamination. These investigations used depth-discrete sampling (DOE/RL-2009-92, Rev. 1). Six of the wells in the project area were sampled at multiple depths with a Kabis® depth-discrete sampler after well completion in Fiscal Year 2007 (FY07) to develop vertical profiles of hexavalent chromium concentrations (DOE/RL-2009-92).

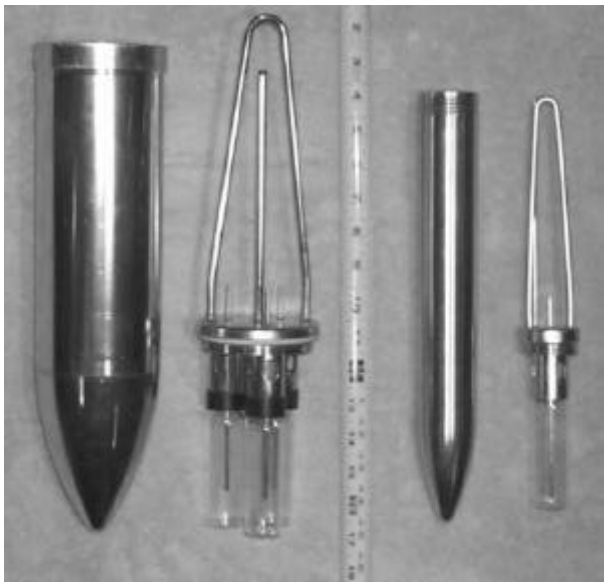

Figure 1. Kabis® depth-discrete sampler

Review of these results raised questions about the representativeness of the data, specifically the potential displacement of the water column by the sampler, which could cause vertical mixing of groundwater in the well.

In FY08, a small-diameter sampler (Solinst® Model 425, see Figure 2) was used to sample seven wells, which resulted in more representative results (DOE/RL-2009-92). The results of the 2008 depth-discrete sampling events showed minimal vertical variation of Cr(VI) in the aquifer, indicating that Cr(VI) is not significantly more concentrated near the top of the water column in wells with high-concentrations of Cr(VI).

Figure 2. Solinst Model 425 Discrete Groundwater Sampler

3 Methodology

Sampling devices used in this study were chosen to minimize or eliminate the possibility of disturbing the hydraulic regime, specifically to avoid mixing any chemical stratification that exists in the well. The selected samplers were diffusion-type devices made of rigid porous polyethylene (RPP) from Columbia Analytical Services. Each of the RPP samplers is a 12.7cm-long (5 inch) by 1.9cm-outer diameter (1.5 inch) porous polyethylene cylinder with a non-porous Delrin® bottom plug and a red non-porous polyethylene top cap (see Figure 3).

Figure 3. RPP Porous Polyethylene Cylinder

The RPP sampler contains approximately 100mL of deionized water. While the sampler is deployed at a discrete depth, pores in the polyethylene (6-20 micron pore size) allow water-soluble analytes in the aquifer to diffuse through the porous walls of the sampler and equilibrate with the water inside.

Each RPP sampler was secured in polyethylene mesh tubing to allow the attachment of the sampler on a cable via clamps (see Figure 4).

Figure 4. RPP Sampler with Polyethylene Mesh Tubing

The RPP sampler(s) were attached to a weighted nylon-coated stainless steel cable suspended from the top of the inner well casing by threading the cable through holes in a circular plastic disk and securing the cable (see Figure 5).

Figure 5. RPP Passive Sampler deployment and Retrieval

This disk rests on the top of the inner well casing and positions the cable in the center of the casing with the clamps at specified depths. Nylon cable ties were threaded through the polyethylene mesh to attach the RPP sampler to clamps on the cable. The clamps were positioned to place the RPP sampler(s) at specific depths in the water column. Borehole logs and recent depth to water measurements were used to position the clamps and the plastic discs on each deployment cable before going into the field.

Sixteen RPP samplers were deployed in monitoring wells 199-D5-99, 199-D5-122, 199-D5-126, and 699-97-45. Well locations are shown in Figure 6 with the Cr(VI) plume at low river stage in 2011. All four of these wells were constructed with continuous screened intervals over the full thickness of the shallow unconfined aquifer overlying the Ringold Formation upper mud unit (RUM).

Four samplers were used per well to evaluate the vertical stratification of Cr(VI) within the unconfined aquifer. Section 3.1 discusses RPP deployment, retrieval, sample collection, and analysis procedures. Samplers were left in each well to equilibrate with the surrounding groundwater for a minimum of fourteen days.

