2.5 100-HR-3-D Operable Unit

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The scope of this section is the 100-HR-3-D groundwater interest area that occupies the west half of the 100-HR-3 Operable Unit (see Figure 2.1-1 in Section 2.1). The Groundwater Performance Assessment Project (groundwater project) defined the "interest areas" informally to facilitate scheduling, data review, and interpretation. Figures 2.5-1 and 2.5-2 show facilities, wells, and shoreline monitoring sites in this region. Hexavalent chromium is the contaminant of greatest significance in groundwater. Groundwater is monitored to assess the performance of two *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA) interim actions for chromium: a pump-and-treat system and an in situ reduction-oxidation manipulation (redox) system. Groundwater also is monitored to track other contaminant plumes including strontium-90, tritium, nitrate, and sulfate.

Hexavalent chromium is the contaminant of greatest concern in the 100-D Area.

Groundwater flows primarily to the north and northwest, to the Columbia River (Figure 2.5-3). Near the Columbia River, including the redox site, the average flow direction is toward the northwest. Farther inland, average flow is northward.

The 182-D reservoir is used to store Columbia River water prior to treatment. The reservoir developed a leak in 2003 and 2004 that was of sufficient volume to create a measurable groundwater mound beneath the reservoir. Data from water-level recorders in new wells 199-D5-32, 199-D5-33, and 199-D5-34 helped define the mound early in fiscal year (FY) 2004. The leak was virtually stopped by lowering the water level in the reservoir, and the mound quickly dissipated. While the mound was present, it created radial groundwater flow locally and contributed to a separation of the north and south chromium plumes.

The remainder of this section describes contaminant plumes and concentration trends for the constituents of interest under CERCLA and *Atomic Energy Act of 1954* (AEA) monitoring.

2.5.1 Groundwater Contaminants

This section describes the distribution and trends of chromium, strontium-90, tritium, nitrate, and sulfate in groundwater in the 100-D Area.

2.5.1.1 Chromium

Chromium contamination underlies most of the 100-D Area in two plumes (Figures 2.5-4 and 2.5-5). The north plume had sources in the central 100-D Area and the south plume had unknown sources near the former 183-DR filter plant. In FY 2002 and 2003, available data suggested that the two plumes had merged at the 100-µg/L contour (drinking water standard) and perhaps the 500-µg/L contour (PNNL-14187; PNNL-14548). However, data from new wells in the central 100-D Area indicated the lobes were separated into two distinct plumes. Chromium concentrations are variable in the central and south 100-D Area and the plumes are dynamic.

Groundwater monitoring in the 100-HR-3-D groundwater interest area includes the following monitoring activities:

- ***A pump-and-treat system in north 100-D Area has operated since 1997, and a second system was added in FY 2004. Wells are monitored monthly to biennially for chromium and co-contaminants.***
- ***An in situ redox system operates in the southwest 100-D Area. Compliance wells, barrier wells, additional wells, and aquifer tubes are monitored monthly to annually.***

At 100-D Area, three remediation systems help reduce the amount of chromium reaching the Columbia River: two pump-and-treat systems in the north and in situ remediation in the southwest.

North Plume. The north chromium plume was formerly oriented south-north, but has spread westward in recent years. At the 100-µg/L contour the plume is roughly triangular, with one corner near the former D Reactor, where waste disposal facilities contaminated the groundwater with chromium, which moved north and west with groundwater flow. The north corner of this plume is influenced by the 100-HR-3-D pump-and-treat system that is designed to reduce the flux of chromium to the river (see Section 2.5.2.1). The highest concentrations in the north plume are on the southwest side of the plume (e.g., 2,400 µg/L in well 199-D5-41).

Near the former sources, chromium continued a gradual decline in most wells (e.g., well 199-D5-16 in Figure 2.5-6). Well 199-D5-15 is an exception to this declining trend, with variable concentrations since FY 1997. Specific conductance and other constituents varied with the chromium, suggesting dilution of groundwater with fresh water. Staff repaired leaking fire hydrants and capped unused water lines in the 100-D Area in FY 2004 to reduce the amount of artificial recharge. Quarterly sampling of well 199-D5-15 in FY 2004 showed higher levels of chromium than in the previous few years (Figure 2.5-6), perhaps in response to these repairs.

In the north 100-D Area near the pump-and-treat system, compliance wells continued to show variable chromium concentrations, with the lowest concentrations in the early summer when river stage was high (Figure 2.5-7). The concentrations remained above the remedial action goal in the compliance wells except for a few samples collected in early summer.

On the southwest side of the north plume, chromium concentrations increased sharply in wells 199-D5-20 and 199-D5-41 beginning in FY 2002 and remained high in FY 2004 (Figure 2.5-8). The high concentrations in well 199-D5-20, which is located near the Columbia River, indicated that chromium was moving between the two remediation systems. In July 2004, a new pump-and-treat system began operating in this region (see Section 2.5.2.1).

New aquifer tubes were installed at three sites in the north 100-D Area in FY 2004. Chromium concentrations in AT-D-2-S and AT-D-3-D were 156 and 294 µg/L, respectively. These are an order of magnitude higher than levels seen in the other aquifer tubes in this region, and higher than concentrations in the compliance wells. Tube site AT-D-2 is located downgradient of well 199-D5-20 and AT-D-3 is located farther north (see Figure 2.5-1 for locations).

South Plume. This chromium plume lies south and southwest of the 182-D reservoir and west of the 183-DR filter plant, extending to the Columbia River (Figures 2.5-4 and 2.5-5). The core of the plume, with concentrations >500 µg/L, is oriented southeast-northwest, perpendicular to the Columbia River. The redox barrier intersects the south chromium plume and terminates the highest-concentration portion of the plume.

Plume areas (square kilometers) above the drinking water standard at the 100-HR-3-D Operable Unit:

Chromium — 0.97
Nitrate — 0.87
Tritium — 0.04

Concentrations dropped nearly 1,000 µg/L in FY 2004 in well 199-D5-38 and more than 2,000 µg/L in well 199-D5-39, near the north edge of the south plume (Figure 2.5-9). Well 199-D5-39 had the highest chromium concentration in the 100-D Area at the beginning of FY 2004 (3,830 µg/L) but finished the year at 1,280 µg/L. The sudden declines are probably related to dilution from the 182-D reservoir, which leaked in FY 2003 and part of FY 2004.

Compliance monitoring wells downgradient of the redox barrier show inconsistent trends (Figure 2.5-10). The northernmost well, 199-D4-83, shows variable chromium concentrations with no clear trend. Well 199-D4-39, near the north end of the barrier, shows the most variability and the concentrations increased 89% between August/September 2003 and August/September 2004. South of well 199-D4-39, wells 199-D4-23, 199-D4-38, 199-D4-84, 199-D4-85, and 199-D4-86 all show an overall decline, although with some variability. Chromium concentrations in these wells declined ~50% between August/September 2003 and August/September 2004.

Aquifer tubes provide additional monitoring points along the 100-D Area shoreline (Figure 2.5-11). Four tube sites in the south chromium plume had concentrations above 100 µg/L, with a FY 2004 maximum of 363 µg/L at tube DD-43-3. Chromium concentrations in several of the tubes in this region have declined since they were first sampled in 1997. The decline may be caused, in part, by remediation effects (Figure 2.5-12).

New aquifer tubes in the north 100-D Area showed higher chromium concentrations than previously measured in other aquifer tubes in that region.

Chromium concentrations have increased in recent years in some of the redox barrier wells, as reported previously (DOE/RL-2003-05). Section 2.5.2.2 contains more information about these wells.

2.5.1.2 Strontium-90

Two locations in the 100-D Area have a history of strontium-90 detections in groundwater: near the former retention basins in the north and near D Reactor in central 100-D Area.

Near the former retention basins, one sample from well 199-D8-68 exceeded the drinking water standard (8 pCi/L) once in FY 2004 (Figure 2.5-13); other samples from that well during the year were below the standard. Strontium-90 was also detected in six other wells in this region, but at levels below the drinking water standard.

Near the former D Reactor, strontium-90 increased to 4.9 pCi/L in well 199-D5-15 (Figure 2.5-14). Nearby well 199-D5-16 continued to have no detectable strontium-90.

2.5.1.3 Tritium

Tritium concentrations in FY 2004 ranged from below detection limits to above the 20,000-pCi/L drinking water standard. The highest concentrations were detected in wells in the south 100-D Area, and are believed to represent groundwater that flowed north from the 100-N Area. Part of the 100-N Area tritium plume moved inland when groundwater mounds were present beneath liquid waste disposal facilities; that contamination is now moving north and northwest. The highest value in the 100-D Area was 25,200 pCi/L in well 199-D4-19, where concentrations are increasing gradually (Figure 2.5-15). The tritium concentration in nearby aquifer tube DD-44-4 was 31,900 pCi/L, and has also increased.

Tritium contamination in the south 100-D Area may have originated in the 100-N Area.

Tritium concentrations continued to be above 10,000 pCi/L near the former reactor buildings in FY 2004. Levels increased to 19,000 pCi/L in well 199-D5-17 near DR Reactor after several years of stability (~15,000 pCi/L).

2.5.1.4 Nitrate and Nitrite

Nitrate distribution (Figure 2.5-16) is generally similar to chromium in the 100-D Area; both constituents form two plumes. Nitrate concentrations continued to exceed the 45-mg/L drinking water standard in both plumes, with a FY 2004 maximum concentration of 74 mg/L in well 199-D5-16 near D Reactor. The south plume is truncated by the redox system, which converts the nitrate to nitrite.

Nitrate trends in the central 100-D Area do not follow chromium trends. Nitrate concentrations are steady in wells 199-D5-20 and 199-D5-41, which showed sharply increasing chromium.

Downgradient of the redox barrier, nitrate concentrations decreased in compliance wells, falling to levels below the drinking water standard for the first time in wells 199-D4-84 and 199-D4-85. As with chromium, these decreases are believed to be related to redox effects.

Like chromium, nitrate concentrations in some redox barrier wells (e.g., 199-D4-26 and 199-D4-32) have risen in recent years, suggesting a loss of reducing conditions.

Samples from four new aquifer tubes were analyzed for nitrate. The highest result was 40.3 mg/L in tube AT-D-1-S in the central shoreline.

Nitrite continued to be detected in redox barrier wells but was below detection limits in downgradient wells. Nitrite concentrations exceeded the 3.3-mg/L drinking water standard three wells (maximum 4.27 mg/L in barrier well 199-D4-32).

2.5.1.5 Sulfate

Sulfate concentrations are >100 mg/L beneath much of the 100-D Area. Excluding wells influenced by the redox system, concentrations all were below the 250-mg/L secondary drinking water standard in FY 2004.

