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, which occupies the west half of the 100-HR-3 Operable Unit (Figure 2.1-1). 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.

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 remainder of this section describes contaminant plumes and concentration trends for the constituents of interest under CERCLA[(a)] 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.

Groundwater monitoring in the 100-HR-3-D groundwater interest area includes CERCLA and AEA monitoring:

CERCLA Monitoring – Pump-and-Treat System

- ***Two compliance wells and 33 monitoring wells are sampled monthly to biennially for chromium and co-contaminants.***
- ***Four extraction wells are sampled quarterly for chromium; co-contaminants are sampled semiannually.***
- ***Four shoreline seeps are sampled annually.***
- ***In fiscal year 2003, all wells were sampled as scheduled; two seeps were not (see Appendix A).***

CERCLA Monitoring – Redox System

- ***Seven compliance wells, 14 barrier wells, and 11 other monitoring wells are sampled quarterly to annually for chromium and co-contaminants.***
- ***Samples are collected at aquifer tubes annually for chromium and field parameters.***
- ***In fiscal year 2003, six wells and three aquifer tubes were not sampled as scheduled (see Appendix A).***

AEA Monitoring

- ***Thirty-five wells are sampled annually to quarterly for contaminants and general chemistry.***
- ***Sampling is coordinated with CERCLA sampling to avoid duplication.***

(a) Past-practice monitoring in this operable unit is regulated under RCRA past-practice monitoring, which follows the same groundwater monitoring activities as CERCLA. This report uses the term CERCLA for simplicity.

2.5.1.1 Chromium

Hexavalent chromium is the contaminant of greatest concern in the 100-D Area. Two remediation systems help reduce the amount of chromium reaching the Columbia River: a pump-and-treat system in the north and in situ remediation in the southwest.

A chromium plume underlies most of the 100-D Area (Figures 2.5-4 and 2.5-5). The plume has two lobes that were formerly separate plumes: a south lobe with unknown sources near the former 183-DR filter plant, and a north lobe with sources in the central 100-D Area. The lobes are joined at the 100-µg/L contour (drinking water standard) and perhaps the 500-µg/L contour.

The south lobe of the chromium plume is oriented southeast-northwest, approximately perpendicular to the Columbia River. The plume has spread northward in recent years. The chromium concentrations here are the highest on the Hanford Site, with a fiscal year 2003 maximum value of 5,440 µg/L in well 199-D5-39 (Figure 2.5-6). Concentrations rose steeply in 2001 as the plume apparently moved northward, and levels have been variable since then. Wells in the south part of the plume, e.g., well 199-D5-43, declined in 2001 and 2002, also as a result of plume migration. Levels remained relatively low in fiscal year 2003.

The south chromium plume is intersected by the redox barrier, which terminates the highest-concentration portion of the plume (Figure 2.5-5). The area downgradient of the initial injection wells (those injected during 1999 and 2000) shows the largest impact of the remediation. For example, wells 199-D4-23 and 199-D4-38 showed steep declines in chromium concentrations in 2000 and 2001 (e.g., Figure 2.5-7). However, in nearby well 199-D4-39, chromium concentrations declined sharply in 2000 but have been highly variable since then. Sulfate concentrations have increased in all these wells in the past 2 years, indicating the presence of residual chemicals from dithionite injection into redox barrier wells. Areas downgradient of portions of the barrier created later (2001 through 2003) show less impact of remediation (e.g., wells 199-D4-83, 199-D4-84, and 199-D4-86; Figure 2.5-8). Well 199-D4-85 is an exception, and shows a sharp decline in chromium and an increase in sulfate in fiscal year 2003. Section 2.5.2 contains more information about the redox system and related impact on the aquifer.

Aquifer sampling tubes provide additional monitoring points along the 100-D Area shoreline (Figure 2.5-9). The highest concentrations are in the southwest chromium plume at the redox site, with a maximum 295 µg/L at tube site 42, sampled in December 2002. Chromium concentrations in several of the tubes in this region have declined in recent years, possibly due, in part, to remediation effects (PNNL-14444).

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

Chromium — 1.11
Nitrate — 0.72
Tritium — 0.04

The north lobe of the chromium plume was formerly oriented south-north, but has spread westward in recent years. Part of this plume is influenced by the 100-HR-3-D pump-and-treat system, which is designed to reduce the flux of chromium to the river (see Section 2.5.2.1).

Chromium concentrations have increased markedly in several wells that formerly were between the south and north plumes. For example, levels exceeded 1,000 µg/L in wells 199-D5-20 and 199-D5-41 in fall 2003 (Figure 2.5-10). These increases are believed to represent westward movement of the north plume, but could also be caused by mobilization of chromium from the vadose zone or movement of the south plume.

2.5.1.2 Strontium-90

Strontium-90 continued to be detected in a few wells in the 100-D Area in fiscal year 2003 at levels below the drinking water standard (8 pCi/L). In the north 100-D Area, several wells detected strontium-90 in the 1 to 3 pCi/L range, and well 199-D8-68 had a result of 7.1 pCi/L. Farther south, strontium-90 was detected in well 199-D5-15 at 3.08 pCi/L, but was undetected in nearby wells. There are no clear increasing or decreasing trends in the data.

2.5.1.3 Tritium

Fiscal year 2003 tritium concentrations 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 flowing northward 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, and that contamination is now moving north and northwest. The highest value in the 100-D Area was 23,700 pCi/L in well 199-D4-19, where concentrations are increasing (Figure 2.5-11). The tritium concentration in an aquifer tube near that well was 29,700 pCi/L.

Tritium concentrations continued to be above 10,000 pCi/L in the central 100-D Area (wells 199-D5-15, 199-D5-16, 199-D5-17, and 199-D5-18) in fiscal year 2003. Levels have been fairly stable in recent years.

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

An area of low tritium concentrations (<2,000 pCi/L) extends from the former 183-DR filter plant to the river and north to the 116-D-7 retention basins. This area formerly had low chromium concentrations as well, possibly because of dilution with clean water that leaked from the 182-D reservoir.

2.5.1.4 Nitrate

Nitrate distribution is generally similar to chromium in the 100-D Area; both constituents form two-lobed plumes. Nitrate concentrations continued to exceed the 45 mg/L drinking water standard in both lobes, with a maximum concentration of 107 mg/L in well 199-D2-6. The south lobe of the plume is truncated by the redox system, which converts the nitrate to nitrite. Nitrite concentrations tend to be elevated in redox injection wells and occasionally in downgradient wells and exceeded the drinking water standard (3.3 mg/L) in two injection wells.

Nitrate trends in the central 100-D Area do not follow chromium trends. Nitrate concentrations are not increasing as sharply as are chromium concentrations.

2.5.1.5 Sulfate

Like chromium and nitrate, the sulfate plume beneath 100-D Area has two lobes. Excluding wells influenced by the redox system, concentrations all were below the 250 mg/L secondary drinking water standard (maximum 196 mg/L in well 199-D2-6 in the south 100-D Area).

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 increased in wells 199-D4-23 and 199-D4-85 in fiscal year 2003 (Figure 2.5-12). The maximum concentration downgradient of the barrier was 390 mg/L in well 199-D4-23.