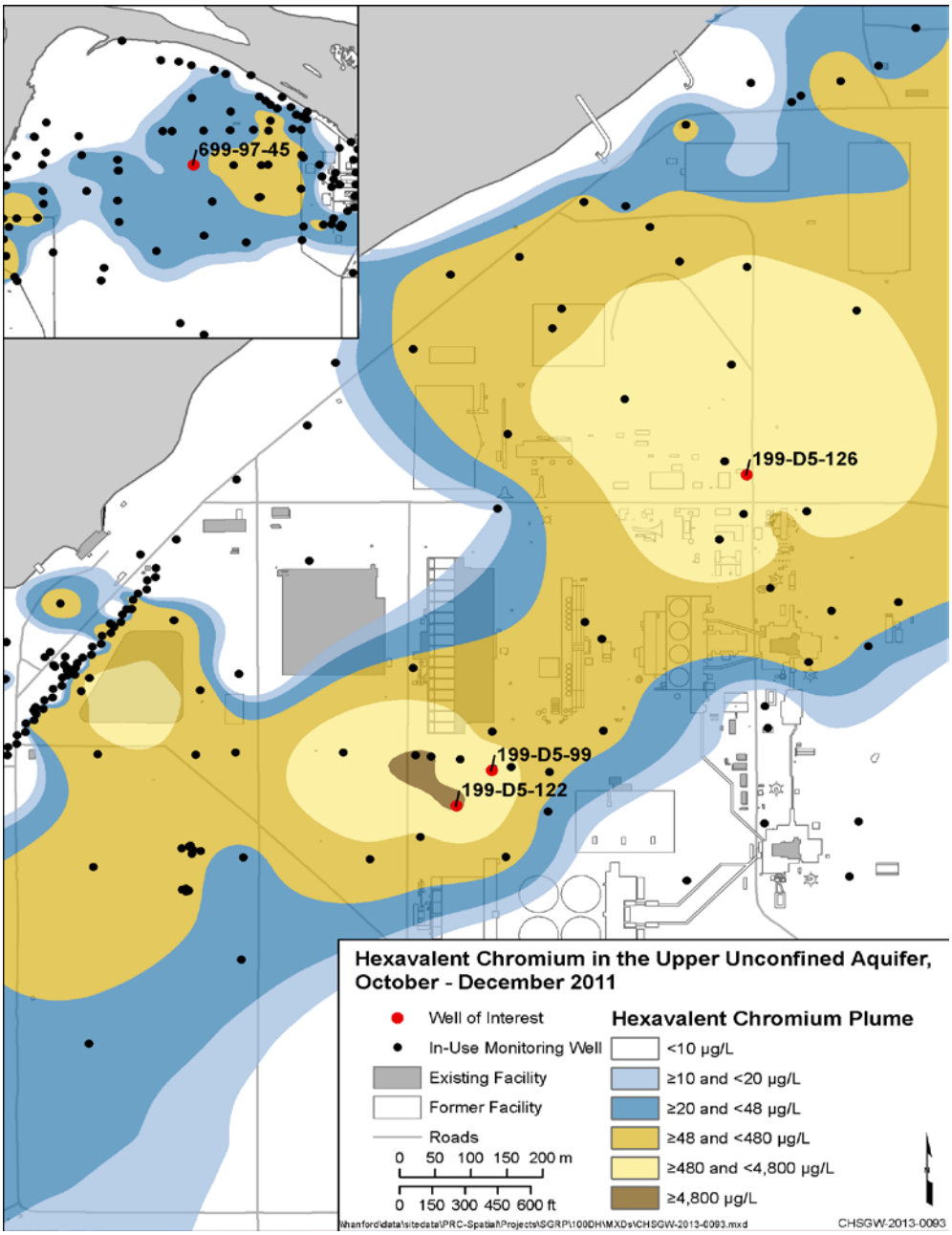

Figure 6. Sample Deployment RPP Monitoring Well Locations at 100-D

3.1 Sampler Deployment, Retrieval and Analysis

The first sampling string was installed in well 199-D5-99 on December 17, 2010. The remaining samplers were installed on December 29, 2010, in wells 199-D5-122, 199-D5-126, and 699-97-45.

The depth interval of each RPP sampler was based on location of the water table and RUM surface as measured in each well. The depth to water was measured with an E-tape and the sample intervals for each RPP were adjusted by moving the cable clamps as necessary. The samplers were placed in the following locations in each well:

- At two feet below the water table
- In an area near a silt layer, if present according to borehole logs
- At a depth three feet above the RUM surface
- At the RUM surface.