Injections of sodium dithionite solution at the redox site increases sulfate concentrations in the barrier and in some downgradient wells and aquifer tubes. For example, sulfate concentrations in downgradient wells 199-D4-23 and 199-D4-84 exceeded the 250-mg/L secondary drinking water standard in FY 2004. The maximum concentration downgradient of the barrier was 580 mg/L in well 199-D4-23 (Figure 2.5-17).

2.5.2 Interim Groundwater Remediation for Chromium

Hexavalent chromium is the contaminant of greatest concern in the 100-D Area. Two CERCLA remediation systems have been implemented as interim actions to reduce the amount of chromium reaching the Columbia River: a pump-and-treat remediation system in the north and in situ redox manipulation barrier in the southwest. A second pump-and-treat system was installed and became operational in FY 2004 between the existing system and the redox barrier.

Fourteen new aquifer tubes at five sites were installed in the 100-D Area shoreline. The new tubes extend from just north of the redox barrier to north of the pump-and-treat system. Pertinent results from aquifer tube sampling were discussed in Section 2.5.1.

In September, 2004, a test of the Enhanced Access Penetration System (EAPS) was conducted in the south chromium plume at 100-D Area. The EAPS combines a cone penetrometer with a small-diameter air-rotary drilling system to allow subsurface access in areas that are not conducive to conventional push technology. The EAPS successfully drilled to the bottom of the unconfined aquifer (>30 meters below the surface) through sand and cobbles. Total drilling time was ~8 hours. A small-diameter well (nominal 2.5-centimeter diameter; 199-D5-93) was installed with a pre-packed sand screen, and the well was completed by sealing with bentonite and grout. A variance for the well was required because the annular seal for the well was thinner than called for in the regulations. Washington State Department of Ecology granted this variance on the condition that a report on the quality of data produced by the well be submitted by September 2006.

The remedial action objectives of the 100-HR-3 Operable Unit (ROD 1996a, 1999a) are:

- ***Protect aquatic receptors in the river bottom from contaminants in groundwater entering the Columbia River.***
- ***Protect human health by preventing exposure to contaminant in the groundwater.***
- ***Provide information that will lead to the final remedy.***

The contaminant of concern is hexavalent chromium. The records of decision set the cleanup goal at compliance wells as 22 µg/L for the pump-and-treat system and 20 µg/L for the redox system. EPA specified enhancements needed to the pump-and-treat system in their 5-year review (EPA 2001).

2.5.2.1 Pump-and-Treat Systems

The original pump-and-treat system in the 100-HR-3-D Operable Unit includes four extraction wells located near the former 116-D-7 and 116-DR-9 retention basins. The system began operating in July 1997. Groundwater is pumped from extraction wells 199-D8-53, 199-D8-54A, 199-D8-68, and 199-D8-72, and then transferred via pipeline to the 100-H Area where it is treated and injected into the aquifer. Monitoring requirements for this system are included in DOE/RL-96-90, as modified by DOE/RL-96-84. Long-term monitoring requirements in the 100-D Area were derived from Change Control Form 107 as modified by Fluor Hanford, Inc.[(a)] Wells, constituents, and sampling frequencies for interim

(a) Letter FH-0205249 from RT Wilde (Fluor Hanford, Inc.) to JS Fruchter (Pacific Northwest National Laboratory), *Revised FY 2003 Sampling Schedule for Groundwater Remediation Monitoring*, dated November 11, 2002.

action monitoring are shown in Appendix A. One well (199-D4-15) scheduled for monthly sampling was not sampled in July because of a pump problem. Details regarding 100-HR-3-D pump-and-treat operations may be found in the annual reports that are issued by the U.S. Department of Energy (DOE). Figure 2.5-1 displays well locations.

A second pump-and-treat system came on-line at the end of July 2004 to address increasing hexavalent chromium levels in monitoring wells southwest of the original pump-and-treat system. The new system is located between the current extraction wells and the redox barrier. Groundwater is withdrawn from wells 199-D5-20, 199-D5-32, and 199-D5-37, treated in the 100-D Area using a metal chelating medium called MR3, and injected into well 199-D5-42. If the small scale system works as planned, the system may be expanded in FY 2005 to remediate a larger area. An upcoming report on the 100 Areas pump-and-treat systems will provide a more detailed discussion of this new technology and its application in the 100-D Area.

During FY 2004, two pump-and-treat system extracted ~181 million liters of groundwater from the 100-D Area, removing ~37.3 kilograms of hexavalent chromium.

Progress During FY 2004. The 100-D Area pump-and-treat system is reducing overall contamination in the operable unit by removing contaminant mass. During FY 2004, the system extracted ~172.8 million liters of groundwater from the 100-D Area, removing ~30.9 kilograms of hexavalent chromium. An additional ~7.9 million liters were processed and ~6.4 kilograms of chromium removed by the new pump-and-treat system.

A total of ~192.2 kilograms of hexavalent chromium has been removed from original targeted plume area since startup of the system in July 1997. An additional ~30 kilograms of hexavalent chromium were removed during a pilot-scale test conducted in the 100-D reactor area between August 1992 and August 1994 (DOE/RL-95-83). The total hexavalent chromium in the plume has been estimated at 590 kilograms (DOE/RL-94-95). This amount does not include the chromium plume in the southwest 100-D Area nor in the vadose zone.

Influence on Aquifer Conditions. In FY 2004, chromium concentrations remained elevated in the 100-D Area. Hexavalent chromium concentrations in compliance wells varied inversely with river stage. The range of concentrations observed in FY 2004 were similar to those observed the previous two years. Figure 2.5-7 shows chromium trends for the two compliance wells, 199-D8-69 and 199-D8-70. Chromium remained above the remedial action goal (22 µg/L) in both of the wells throughout FY 2004 except for one measurement in each well in the early summer when Columbia River run-off was greatest. Results of performance monitoring are incorporated with the discussion of general contamination in Section 2.5.1.

DOE/RL-2004-21 presents results of operational monitoring and additional details about the pump-and-treat system for calendar year 2003. Results for 2004 will be included in an upcoming report on the 100 Areas pump-and-treat systems.

2.5.2.2 In Situ Redox Manipulation System

This treatment system uses a change in redox potential to reduce dissolved hexavalent chromium in groundwater to trivalent chromium, a much less soluble and less toxic species. Objectives of the redox interim action are the same as for the 100-D Area pump-and-treat system except that the remedial action goal for chromium at the redox site is 20 µg/L. Remedial action monitoring is described in DOE/RL-99-51. Wells, constituents, and sampling frequencies are listed in Appendix A.

Progress During FY 2004. The redox treatment zone is ~680 meters in length, aligned parallel to the Columbia River shoreline and ~100 to 200 meters inland. The treatment zone is designed to reduce the concentration of hexavalent chromium in groundwater to ≤20 µg/L at seven compliance wells situated between the treatment zone and Columbia River. The 20-µg/L goal was met at only one of the seven compliance wells, 199-D4-86, located at the southwest extent of the barrier. Concentrations in the other compliance wells were generally decreasing except for well 199-D4-39, as discussed in Section 2.5.1 (Figure 2.5-10). The reason for the increase is not understood at this time.

Institutional controls continue to protect the public by preventing access to hexavalent chromium in the groundwater. Sampling and analysis of groundwater from compliance wells, monitoring wells, aquifer tubes, and redox treatment zone wells continues to provide information leading to selection of the final remedy.

An automated water-level monitoring system installed in eleven wells and at the Columbia River also provide information leading to selection of the final remedy. Hydrographs of data from the automated water-level monitoring systems installed in four wells showed responses to the re-filling of the 182-D reservoir in July 2003 and the subsequent decline and dissipation of that mound into FY 2004.

Chromium concentrations have increased sharply in one redox compliance well but continued decreasing in other compliance wells. Concentrations increased in some barrier wells.

Influence on Aquifer Conditions. In FY 2004, as well as in previous years, chromium concentrations increased in redox barrier wells beyond what was expected based on the design. At the end of the fourth quarter, ~85% of the barrier wells were below the remedial action goal of 20 µg/L. Chromium concentrations in the barrier wells ranged from below detection limits to 1,380 µg/L.[(b)] Almost all of the elevated concentrations are in the northeast part of the barrier.

To evaluate the reason for the increasing concentrations a team of experts convened with key Hanford Site technical personnel to review site conditions and processes in establishing the barrier. The panel concluded that the primary cause of the premature breakdown in reductive capacity was physical and chemical aquifer heterogeneity. These conditions lead to the following:

- Lack of ferrous iron in some intervals (needed for long-term reducing conditions).
- High flow rates through preferential pathways (incomplete reducing conditions).
- Presence of competing oxidants (uses up reductant targeted for hexavalent chromium).

The remaining wells in the barrier treatment zone appear to be intact and functioning as designed. DOE is working with the regulatory agencies and technical experts to develop corrective actions to mend the barrier where hexavalent chromium concentrations are elevated.

2.5.3 Chromium Sensor Deployment

As part of the Advanced Monitoring Systems Initiative, DOE deployed a chromium sensor on the 100-D Area shoreline in FY 2004. The purpose of the deployment was to demonstrate the efficacy of such a system in the field. Chromium sensors could be used routinely in the 100-D Area to measure chromium concentrations in monitoring wells and aquifer tubes at more frequent intervals than is practical using manual sampling techniques.

Burge Environmental developed a universal platform to use with various types of analytical sensors in the field. The platform was previously used at other locations to monitor trichloroethene in monitoring wells and at groundwater treatment systems. For the 100-D Area deployment, Burge Environmental coupled the platform with analytical systems for hexavalent chromium and specific conductance. Two aquifer tubes downgradient of the redox site, DD-39-1 and DD-39-3, were plumbed into the sensor.

Figure 2.5-18 illustrates the complete universal platform deployed in the field. The monitoring system comprises several modules for sample collection, calibration, analysis, data acquisition/control, and communication. A field deployment box was used to mount solar cell panels and house the batteries, air system, and communication module. A piece of plastic casing passed through the bottom of the field deployment box and ~1 meter into the soil. The analytical and calibration modules were mounted inside the casing for temperature control.

(b) Redox operational data; not in Hanford Environmental Information System (HEIS).

The system collected samples with a peristaltic pump that ran off batteries charged by solar cells. A valve directed the sample to either the calibration module or the analytical chamber. The calibration module performed two functions: creating blank water and creating three-step calibration curves. Sample water diverted to the calibration module was passed through a filter of granular ferric hydroxide to remove the hexavalent chromium from the water, creating the "blank water." Blank water was used to clean the system and create the three-step calibration curve. After the initial deployment, the system was modified to include a specific conductance sensor.

