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Pacific Northwest National Laboratory
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Results of Tritium Tracking and Groundwater Monitoring at the Hanford Site 200 Area State-Approved Land Disposal Site—Fiscal Year 2003

D. B. Barnett
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November 2003

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RL01830

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Summary

The Hanford Site 200 Area Effluent Treatment Facility (ETF) processes contaminated aqueous wastes derived from Hanford Site facilities. The treated wastewater occasionally contains tritium, which is not removed by the ETF, and is discharged to the 200 Area State-Approved Land Disposal Site (SALDS). During fiscal year (FY) 2003 to date (through August 31, 2003), approximately 96-million liters (25.3-million gallons) of water have been discharged to the SALDS.

Groundwater monitoring for tritium and other constituents, and water-level measurements are required by the state-issued permit at the SALDS. The current network consists of 3 proximal monitoring wells and 16 tritium-tracking wells. Proximal wells were sampled in October 2002, and January, February, April, and September of 2003. Tritium-tracking wells were sampled in January and September of 2003, but September results were delayed because of fire hazards near the wellheads. Water-level measurements in three wells nearest the SALDS indicate the continuation of a small hydraulic mound beneath the SALDS facility as a result of discharges. This feature is directing groundwater flow radially outward a short distance before the regional northeasterly flow predominates. This condition also places several wells south of the SALDS hydraulically downgradient of the facility. Some of the wells south of the SALDS in the tritium-tracking network have dried or are projected to soon be dry. Well 299-W7-6 went dry during FY 2003, preventing collection of the September sample from this well. Likewise, difficulties in obtaining a sample from well 299-W7-9 suggest that this well may have produced its final sample in January 2003. So far, the tritium-tracking network remains adequate to track effluent from the SALDS, but the loss of these wells could affect numerical modeling results.

Average tritium activities decreased in all three SALDS proximal wells during FY 2003, compared with FY 2002. Sporadic detections in well 299-W7-5 suggest that tritium from SALDS may be reaching the northern edge of the 200-West Area (due south of the facility), or that this well is peripherally influenced by the tritium plume from the 200-West Area. Maximum FY 2003 tritium activities for SALDS proximal wells were 189,000 pCi/L in well 699-48-77A, (February 2003), 430,000 pCi/L in well 699-48-77C (October 2002), and 220,000 pCi/L in well 699-48-77D (October 2002).

Concentrations of all chemical constituents with permit limits were well within those limits during all of FY 2003. Acetone, benzene, tetrahydrofuran, cadmium, chloroform, lead, and mercury were below method detection limits in all samples. Concentrations of major cations and anions are mostly below background concentrations due to dilution by the clean water discharged to the SALDS.

Comparison of head distribution in March 2003 and reported FY 2003 tritium activities, with numerical predictions of these quantities for 2000 and 2005, suggests that modeling performed in 1997 only slightly overestimated the areal spread of tritium around the SALDS to date. Contouring of March 2003 groundwater flow potential near the SALDS (but away from the mound) appears to show a more easterly component compared with both 2000 and 2005 model times and the FY 2002 potential map.

Acronyms

DMR	Discharge Monitoring Report
ETF	Hanford Site 200 Area Effluent Treatment Facility
FY	fiscal year
LLBG	low-level burial ground
MDA	minimum detectable activity
MDL	method detection limit
SALDS	200 Area State-Approved Land Disposal Site
TDS	total dissolved solids

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1.0 Introduction

Treated water from the Hanford Site 200 Area Effluent Treatment Facility (ETF) is discharged to a drainfield as allowed by State Waste Discharge Permit ST-4500 (ST-4500; Ecology 2000). The permit allows disposal of tritium to the site, which is named the State-Approved Land Disposal Site (SALDS), and is located immediately north of the 200-West Area of the Hanford Site (Figure 1). In accordance with ST-4500, the groundwater in the vicinity of the SALDS is routinely sampled, and water levels in wells are measured. The permit also requires the submission of an annual tritium-tracking report and a groundwater monitoring plan that covers the 5-year period of the permit. The current plan (Barnett 2000) provides additional guidance for selecting and reporting groundwater analyses. The results of the groundwater sampling and analysis are also reported in quarterly Discharge Monitoring Reports issued by Fluor Hanford.