Signs were attached to each of the four wells to notify personnel that a study was being performed on the well and it was not to be disturbed. The RPP samplers were retrieved after the minimum 14-day period. Dates of recovery are noted on Table 1. The retrieval process involved carefully pulling the cable up from each well and detaching the RPP samplers one at a time. Sample collection was conducted in accordance with EPA SW-846 Method 7196. All sampling quality assurance/quality control procedures were followed and the samples were transported to the Waste Sampling and Characterization Facility for analysis within the 24-hour holding period.

3.2 Pump and Treat System Effects

The DR-5 pump-and-treat (P&T) system operated within the 100-D Area to treat Cr(VI) in groundwater from the unconfined aquifer from December 28, 2004 until April 19, 2011. Some of these wells are in the vicinity of this study, so the potential for their hydraulic influence was appraised.

In the last configuration before it was shut down, the DR-5 system operated with five extraction wells (199-D5-20, 199-D5-32, 199-D5-39, 199-D5-92, and 199-D5-104) and two injection wells (199-D5-41 and 199-D5-42). Extraction wells 199-D5-39 and 199-D5-104 are located downgradient of the southern plume hot spot, approximately 210 and 85 m, respectively, from waste site 100-D-12. Injection well 199-D5-42 is located approximately 255 m cross-gradient to 100-D-12. Before this sampling study began, approximately 8 gallons per minute (gpm) was being extracted from well 199-D5-39. Extraction well 199-D5-104 was offline from December 17, 2010 to January 31, 2011; before going off-line approximately 4 gpm was being extracted from this well. The injection well received treated water at a rate of approximately 13.5 gpm.

It is unlikely that DR-5 pump and treat operations impacted the results of this study, since the operating wells were over 200 m away from the study site and the only nearby extraction well, 199-D5-104, was offline during the experiment.

4 Summary of Results

Sixteen groundwater samples collected using the RPP samplers were analyzed for Cr(VI). The results are summarized in Table 1. While Cr(VI) concentrations appear to fluctuate with depth, no consistent pattern was identified. The largest ranges in vertical Cr(VI) distribution were observed in wells 199-D5-99 (which exhibited the highest concentration in the deepest sample) and 199-D5-122 (which exhibited the lowest concentration in the uppermost sample).

Although these wells did exhibit depth-varying Cr(VI) concentrations, the magnitude of the concentrations are consistent with routine monitoring results. The highest concentrations observed are more than four orders of magnitude smaller than the concentration expected of a sodium dichromate dense brine solution. The changes in concentration over time and depth are consistent with seasonal variability associated with plume migration and potential contributions from secondary sources within the vadose or periodically-rewetted zone near these wells.

Table 1. Summary of Vertical Cr(VI) Distribution Results for Selected Wells at 100-D Area.

Well Name	Date Samplers Installed	Date Sample Analyzed	Depth below TOC m (ft)	Cr(VI) Concentration (µg/L)
199-D5-99	12/29/2010	1/17/2011	27.36 (89.76)	1440
			29.64 (97.24)	1460
			33.30 (109.25)	1490
			34.37 (112.76)	9960
199-D5-122	12/17/2010	1/17/2011	27.20 (89.24)	6590
			29.64 (97.24)	25700
			32.54 (106.76)	26200
			33.45 ((109.74)	26900
199-D5-126	12/29/2010	1/31/2011	27.13 (89.01)	1510
			29.57 (97.01)	1510
			33.22 (108.99)	1520
			34.14 (112.01)	1510
699-97-45	12/29/2010	1/31/2011	9.75 (31.99)	53.9
			9.91 (32.51)	53.2
			11.09 (36.38)	55.6
			12.01 (39.40)	24.1

Figure 7 illustrates the observed variations in the vertical distribution of Cr(VI) in Well 199-D5-99. The figure includes a plot of all vertical Cr(VI) distribution measurements taken. This includes the results of grab samples collected during drilling, samples with the Kabis® device, and diffusion sampler results discussed above. The results of the routine groundwater monitoring analyses for samples collected at times close to the vertical samples are also posted in Figure 7. The observed values range from the lowest concentrations measured in the January 2011 vertical profile samples (i.e., 1,400 µg/L to 9,960 µg/L as shown in Table 1), to the highest concentrations measured in March 2008, when both the vertical distribution samples and the routine monitoring sample exhibited Cr(VI) at about 30,000 µg/L.