A serial cable connected a modem, located in the field deployment box, to a small programmable logic controller located on the analytical/calibration unit. A computer located at a trailer ~0.8 kilometer from the monitoring location controlled the monitoring system via a radio modem. The program on the computer sent commands and received data via the radio modem. The modem was capable of operating at distances of 20 kilometers. The computer located in the trailer was remotely controlled by users in more distant locations.

A chromium sensor was installed at an aquifer tube site on the 100-D Area shoreline to measure chromium concentrations automatically.

Deployment of the sensor demonstrated that the system can

- Measure chromium concentrations reliably. Data compared favorably to laboratory data from samples collected during installation and to historical data.
- Measure specific conductance, which gives information on the source of the water (river or groundwater).
- Create calibration curves.
- Perform 90 to 100 analyses before replenishing reagent.
- Operate using solar cells for power.
- Be controlled and data can be accessed from remote locations.

The deployment encountered the following difficulties:

- The volume of water that had to be pumped to purge the system was initially too high. This problem related to the diameter of the aquifer tubes. Smaller-diameter tubes were inserted inside the aquifer tubes to reduce the volume of water pumped to flush the system and analyze the sample.
- The compressor overheated. A cooling fan was installed and a regulatory switch was replaced.
- A leak developed in the reaction chamber and was repaired.
- Communication difficulties associated with use of a non-dedicated phone line to access the computer arose. Staff resolved the problem.
- Air bubbles in the line affected specific conductance measurements. This problem could be solved by changing the design of the conductivity sensor.

Results of this limited deployment showed that this type of sensor is a viable alternative to manual sampling and analysis of chromium at shoreline sites at the Hanford Site. The system can be designed to measure other constituents and to sample monitoring wells also.