2.5.2 CERCLA Interim Groundwater Remediation for Chromium

Two interim remedial actions operate in the 100-D Area: a pump-and-treat system in the north 100-D Area and an in situ remediation treatment system in the southwest 100-D Area.

2.5.2.1 Pump-and-Treat System

The 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 is pumped to the 100-H Area where it is treated and injected into the aquifer. Details regarding 100-HR-3-D pump-and-treat operations may be found in an upcoming interim action report that will be issued by the U.S. Department of Energy (DOE).

Remedial action monitoring is described in DOE/RL-96-90. Figure 2.5-1 displays well locations and Appendix A lists sampling frequencies and constituents.

Progress During Fiscal Year 2003

The 100-D Area pump-and-treat system is reducing overall contamination in the operable unit by removing contaminant mass. During fiscal year 2003, the system extracted ~241 million liters of groundwater from the 100-D Area, removing ~39.2 kilograms of hexavalent chromium. The withdrawn water was piped to the 100-H Area where it was treated and injected into the aquifer.

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 record of decision sets 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).

A total of ~161.3 kilograms of hexavalent chromium has been removed from the plume targeted for interim action 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 is not including the chromium plume in the southwest 100-D Area nor in the vadose zone.

All of the wells scheduled for sampling under CERCLA were sampled as scheduled in fiscal year 2003. Two seeps could not be sampled (see Appendix A).

Influence on Aquifer Conditions

Chromium concentrations remain elevated in the north 100-D Area. The plume continued to move in fiscal year 2003 (see Section 2.5.1.1).

Hexavalent chromium concentrations in compliance wells vary inversely with river stage. The ranges of concentration observed in fiscal year 2003 were similar to those observed in fiscal year 2002. Figure 2.5-13 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 fiscal year 2003. Concentrations were lowest in the spring and early summer.

During fiscal year 2003, the pump-and-treat system extracted ~241 million liters of groundwater from the 100-D Area, removing ~39.2 kilograms of hexavalent chromium.

Results of performance monitoring are incorporated with the discussion of general contamination in Section 2.5.1.

Results of operational monitoring, and additional details about the pump-and-treat system, will be included in an annual report on the 100-HR-3, 100-KR-4, and 100-NR-2 pump-and-treat systems.

2.5.2.2 In Situ Redox Manipulation System

This treatment system uses a change in reduction-oxidation (redox) potential to reduce dissolved hexavalent chromium in groundwater to trivalent chromium, a much less soluble 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 and Appendix A.

Progress During Fiscal Year 2003

Treatment of the aquifer surrounding the last five treatment zone wells was completed in fiscal year 2003. The treatment zone is now ~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 one of the seven compliance wells at the end of fiscal year 2003. Institutional controls continue to protect the public by preventing exposure to hexavalent chromium in the groundwater. Sampling and analysis of groundwater from compliance wells, monitoring wells, aquifer sampling 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 provides information leading to selection of the final remedy. The network was expanded from nine wells to eleven wells in fiscal year 2003. 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 and the development of a low groundwater mound below the reservoir.

Six wells were not sampled one of the four quarters scheduled (see Appendix A). Three aquifer tubes could not be sampled because they did not produce water.

DOE completed the redox treatment barrier in fiscal year 2003. Chromium concentrations declined in some downgradient wells.

Influence on Aquifer Conditions

Chromium concentrations in compliance wells have been variable or decreasing since monitoring began (see Section 2.6.1.1 for more discussion and Figure 2.5-7 for examples of trends). Wells 199-D4-23, 199-D4-38, and 199-D4-85 show overall decreasing trends. Wells 199-D4-39, 199-D4-83, and 199-D4-86 show large variations in chromium concentrations. Chromium concentrations in well 199-D4-84 are fairly steady. Only in well 199-D4-86 did the concentration of hexavalent chromium decrease to less than the goal of 20 µg/L in fiscal year 2003. Chromium concentrations in the redox compliance wells are not affected as strongly by bank storage effects as are the pump-and-treat compliance wells. Specific conductance and chromium concentrations in the redox compliance wells do not correlate with water levels.

In recent years, chromium concentrations increased unexpectedly within the redox treatment zone in wells 199-D4-26, 199-D4-31, and 199-D4-37, based on operational monitoring data (not in the Hanford Environmental Information System database). The remaining areas of the in situ redox manipulation treatment zone appear to be intact and functioning as designed. DOE is working with the regulators to develop a corrective action to the apparent breakdown of portions of the barrier, as well as to the movement of chromium past the north end of the redox barrier.

Other effects of the redox system observed in wells within and downgradient of the treatment zone include decreases in dissolved oxygen and nitrate and increases in arsenic, gross beta, nitrite, sulfate, and some metals. The increases in metals are due to increased solubility in the reducing aquifer conditions. Increased sulfate is a result of incomplete recovery of the reaction products following the reduction treatment. Elevated gross beta activity (up to 466 pCi/L) is due to potassium-40 naturally present in the injected solution.