1.1 Objectives and Scope

This report presents the results of groundwater monitoring and tracking of tritium-enriched discharges in groundwater for the SALDS facility during fiscal year (FY) 2003. The period covered by the data in this document is October 1, 2002 through September 2, 2003. The report also provides the updated background information on the facility operations necessary to understand the results of the groundwater analyses. Interpretive discussions and recommendations for future monitoring are also provided where possible. Semiannual results for four tritium-tracking wells (see Section 3) had not been received at the time of this report due to fire restrictions near the wellheads and laboratory delays. These results will be included in the FY 2004 report.

1.2 Background

The background information is mostly based on a synopsis of *Groundwater Monitoring and Tritium-Tracking Plan for the 200 Area State-Approved Land Disposal Site* (Barnett 2000). New information on hydrogeology, modeling comparison, and discharges is also provided where available.

The primary requirements of the permit are that a groundwater monitoring plan must be regulator-approved and that analytical results must be compared annually with permit-prescribed limits; these comparisons are presented in tabular form and discussed in Section 3 of this report. The groundwater monitoring plan requires:

- Tracking changes in groundwater quality associated with the SALDS discharges
- Determining how these changes have occurred, e.g., from discharges versus soil chemistry
- Tracking of the migration rate of tritium in groundwater originating from the SALDS
- Comparison of model predictions with observation for purposes of refining predictive capability
- Correlation of discharge events at SALDS with analytical results from groundwater monitoring
- Ensuring that groundwater data are accurately interpreted.