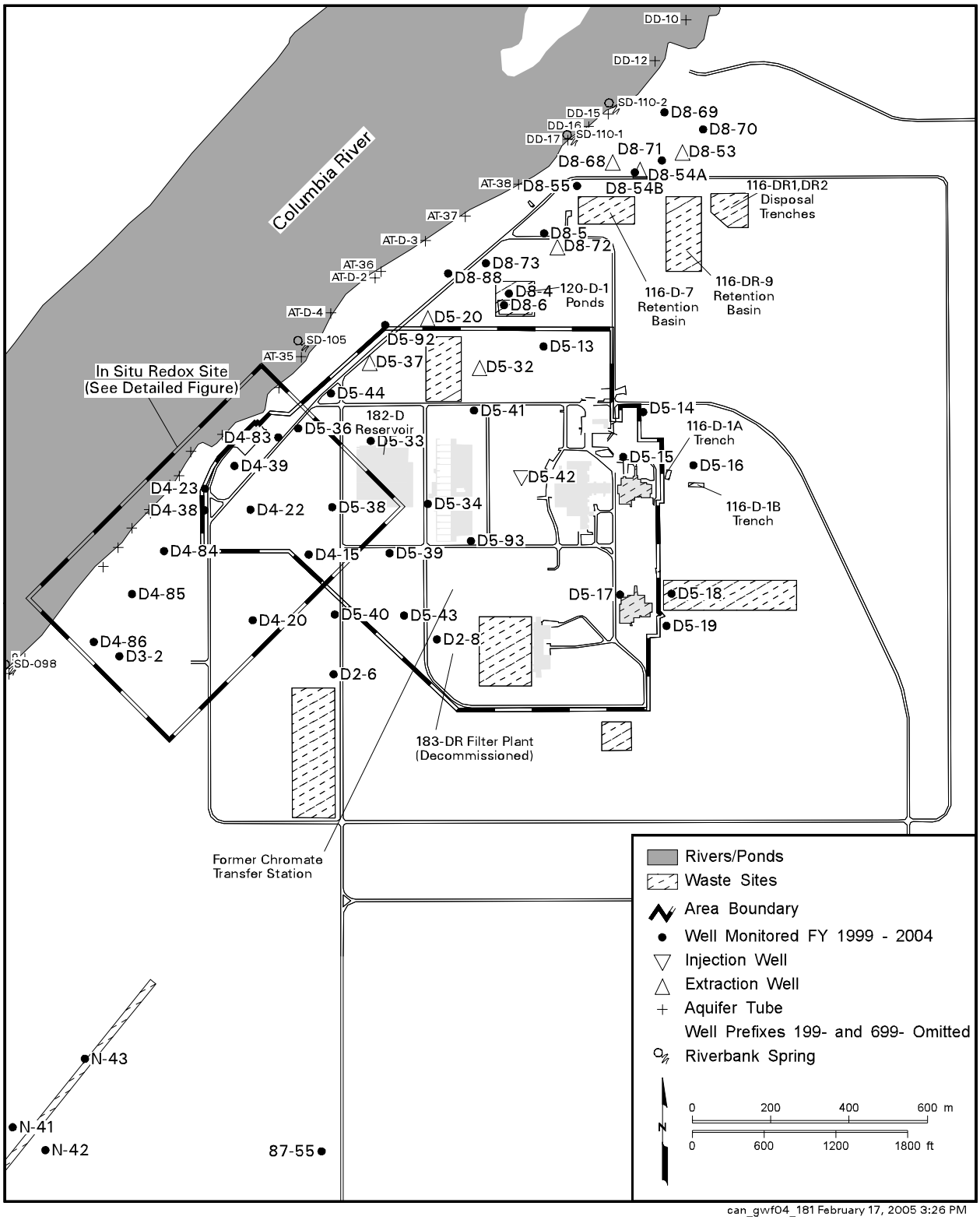

Figure 2.5-1. Groundwater Monitoring Wells in the 100-D Area

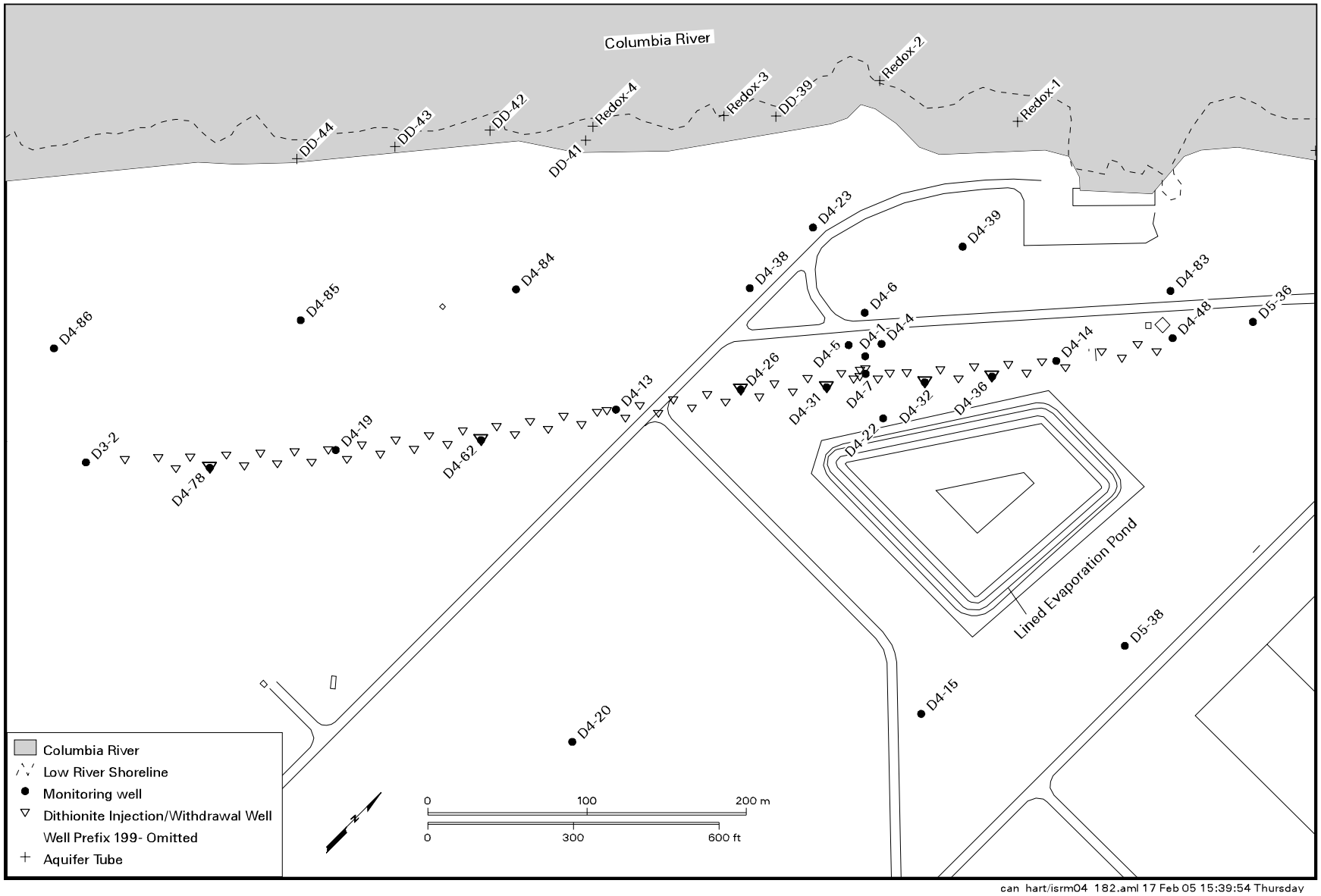

Figure 2.5-2. Groundwater Monitoring Wells Near the Redox Site in 100-D Area

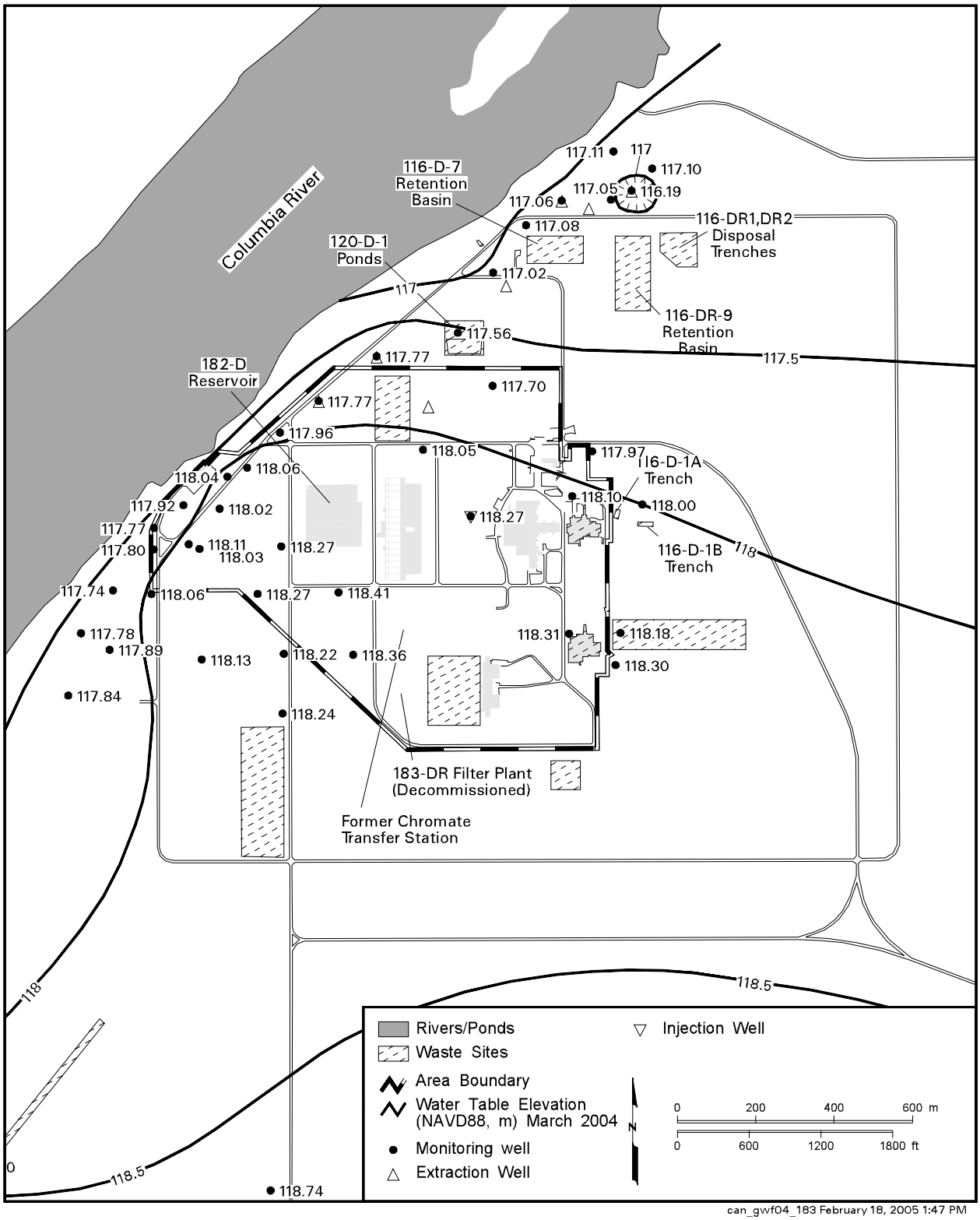

Figure 2.5-3. 100-D Area Water-Table Map, March 2004

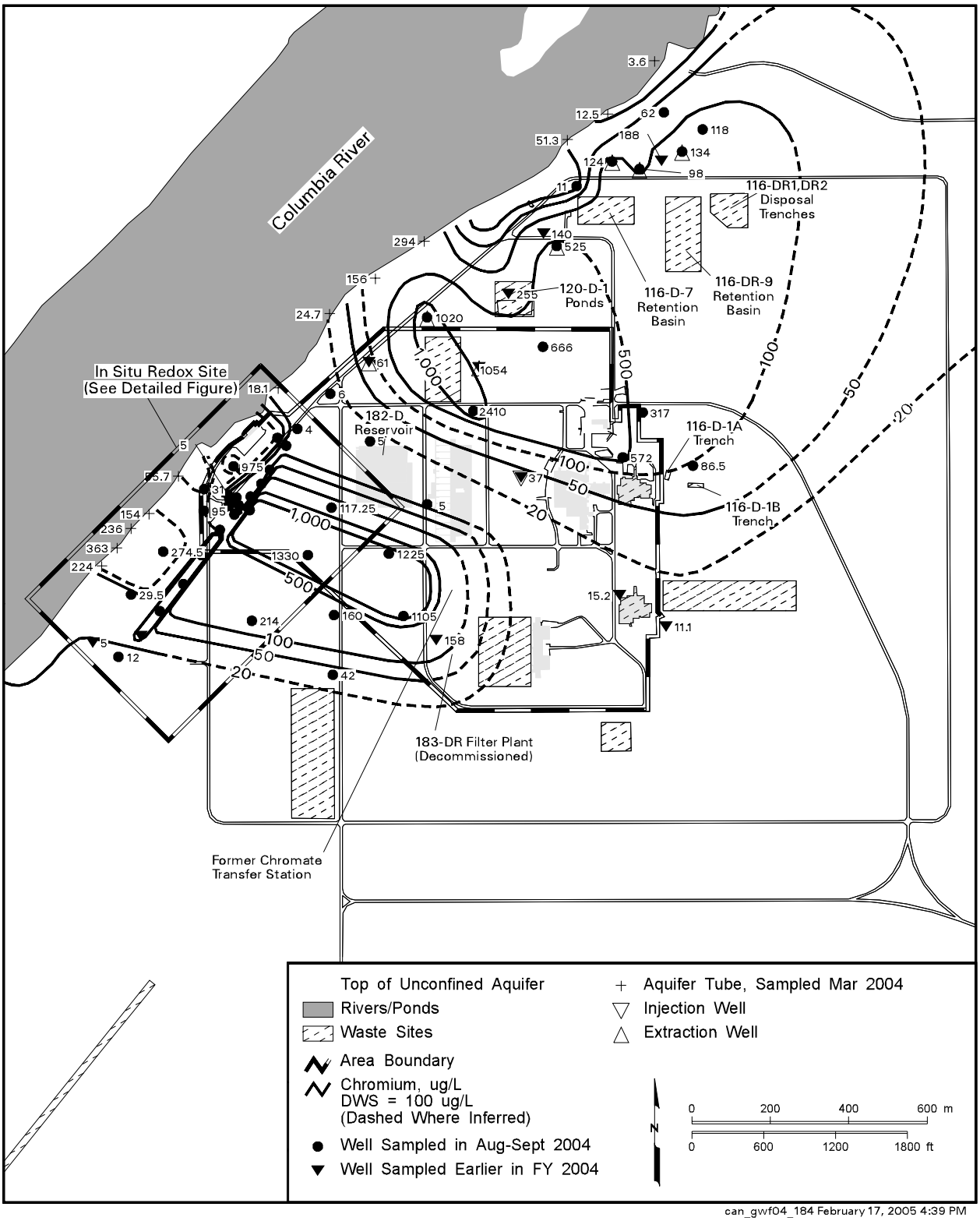

Figure 2.5-4. Dissolved Chromium Concentrations in the 100-D Area, Top of Unconfined Aquifer, August-September 2004

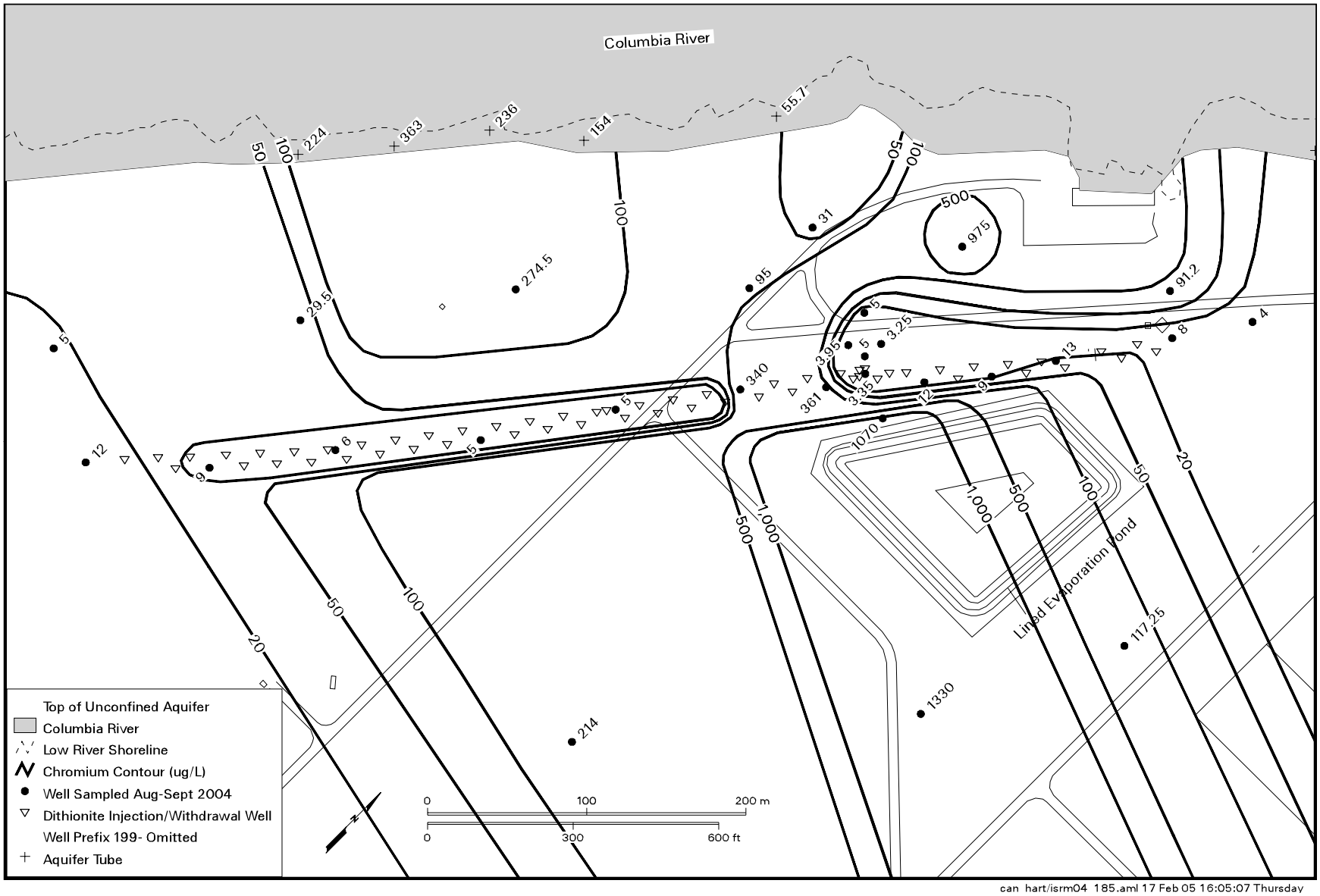

Figure 2.5-5. Dissolved Chromium Concentrations Near the Redox Site, 100-D Area, August-September 2004