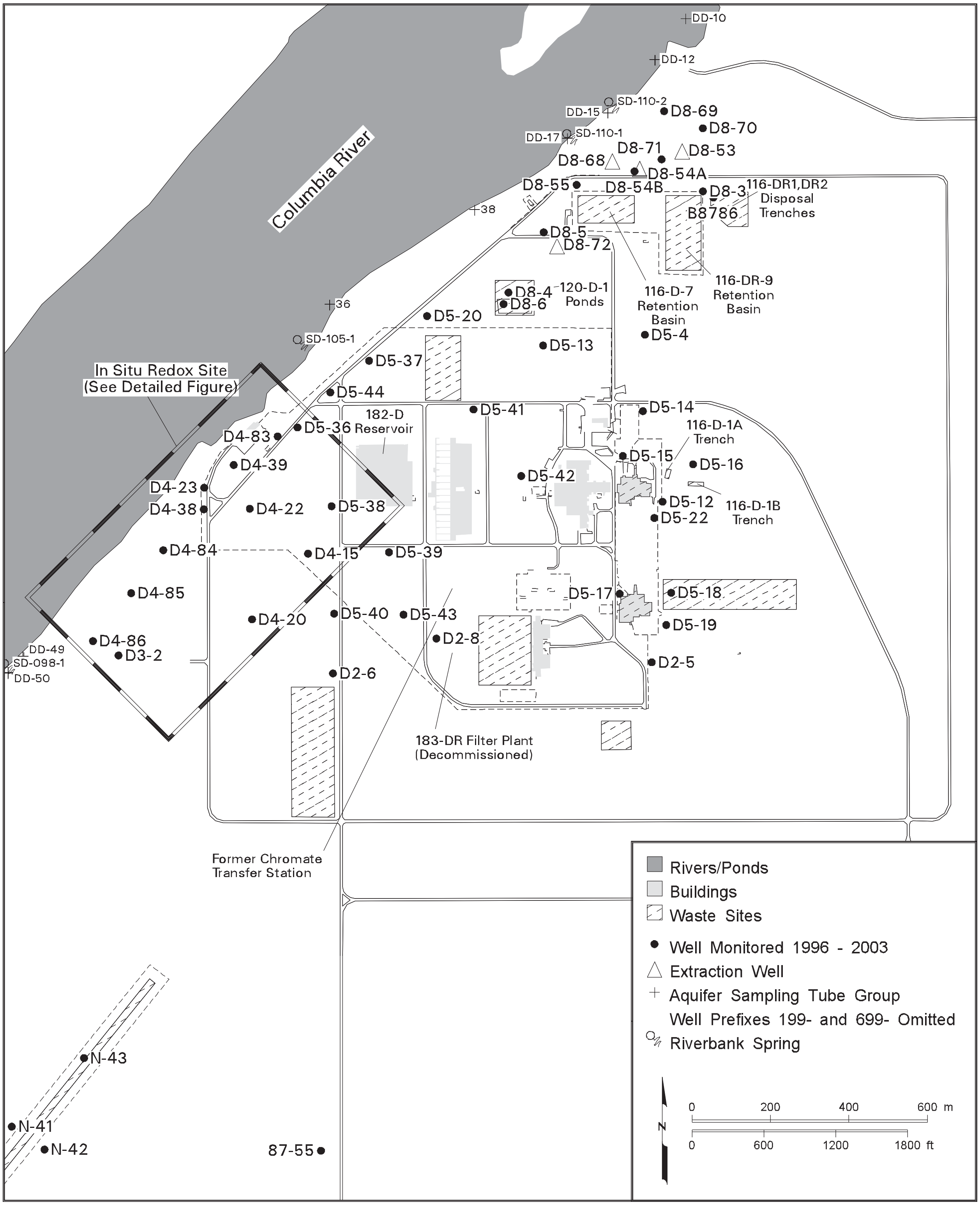

Figure 2.5-1. Groundwater Monitoring Wells in the 100-D Area

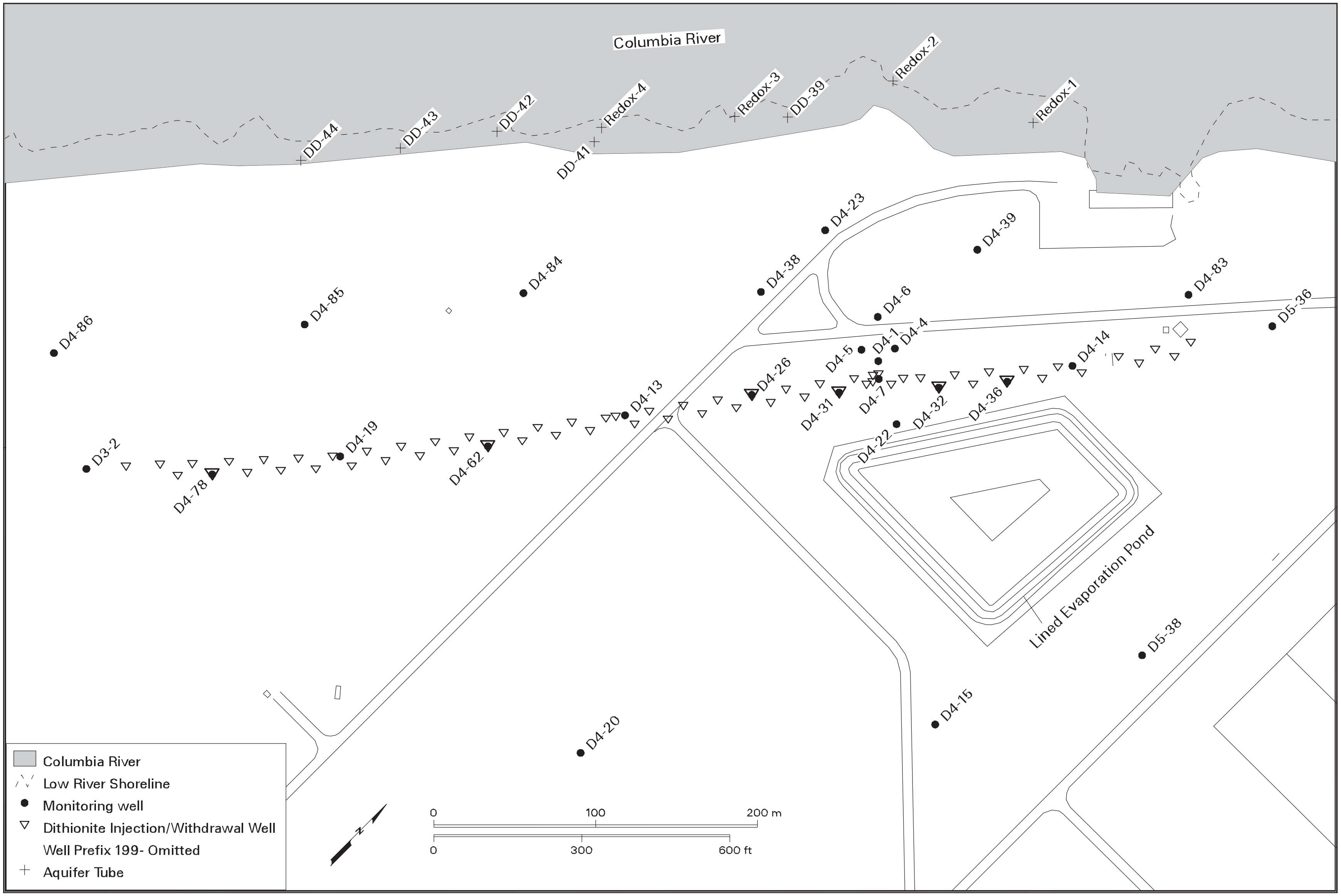

Figure 2.5-2. Groundwater Monitoring Wells Near the Redox Site in 100-D Area

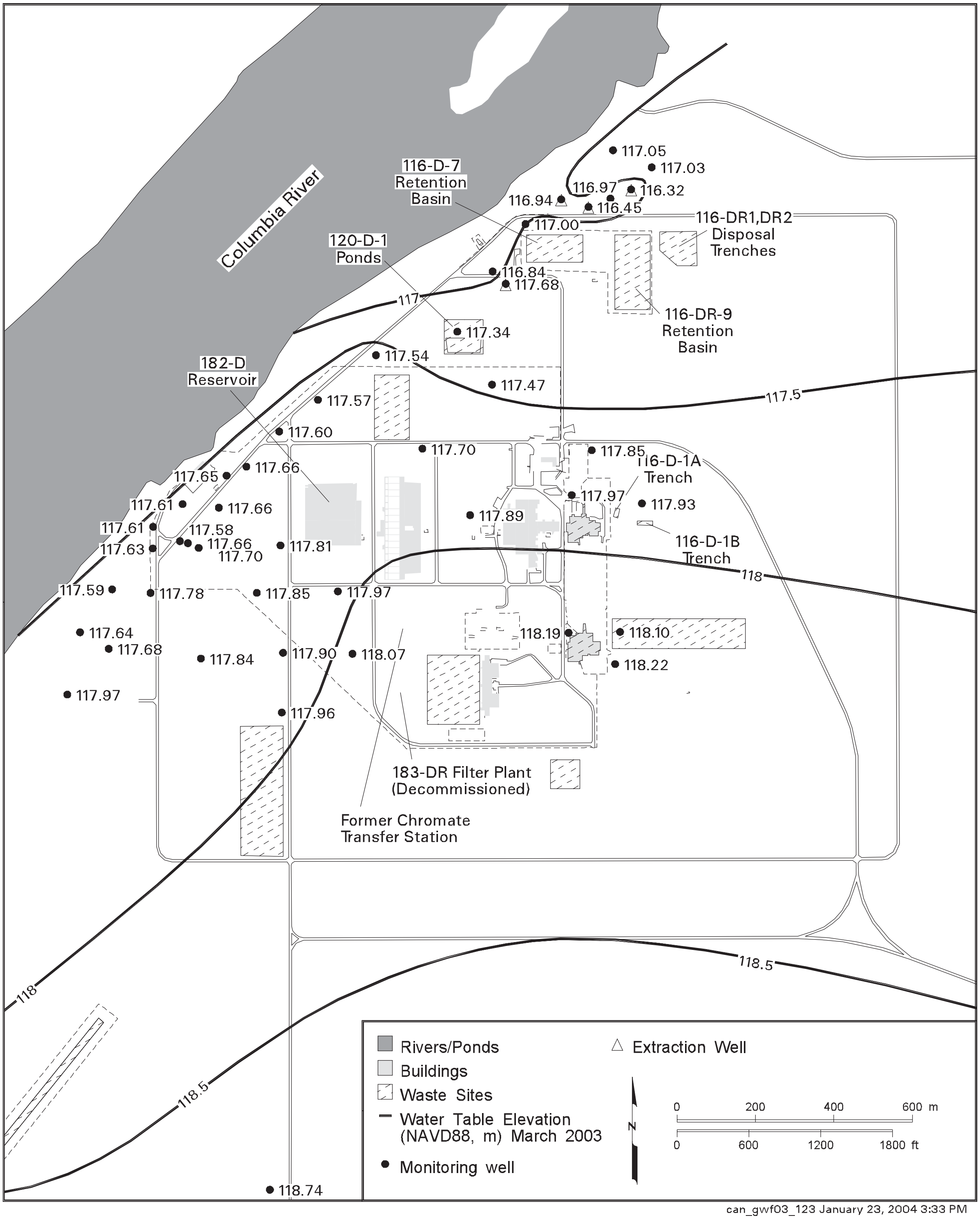