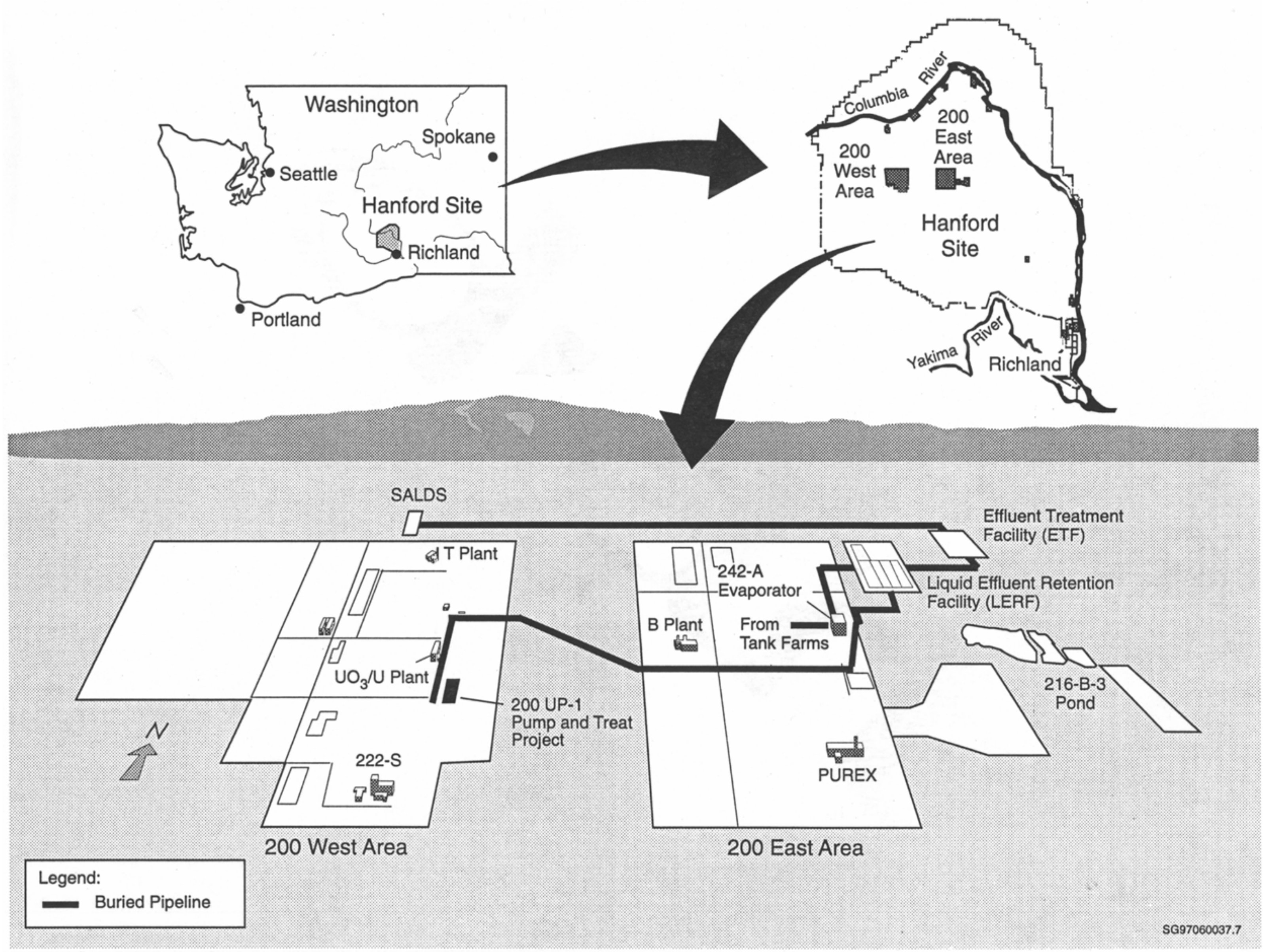


Figure 1. Location of the State-Approved Land Disposal Site and Related Infrastructure

The groundwater monitoring well network (Figure 2) was designed to address these objectives using existing wells shared with other nearby facilities, e.g., low-level burial grounds (LLBGs), and dedicated wells drilled specifically for monitoring SALDS.

1.2.1 Hydrogeologic Setting

The nature of the geologic formations beneath the SALDS facility accounts for peculiarities in the movement of the SALDS effluent downward to the groundwater, and is described in detail by Barnett (2000). Groundwater chemical analyses indicate that the well farthest from the SALDS (699-48-77A) responds to SALDS discharges several months earlier than well 699-48-77D, and approximately 2 years earlier than in well 699-48-77C (see Section 3). Of particular importance are the carbonate-cemented horizons of the Cold Creek Unit (formerly known as the Plio-Pleistocene Unit—see DOE-RL, 2002) that lies within the vadose zone a few feet below the bottom of the SALDS drainfield. This stratum consists of a thick, but locally discontinuous layer of highly impermeable silt, gravel, and sand with significant interstitial calcium carbonate and other minerals as cementation. Effluent from the SALDS is diverted southward along the gentle dip of this horizon until a discontinuity or significant fracture is reached, whereupon it migrates further downward into the Ringold Formation. This circumstance allows the infiltrating effluent to reach the southernmost proximal well (699-48-77A) first.

Sedimentary units beneath the SALDS (i.e, Ringold Formation, Cold Creek Unit, and Hanford formation) have been shown to host leachable minerals, such as calcium carbonate and sulfate-bearing minerals (Reidel and Thornton 1993; Serne et al. 2002). All three of these strata occur beneath the SALDS, extending from near the surface to approximately 75 m depth in the vadose zone. Natural mineral accumulations in these formations have contributed a considerable load of dissolved solids to the groundwater in the vicinity of the SALDS as the effluent infiltrates to the water table. An updated discussion of this topic, in terms of its relation to SALDS operations, is provided in Section 4.

1.2.2 Groundwater Modeling

Permit ST-4500 requires an updated numerical groundwater model run at least once during a permit cycle (every 5 years) to predict tritium movement and distribution in the aquifer resulting from SALDS discharges. The permit also requires that the model be reapplied "within 6 months of detection of the tritium plume in a new monitoring well." This requirement indicates that the numerical model will be reapplied when the tritium plume associated with the SALDS is positively identified in a location not predicted by the most recent model run, or within a well not previously affected by an incursion of SALDS-derived tritium.

The most recent model application was conducted in 1997 (Barnett et al. 1997), two years after the beginning of SALDS discharges. The model output graphically illustrates the predicted head distribution and tritium concentrations in groundwater near the SALDS for selected time frames between 1996 and 2095. Section 4 compares the most recent results of monitoring with the contemporaneous model predictions.