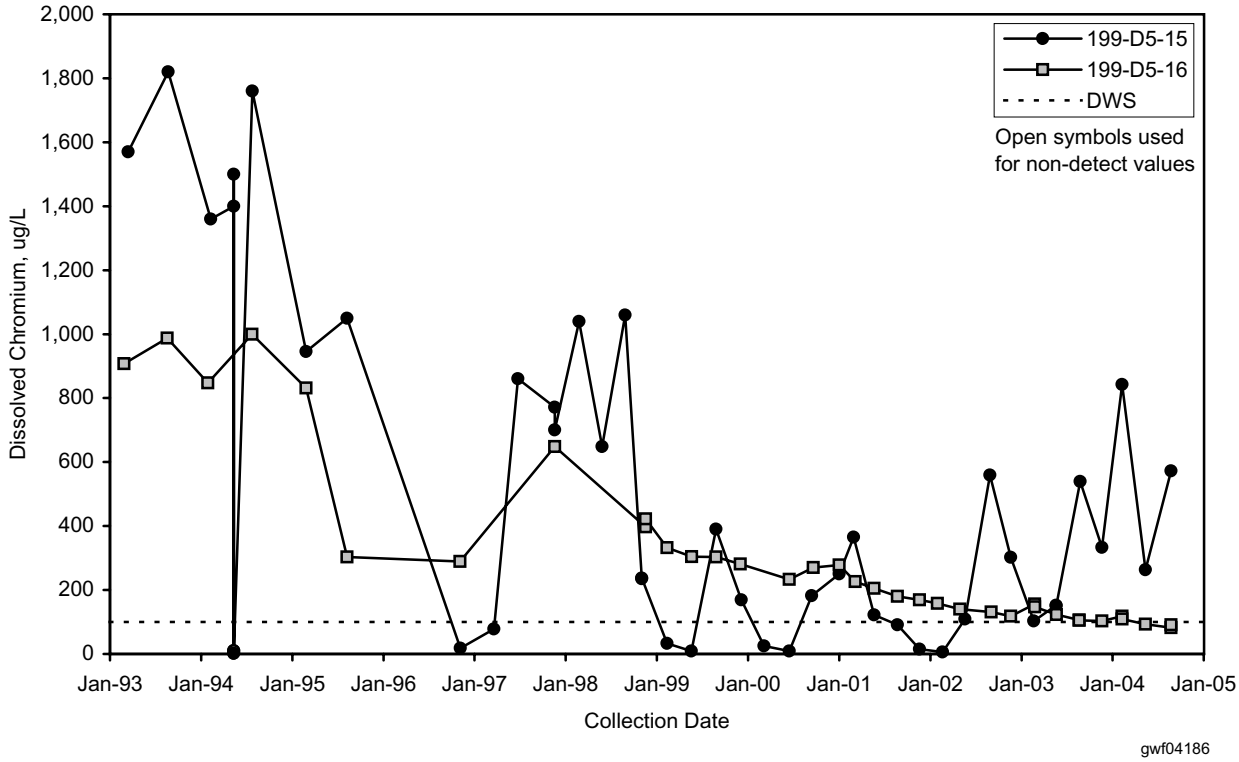

Figure 2.5-6. Chromium Concentrations in Wells Near the Former D Reactor

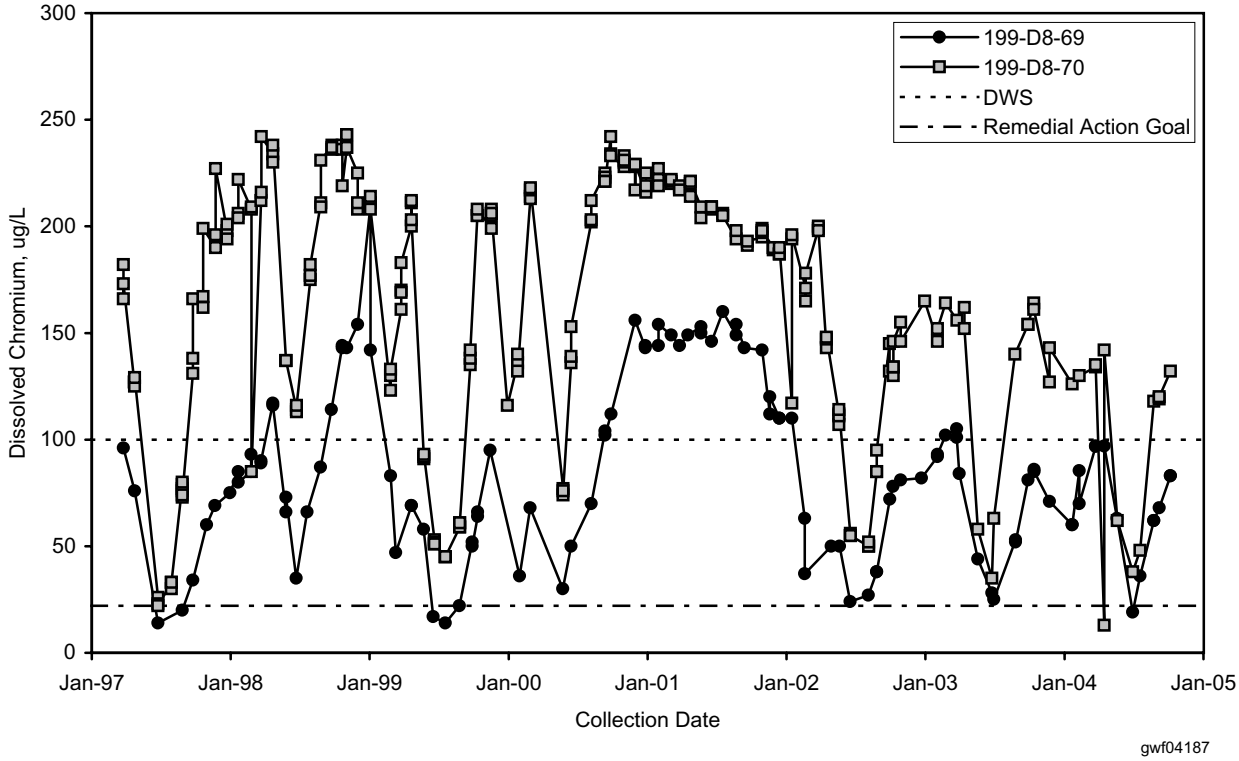

Figure 2.5-7. Dissolved Chromium Concentrations in Compliance Wells for the 100-HR-3 Pump-and-Treat System at 100-D Area