Figure 2.5-3. 100-D Area Water-Table Map, March 2003

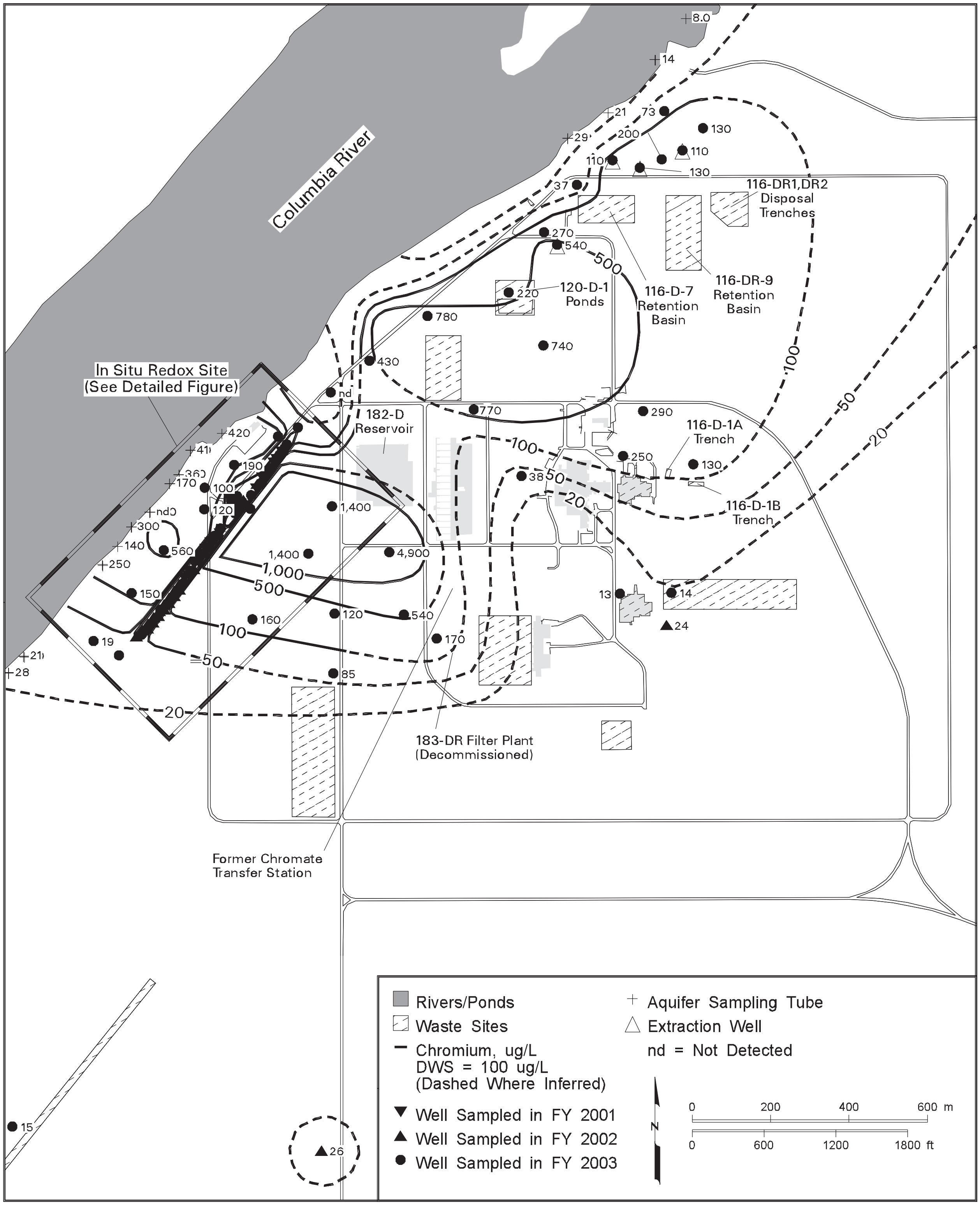

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Figure 2.5-4. Average Dissolved Chromium Concentrations in the 100-D Area, Top of Unconfined Aquifer