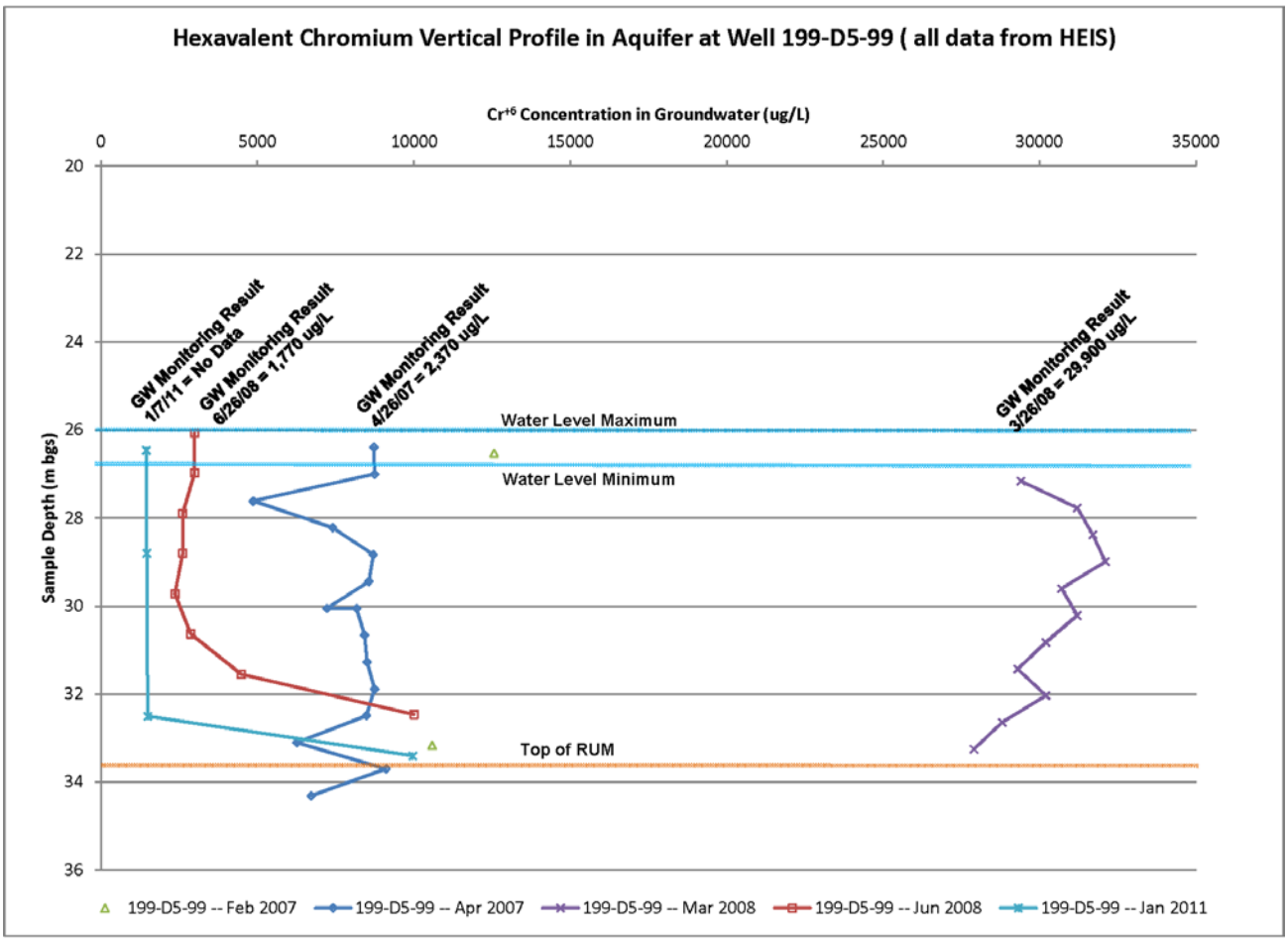

Figure 7. Vertical Distribution Profiles of Cr(VI) in Well 199-D5-99.

Figure 8 illustrates the Cr(VI) concentration as a function of time in Well 199-D5-99; the dates of the vertical profile samples are indicated in the graph. The Cr(VI) concentration observed in the well exhibits an inverse relationship with groundwater elevation (i.e., lowest concentrations are associated with the highest head and vice versa). This condition is observed at other locations where wells are closely downgradient from contaminant sources. This pattern is inferred to represent the following condition:

1. Water level rises seasonally as groundwater elevation equilibrates to the rising stage of the nearby Columbia River. At this time, the overall groundwater gradient decreases, with slowing of the groundwater flow toward the river.