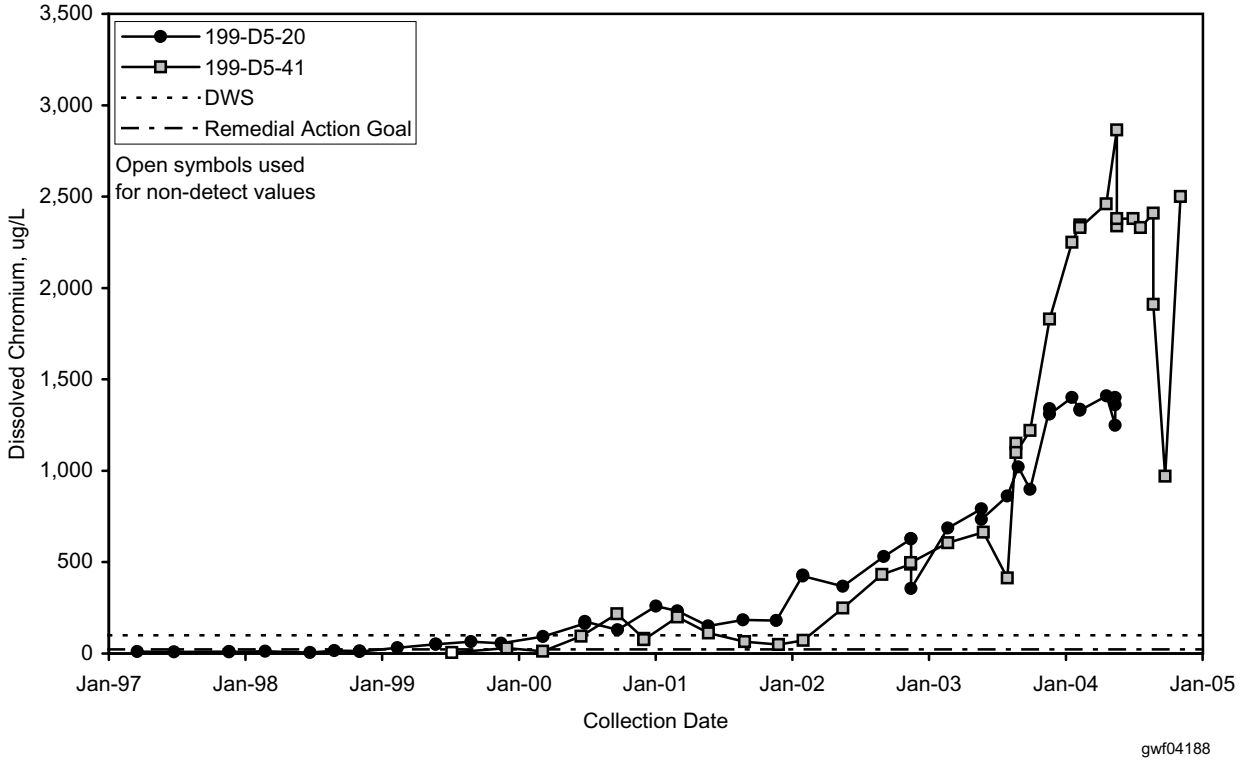

Figure 2.5-8. Dissolved Chromium Concentrations in Central 100-D Area

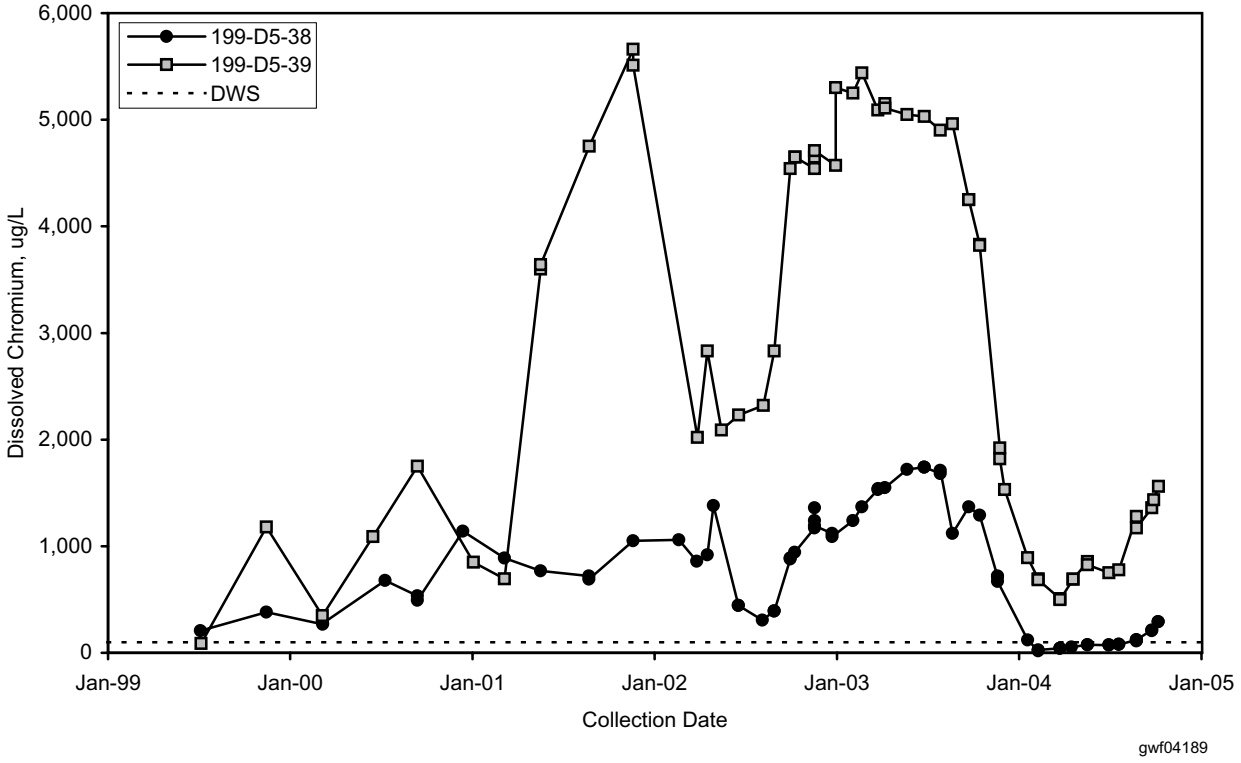

Figure 2.5-9. Dissolved Chromium Concentrations in South 100-D Area

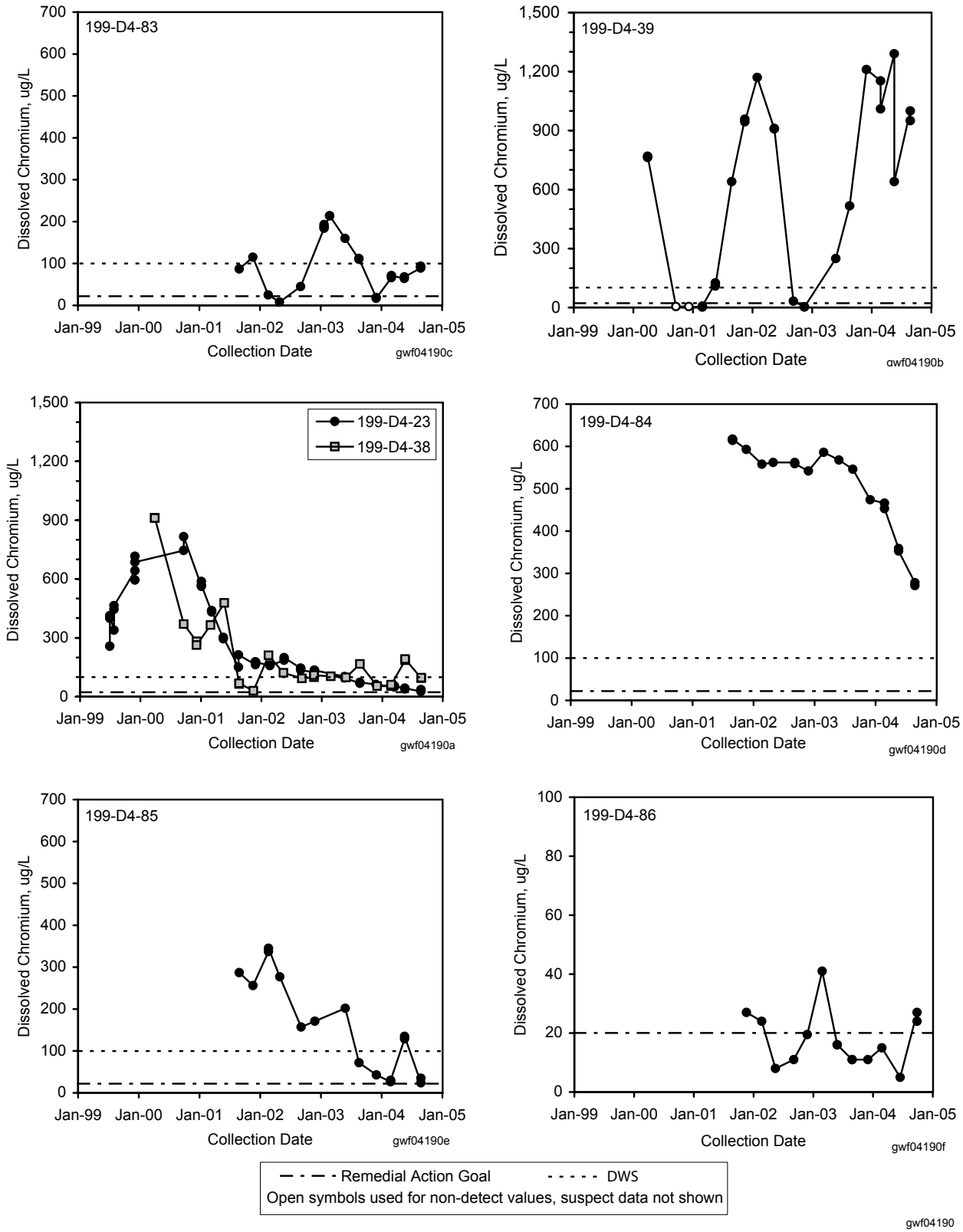

Figure 2.5-10. Dissolved Chromium Concentrations in Compliance Wells Downgradient of the Redox Barrier

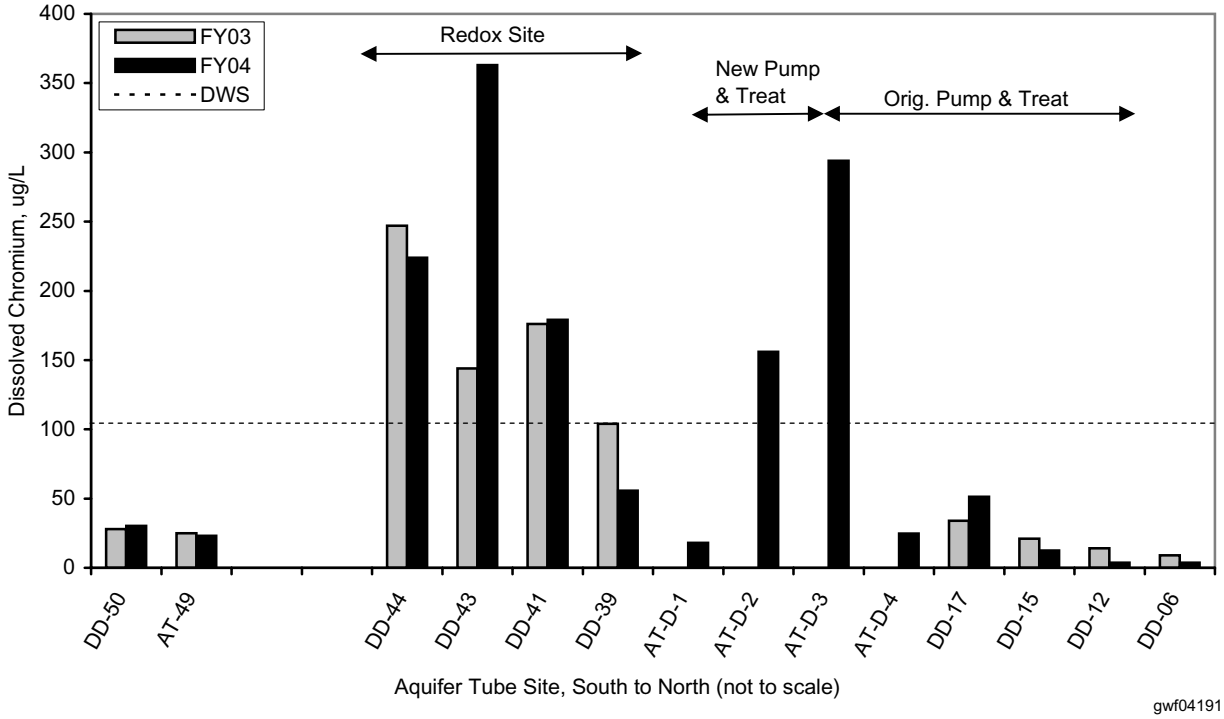

Figure 2.5-11. Hexavalent Chromium in Aquifer Tubes at 100-D Area, FY 2004

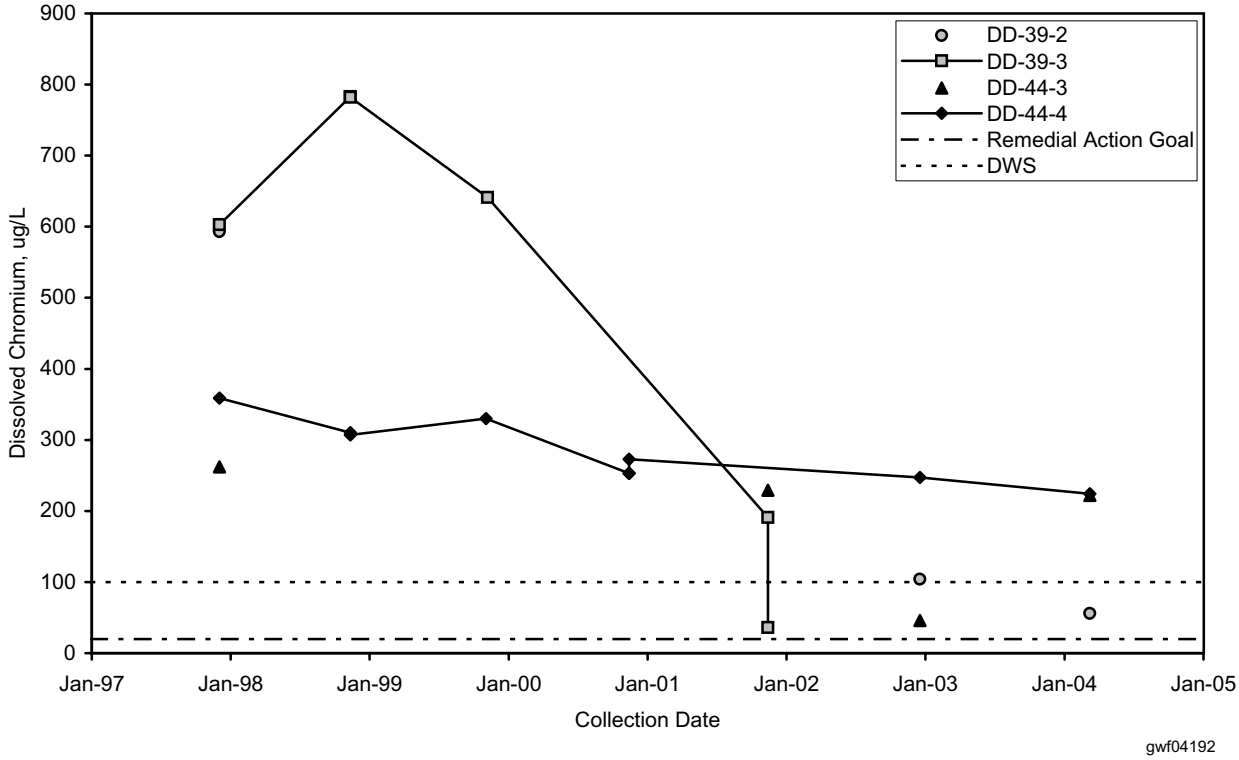

Figure 2.5-12. Hexavalent Chromium in Aquifer Tubes Downgradient of Redox Barrier