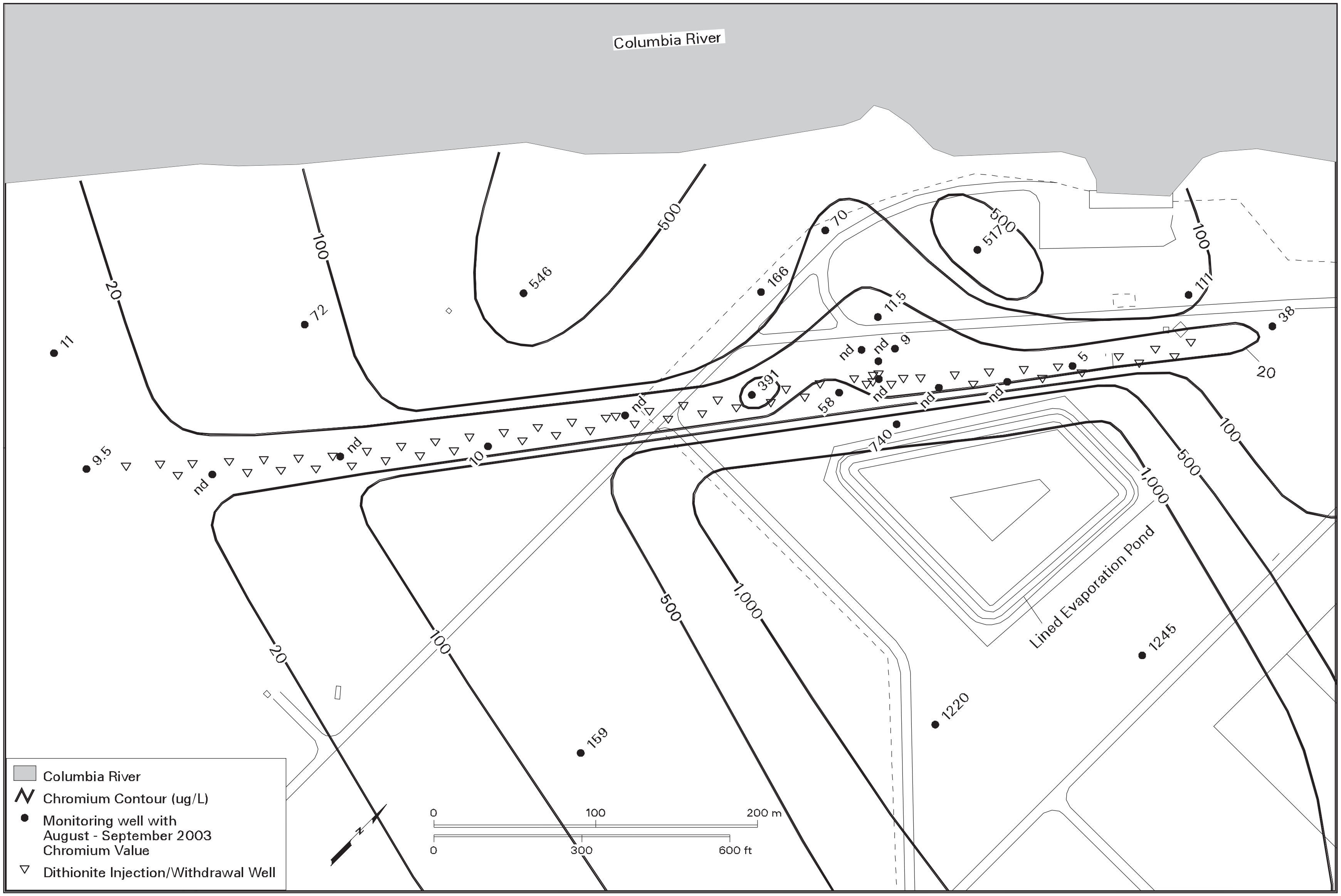

Figure 2.5-5. Average Dissolved Chromium Concentrations Near the Redox Site, 100-D Area, August-September 2003