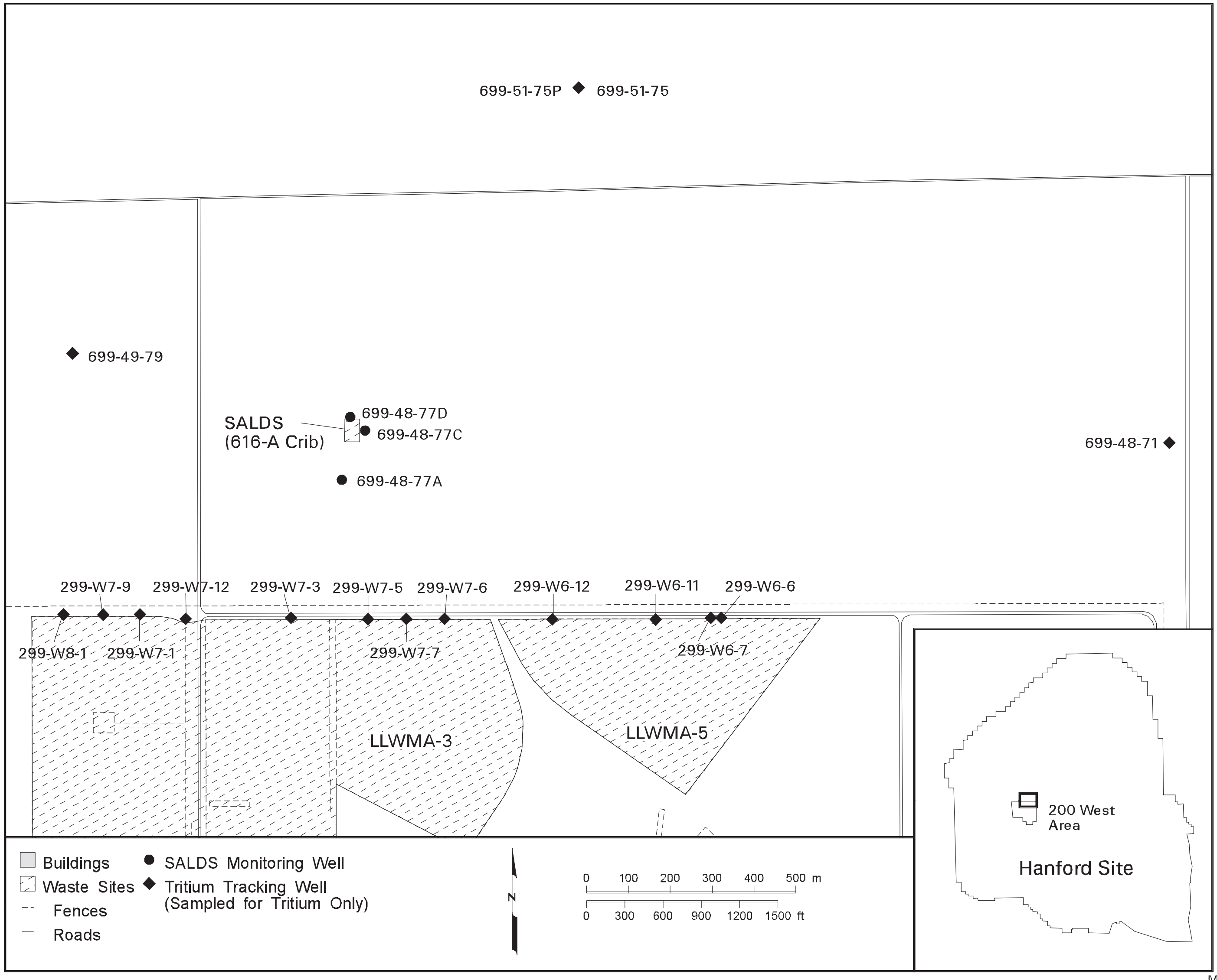


Figure 2. Locations of SALDS Groundwater-Monitoring and Tritium-Tracking Network Wells

1.2.3 SALDS Discharge Information

During FY 2003 (from October 1, 2002 through August 2003), approximately 96-million liters (25.4-million gallons) of water were discharged to the SALDS, compared with approximately 91-million liters (24-million gallons) discharged during all of FY 2002. July 2003 was the month with the highest discharge total – approximately 14-million liters (3.7 million gallons). Total discharge volume to the SALDS is over 600-million liters (approximately 160-million gallons) since December 1995 (Figure 3).