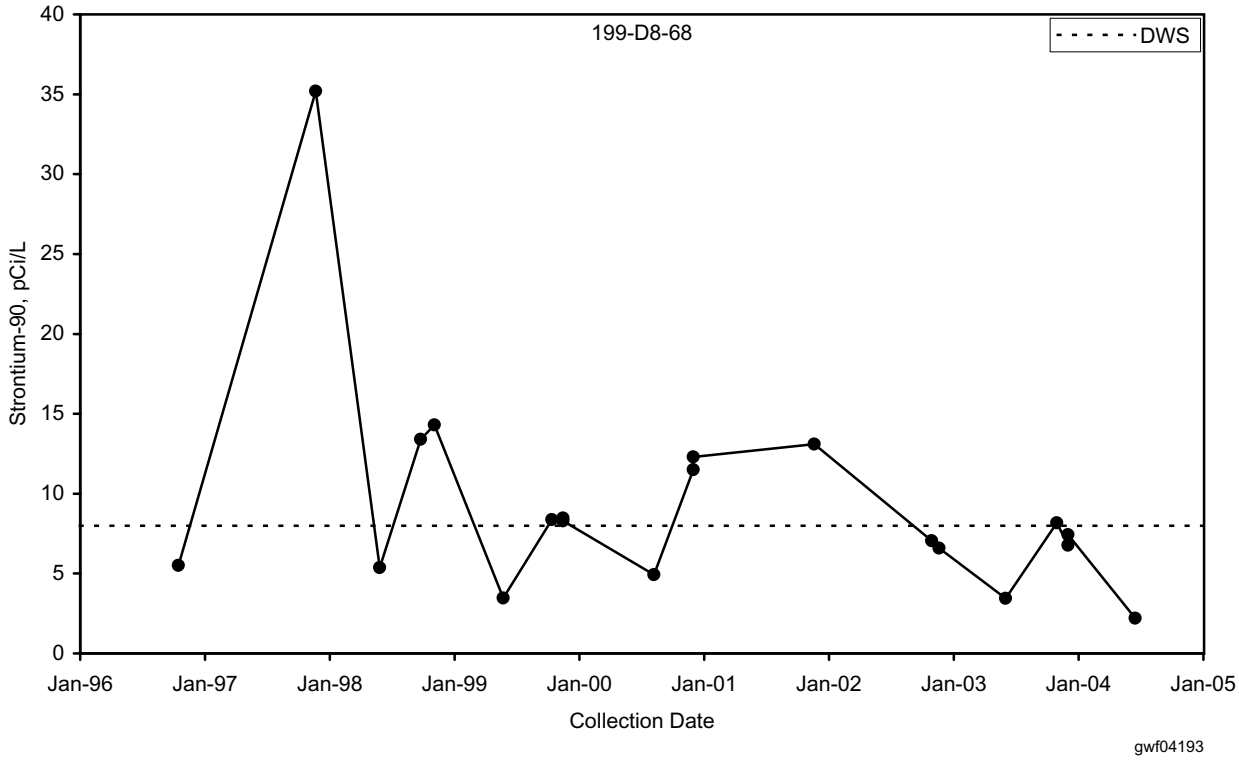

Figure 2.5-13. Strontium-90 Concentrations in Well 199-D8-68 Near Former Retention Basin

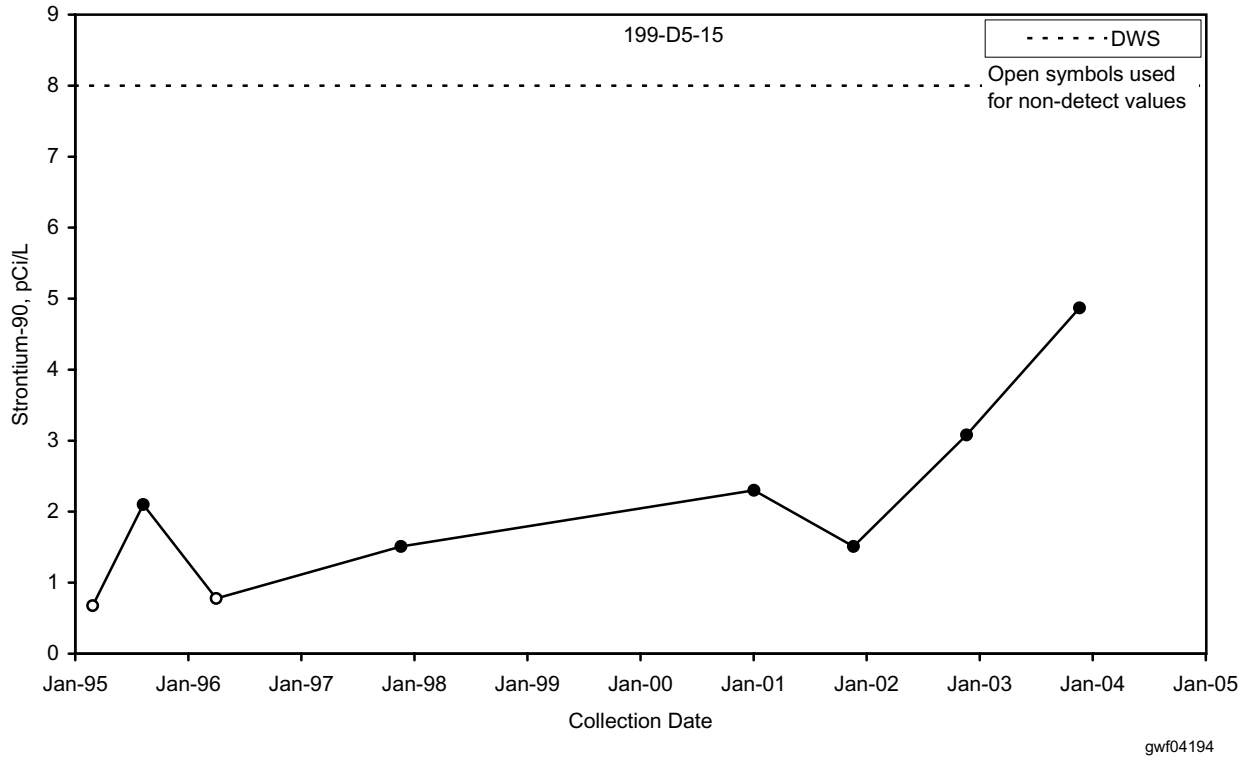

Figure 2.5-14. Strontium-90 Concentrations in Well 199-D5-15 Near Former D Reactor

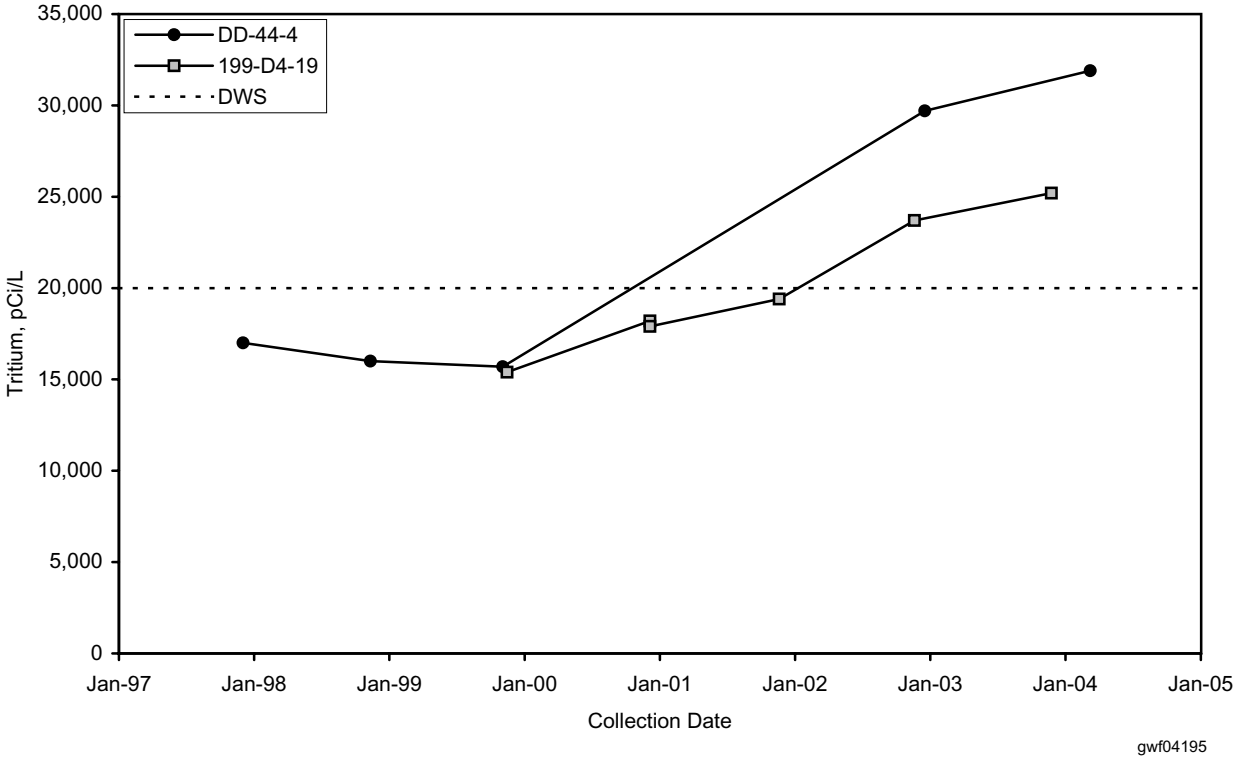

Figure 2.5-15. Tritium Concentrations in the South 100-D Area Near Columbia River