2. Groundwater near the well, and in the vicinity of a secondary contaminant source within the periodically-rewetted zone, rises into the secondary source material. The contaminant concentration in groundwater at the source area increases dramatically.

3. As the river stage decreases over the fall and winter, groundwater elevation declines and the gradient increases toward the river. The groundwater beneath the source area now contains a freshly-elevated concentration of Cr(VI) after its contact with the overlying contamination.

4. The accelerated flow subsequently brings the water (exhibiting the newly elevated concentration of Cr(VI) to the downgradient monitoring well (in this instance 199-D5-99), resulting in the transient concentration peaks exhibited during the period of low water.

5. It is hypothesized this cycle occurs when the groundwater enters the contaminated rewetted zone, which is likely encountered at a specific elevation. Seasonal changes that produce lower groundwater elevations may not result in such dramatic concentration transients. This condition is illustrated by the substantially smaller concentration transient peak following the lowest groundwater elevation peaks in this dataset (i.e., 22 July 2009 and 13 August 2010).

6. These observations are consistent with episodic releases from the overlying vadose zone.

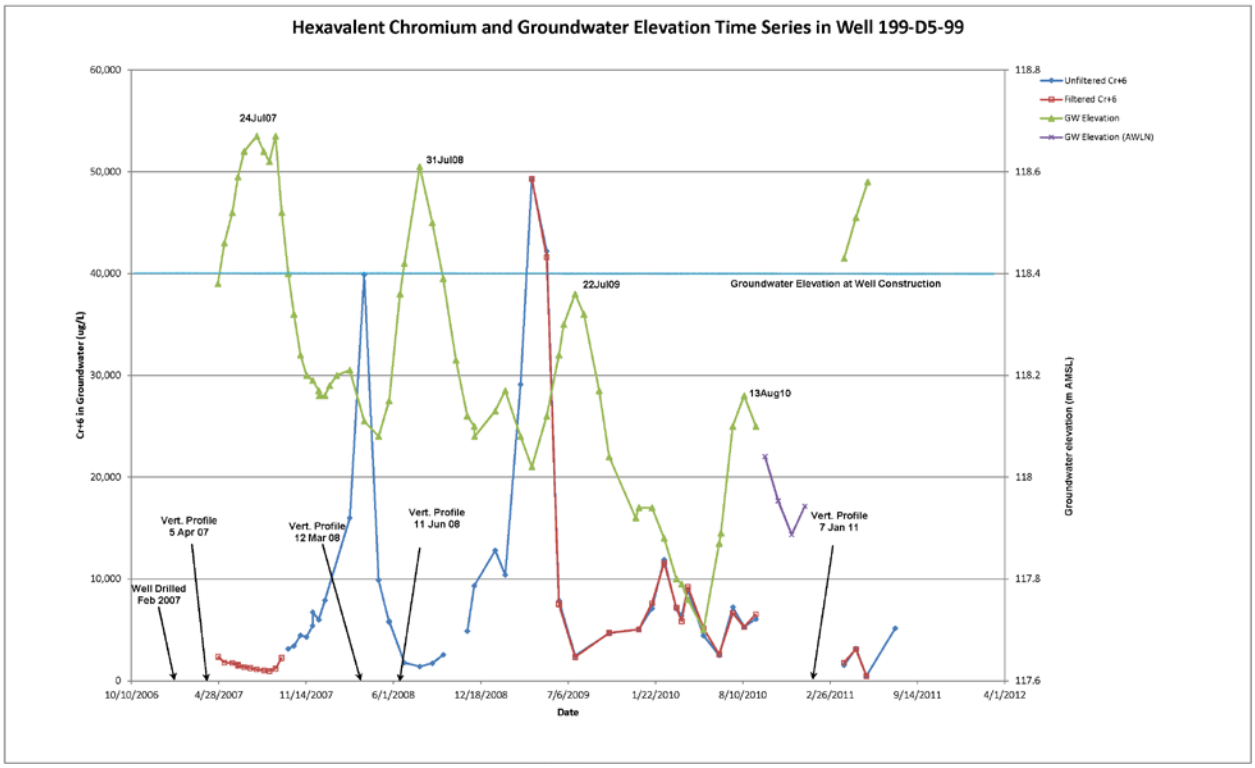

Figure 8. Hexavalent Chromium and Groundwater Elevation Time Series in Well 199-D5-99

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