The first release of clean, tritium-rich water from the ETF to the SALDS occurred in December 1995. During that month and the subsequent six months, a total of 218 curies of tritium were released, an amount that comprises about 65% of the total inventory released to date. Although discharge volumes of clean water have remained relatively constant during the past 6 years (average ~95M liters [~25M gallons] per year), tritium consignments discharged to the site have been sporadic since the 7-month period at the beginning of operations, and are now punctuated by annual campaigns of the 242-A Evaporator, which supplies most of the tritium to the process.

Calculations of the total quantity of tritium discharged to the SALDS during FY 2003 were unavailable as of this writing. Total tritium quantity discharged to the SALDS from December 1995 through the end of FY 2002 was approximately 333 curies.

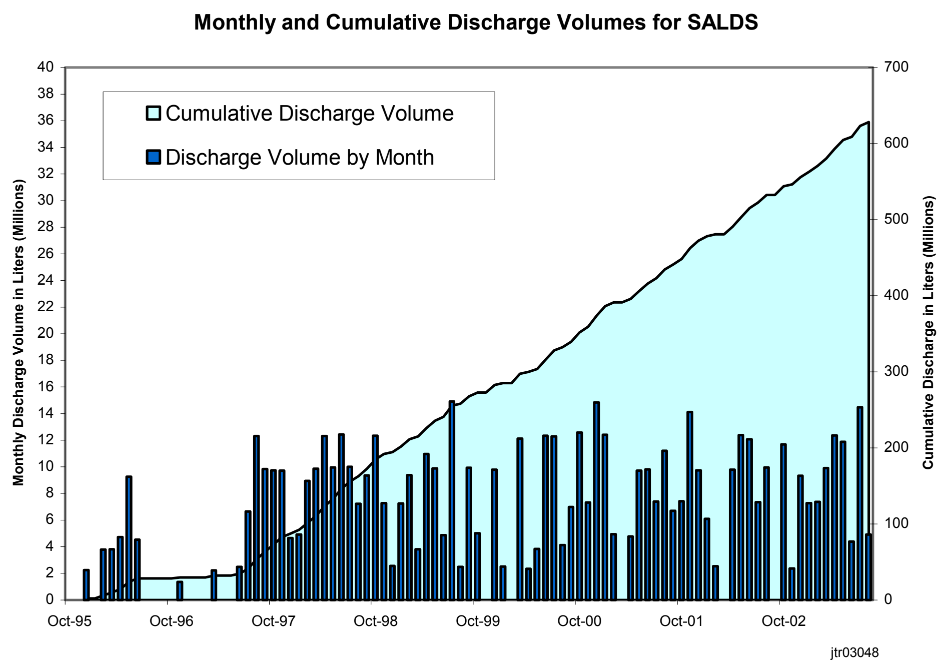


Figure 3. Monthly and Cumulative Discharge Volumes for SALDS through August 2003

2.0 Results of FY 2003 Water-Level Measurements

Measurements of water levels in wells surrounding the SALDS are necessary for local and regional interpretation of head and potential groundwater flow directions. These measurements are used in combination with groundwater chemistry analyses to feed conceptual and predictive models to forecast the possible movement of tritium from the SALDS facility.

2.1 Schedule of Water-Level Measurements

Water levels are measured in all wells prior to each sampling event, and have been measured monthly since January 1997 in the proximal SALDS wells (699-48-77A, 699-48-77C, and 699-48-77D). Because SALDS proximal and tritium tracking wells are also sampled for other programs (LLBG and surveillance), water levels in each well may be measured several times per year.