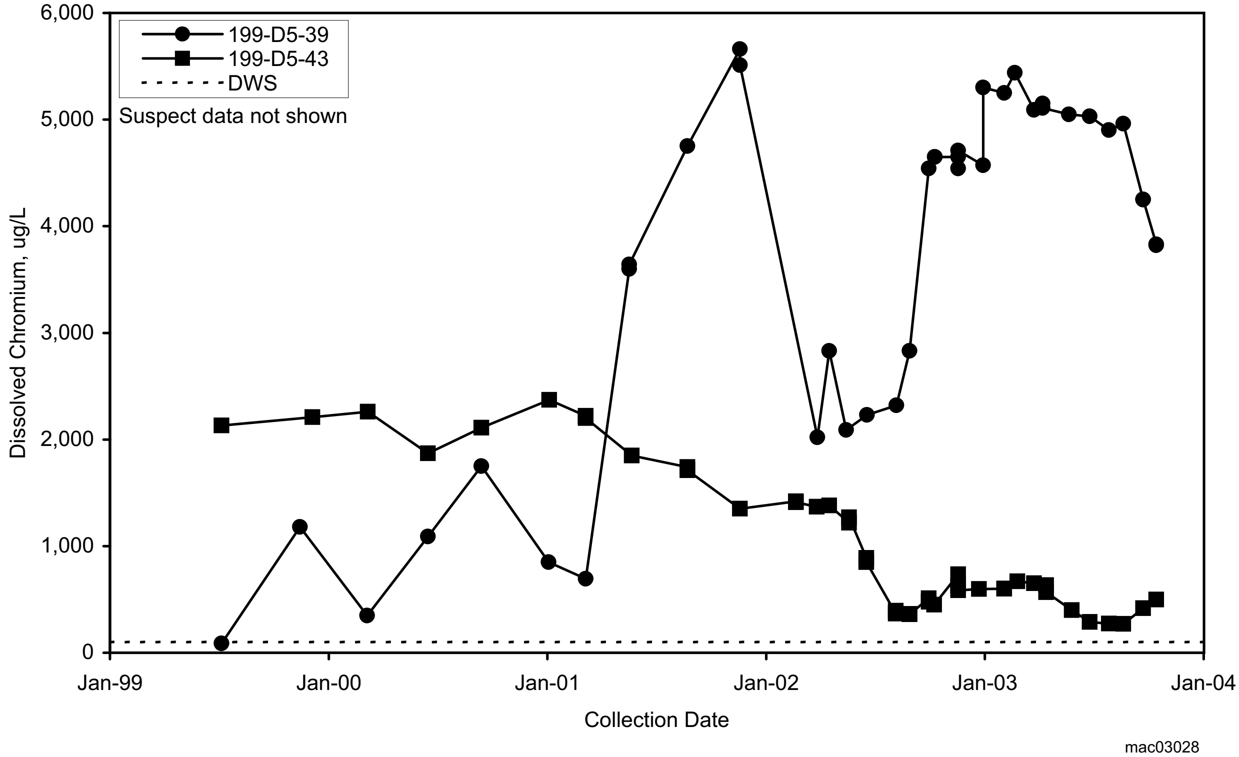

Figure 2.5-6. Dissolved Chromium Concentrations in South 100-D Area

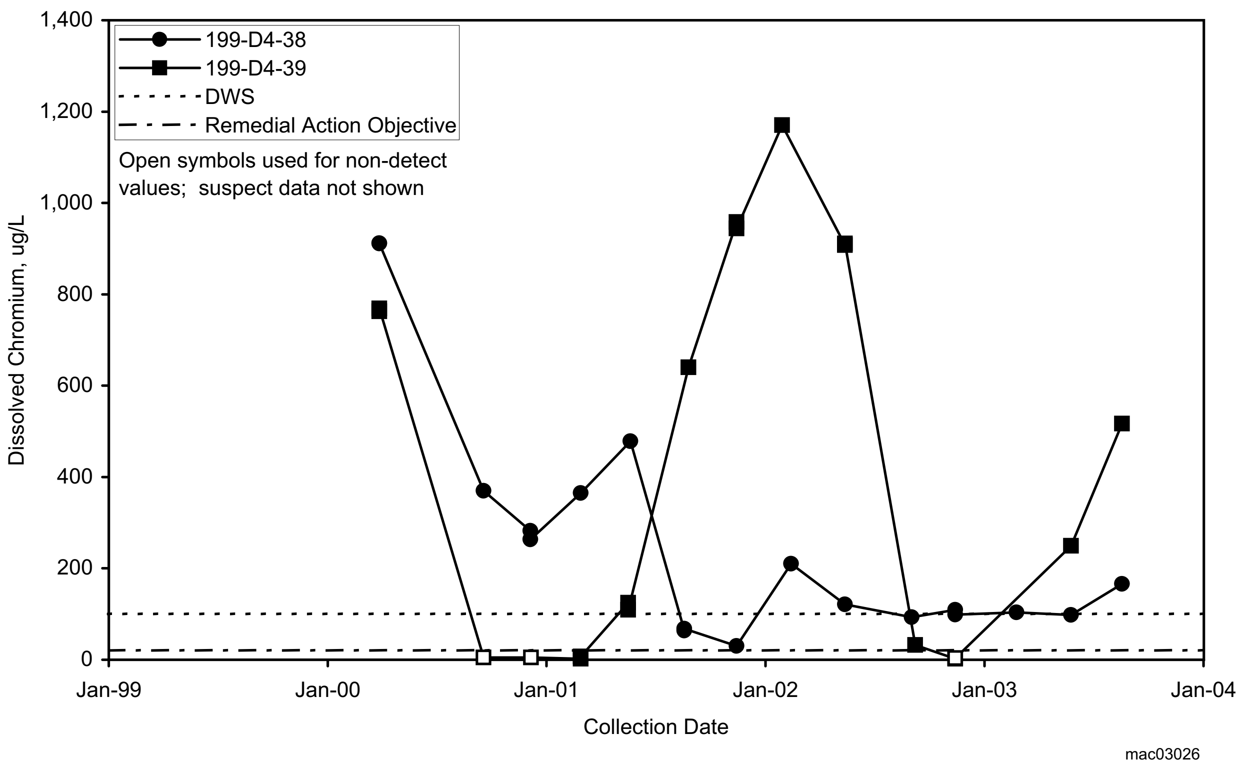

Figure 2.5-7. Dissolved Chromium Concentrations in Compliance Wells Downgradient of Early-Emplaced Redox Barrier

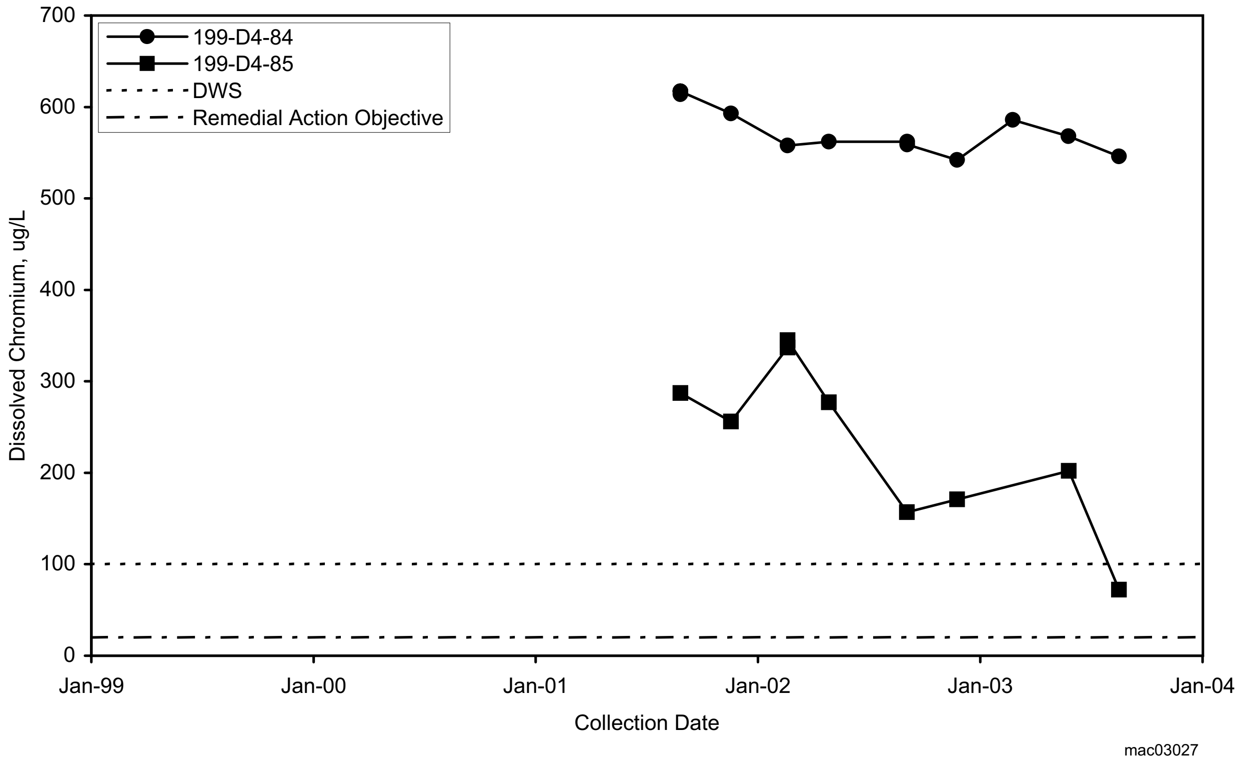

Figure 2.5-8. Dissolved Chromium Concentrations in Compliance Wells Downgradient of Late-Emplaced Redox Barrier