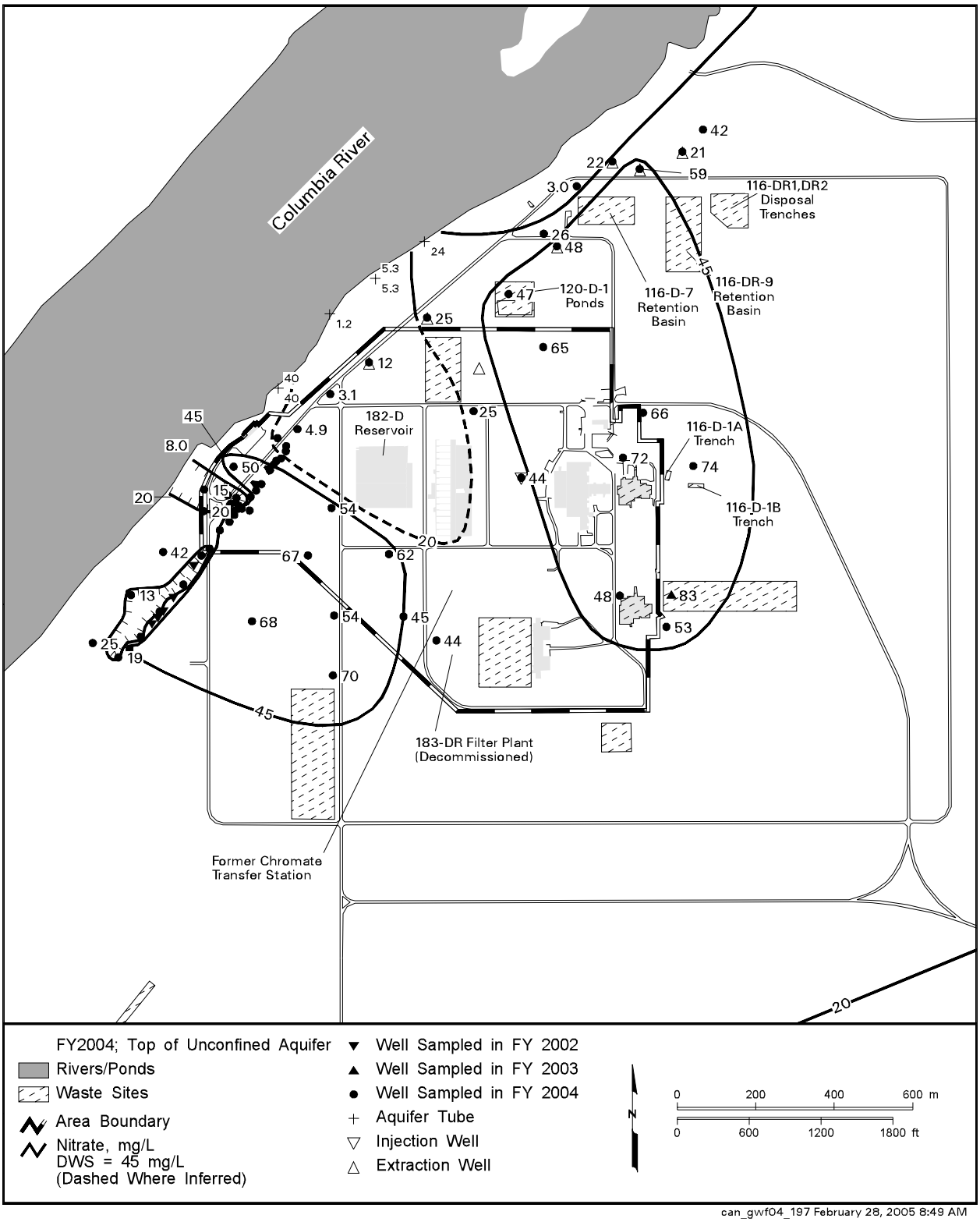

Figure 2.5-16. Average Nitrate Concentrations in the 100-D Area, Top of Unconfined Aquifer

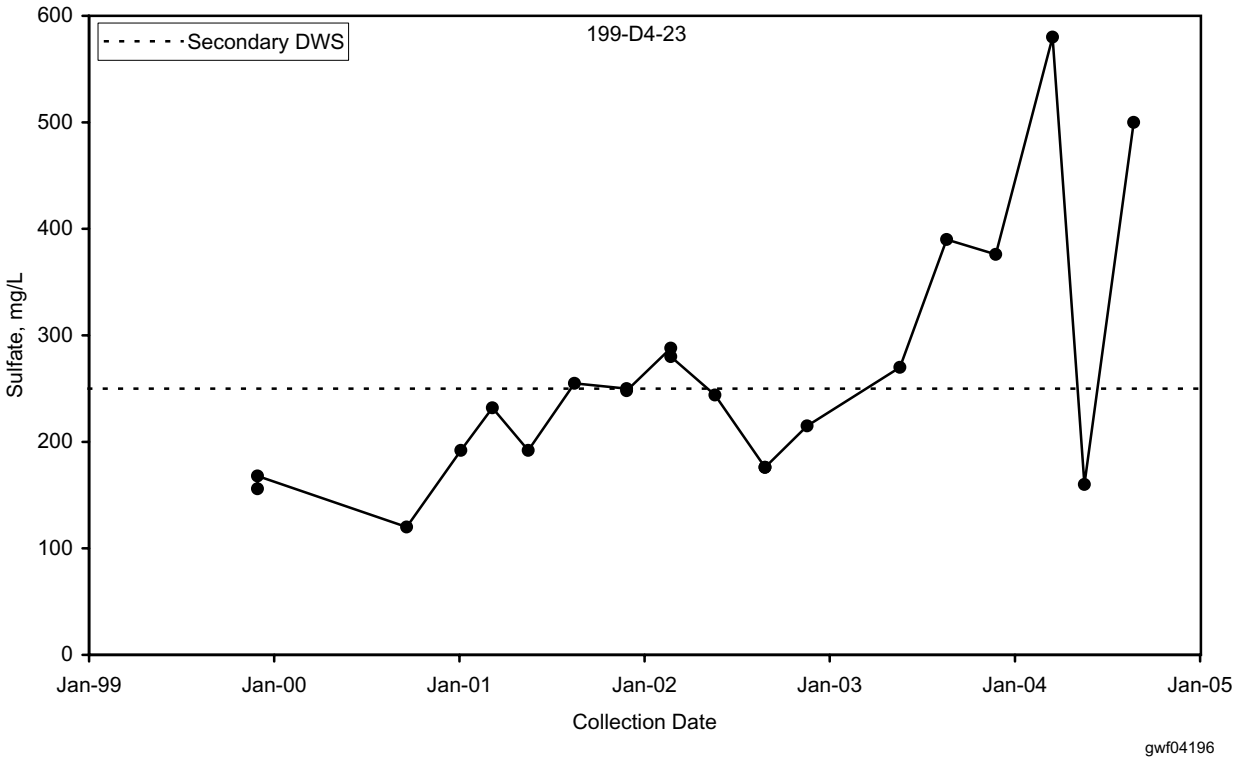

Figure 2.5-17. Sulfate Concentrations Downgradient of the Redox Barrier

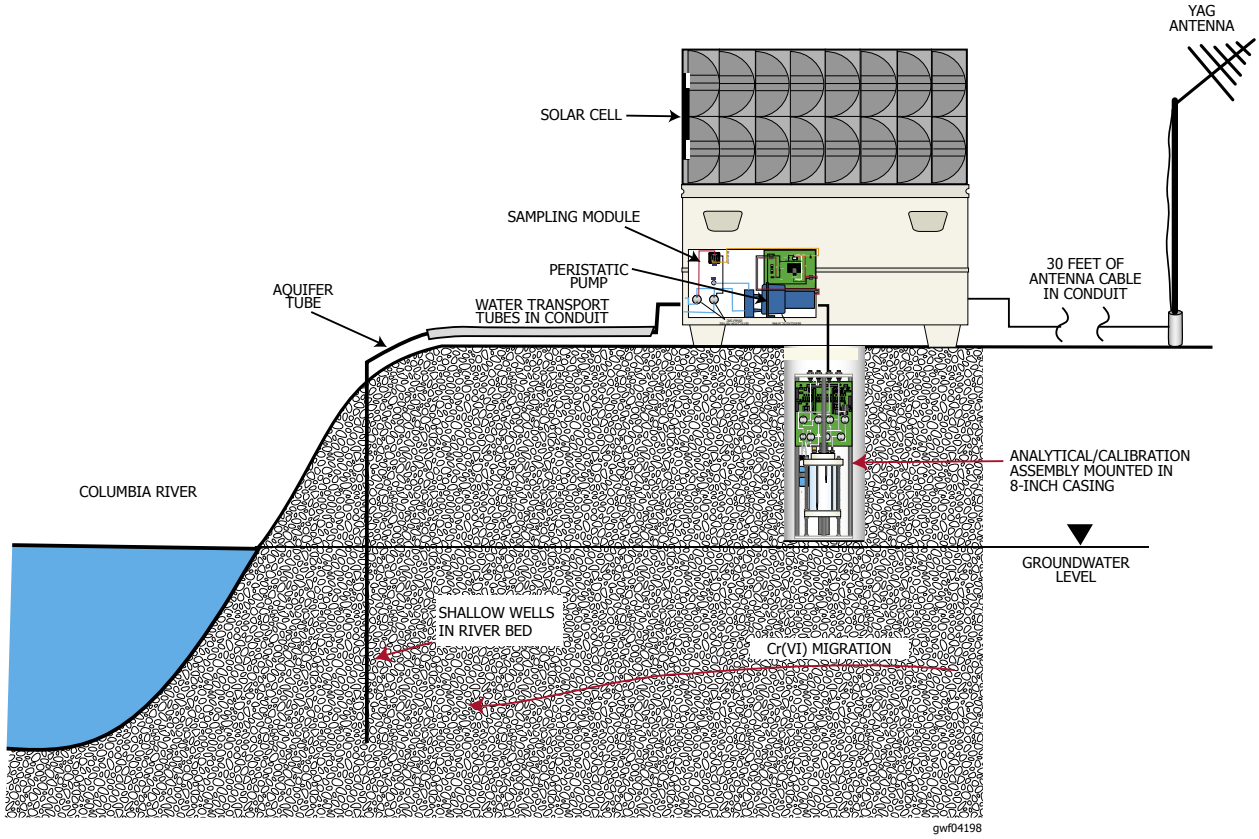

Figure 2.5-18. Field Deployment of Chromium Sensor (Burge Environmental)