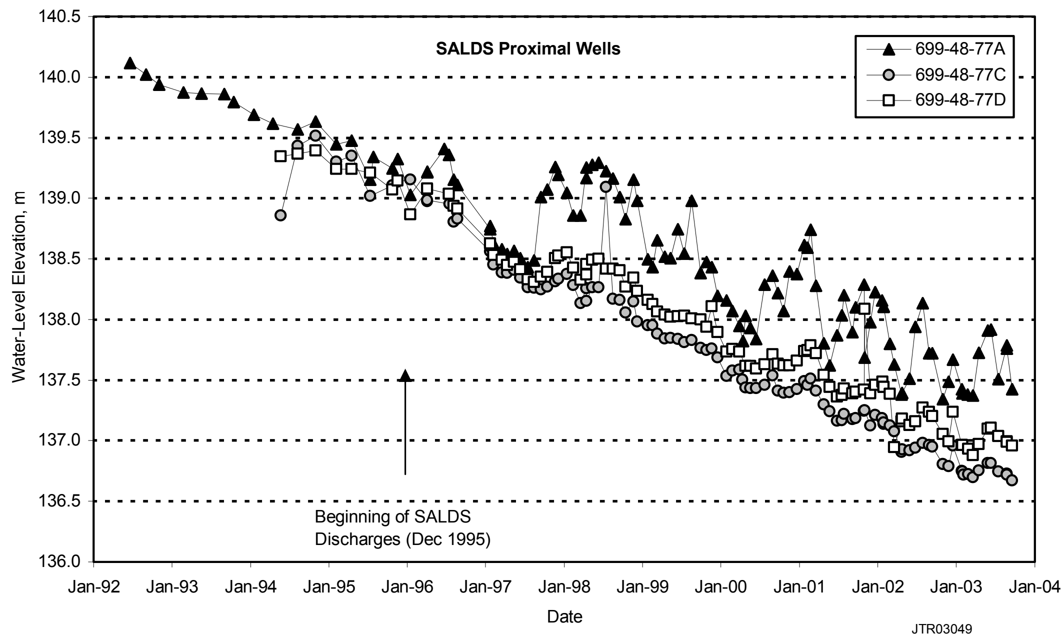
Water levels have fallen in recent years to the point where some tritium-tracking wells have become unserviceable for sampling (see Section 3.1). As this occurs, water-level measurement in these wells will also be discontinued.

2.2 Measurement Results and Hydraulic-Head Distribution

Current hydrographs (through August 2003) for the SALDS proximal wells and tritium-tracking network, grouped by relative position to the SALDS, are shown in Figures 4 through 6. Since late 1997, hydraulic head in well 699-48-77A has remained higher than other nearby wells as a result of the continuing general decline in water levels in the 200-West Area and the increased head near the SALDS from SALDS discharges. The occasional exceptions are the wells southwest of the SALDS. In these wells, water-level elevations are only intermittently lower than those in well 699-48-77A, depending on the magnitude and timing of discharges to the SALDS.

Deep and shallow tritium-tracking network wells 299-W6-6 and 299-W6-7, respectively, indicate that almost no vertical gradient exists in this portion of the aquifer away from the SALDS vicinity (see Figure 6). Well 299-W6-7 is completed at the water table; well 299-W6-6 is completed 49 meters deeper in the aquifer. The slight departure from trend of well 299-W6-6 in March of 2002 may be due to a measurement error or a barometric response.

Near the SALDS, there remains a consistently downward hydraulic potential in the uppermost aquifer, as indicated by the head differences between the shallow proximal wells 699-48-77A and 699-48-77D, and deep proximal well 699-48-77C (see Figure 4).