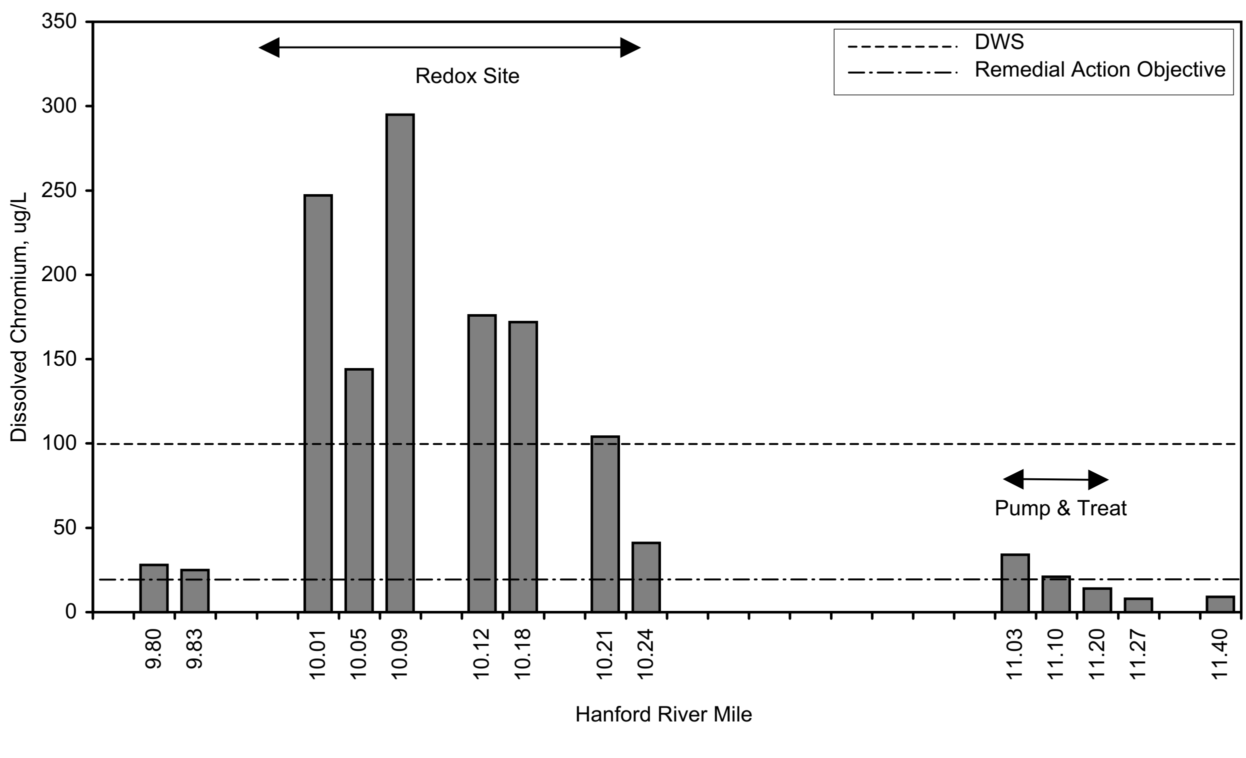

Figure 2.5-9. Hexavalent Chromium in Aquifer Tubes at 100-D Area, Fiscal Year 2003

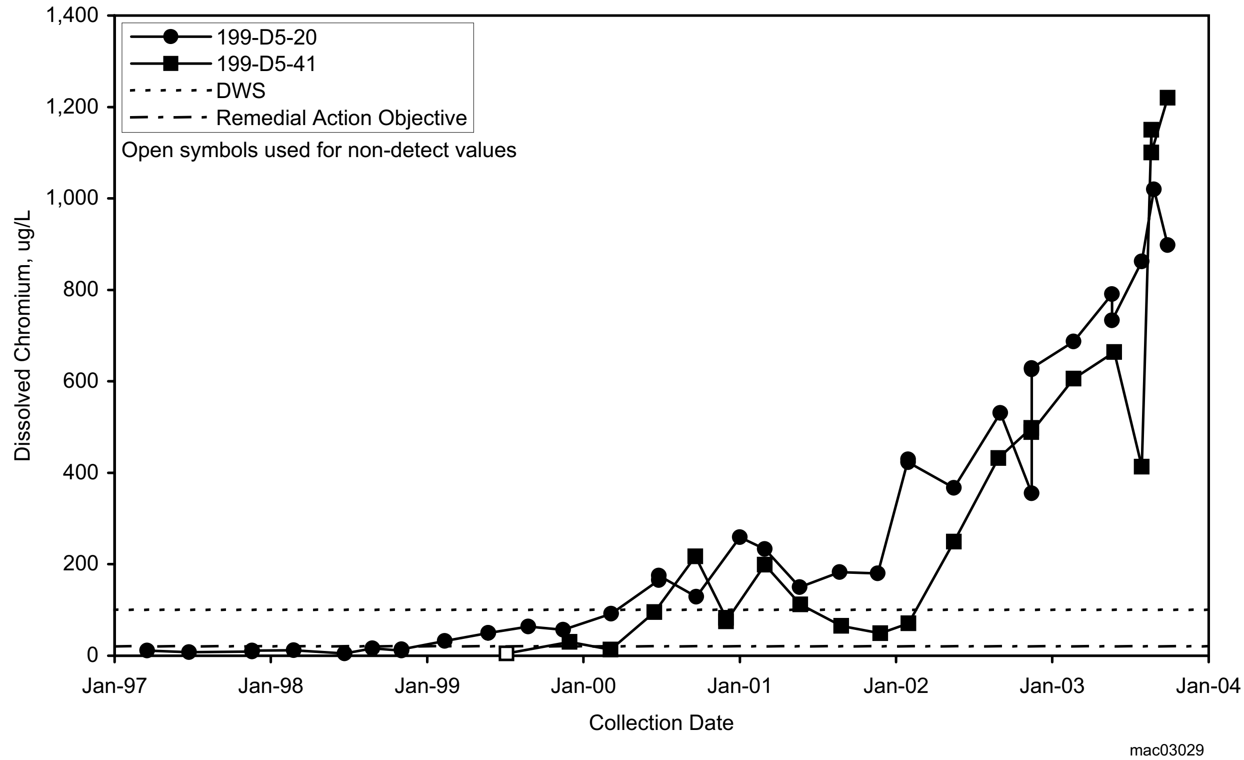

Figure 2.5-10. Dissolved Chromium Concentrations in Central 100-D Area

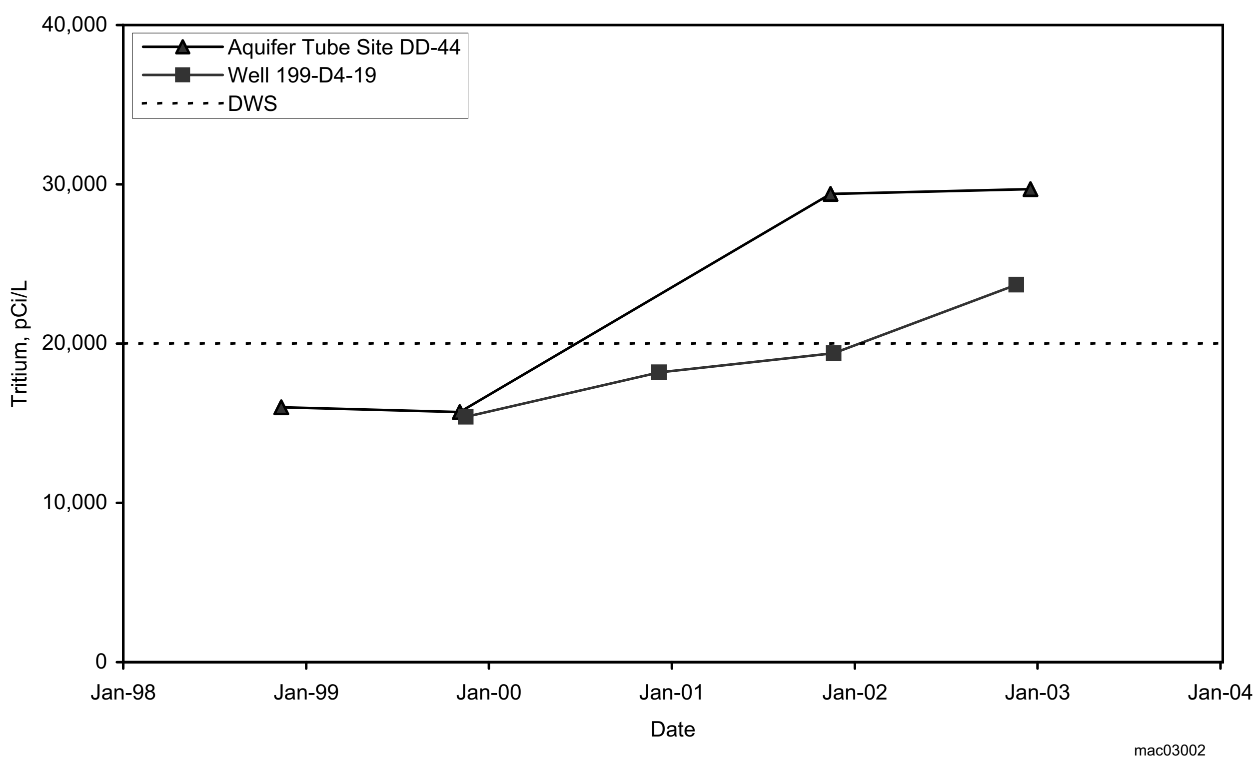

Figure 2.5-11. Tritium Concentrations in the South 100-D Area

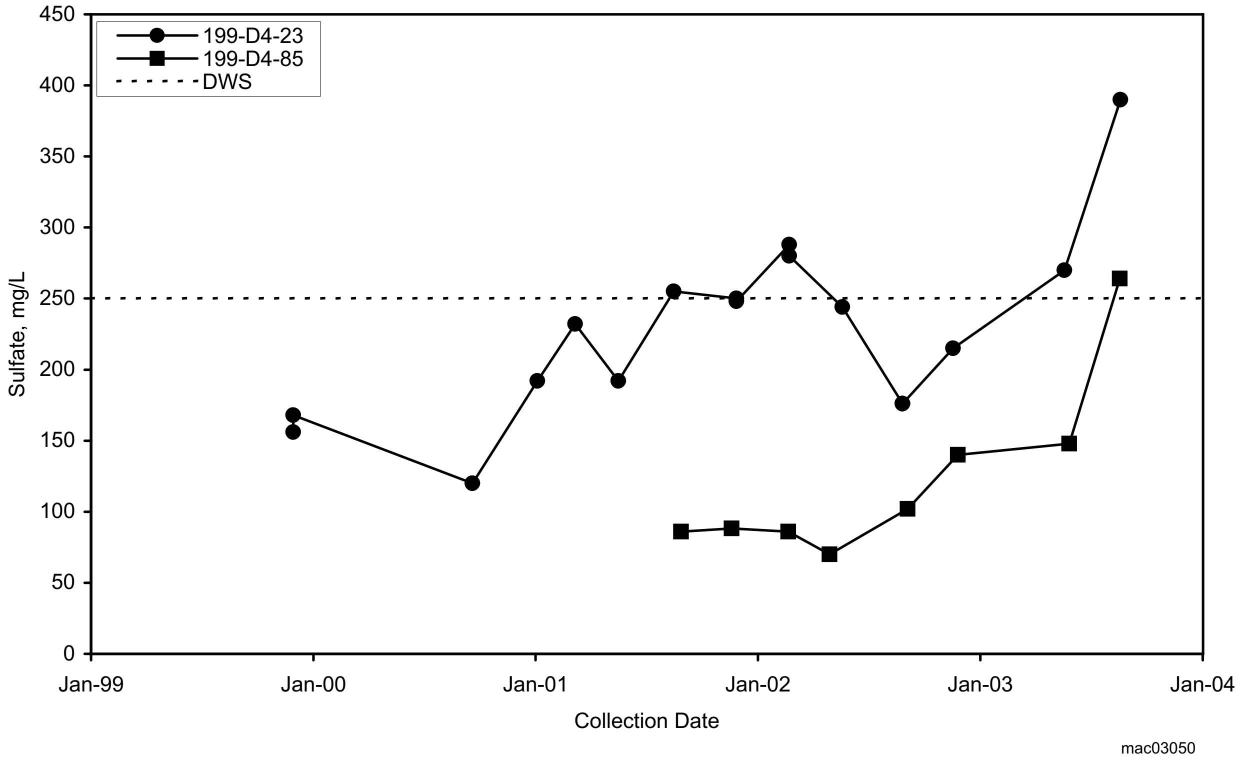

Figure 2.5-12. Sulfate Concentrations Downgradient of the Redox Barrier

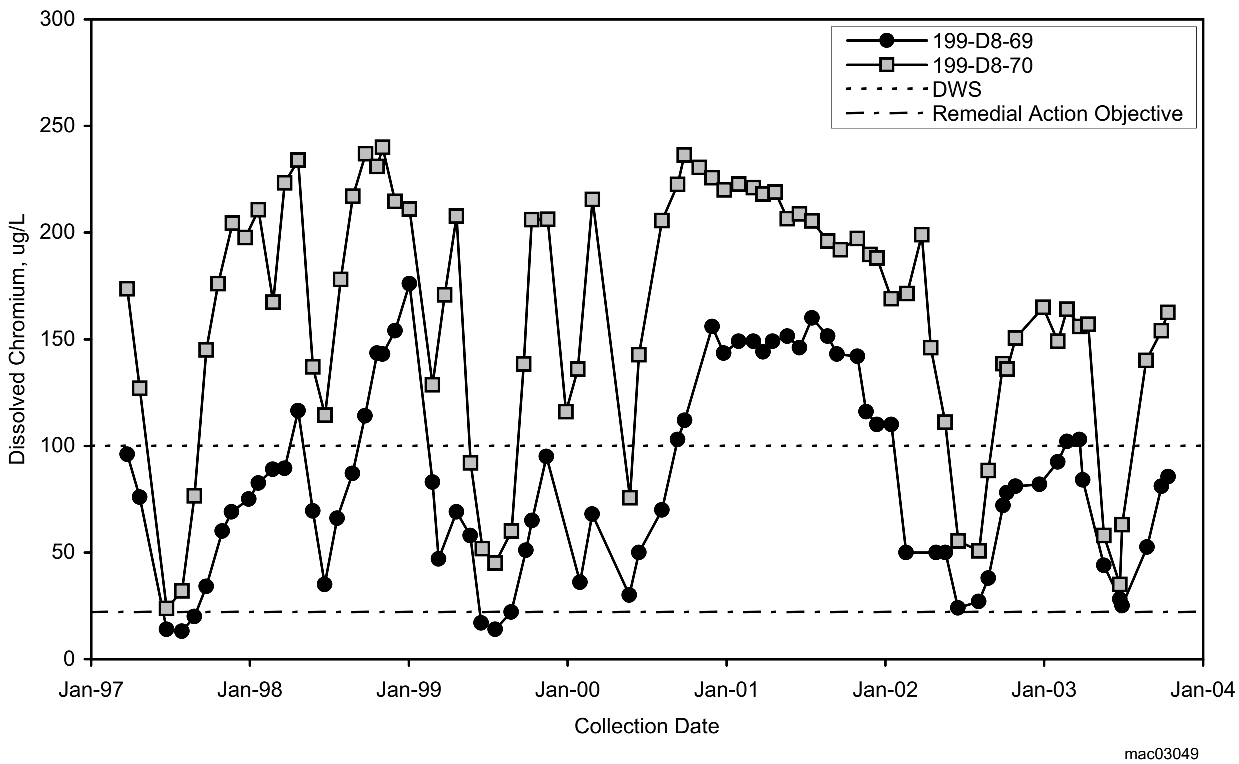

Figure 2.5-13. Dissolved Chromium Concentrations in Compliance Wells for the 100-HR-3 Pump-and-Treat System at 100-D Area