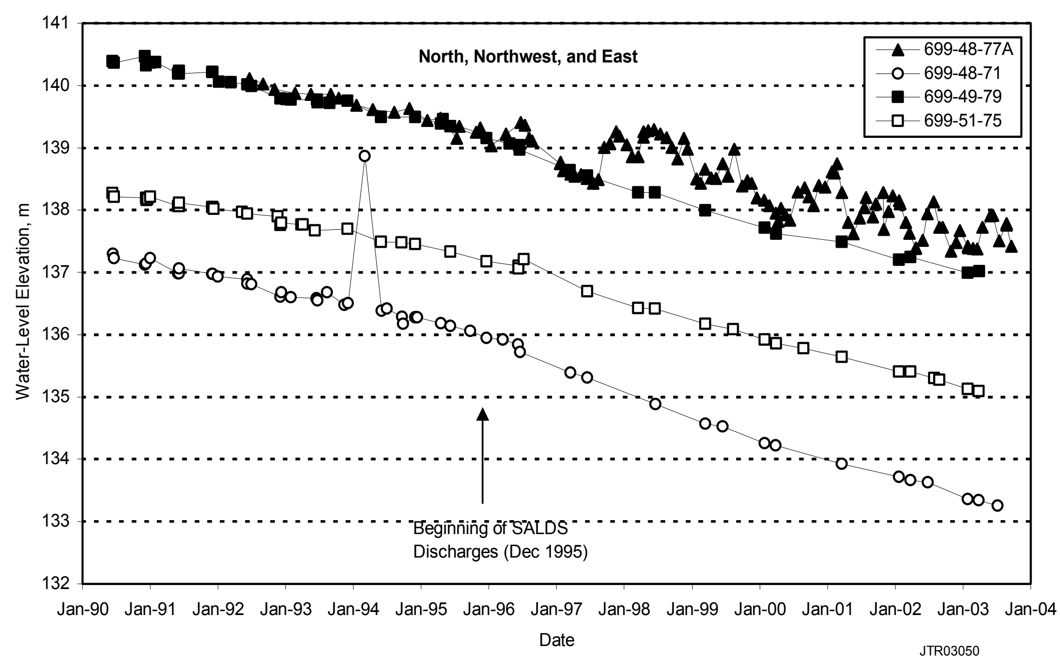
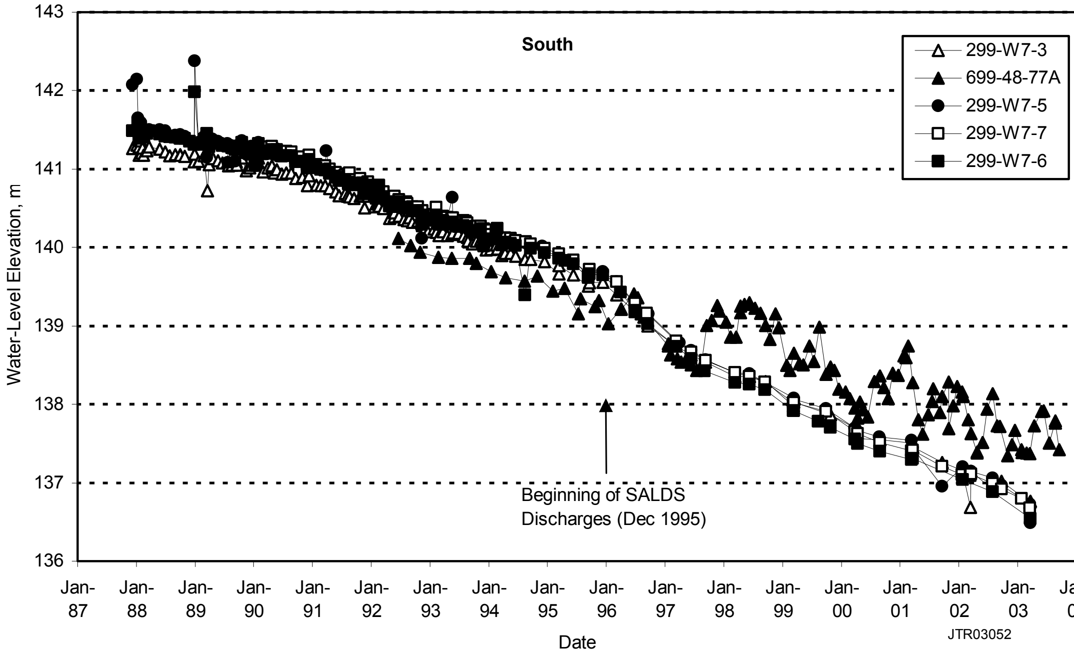


Figure 4. Hydrographs of SALDS Proximal Wells (top) and Tritium-Tracking Wells North, Northwest, and East of the SALDS, Compared with Well 699-48-77A (bottom). Well 699-48-77C is completed (screened) ~20 meters deeper within the aquifer than the other two proximal wells.



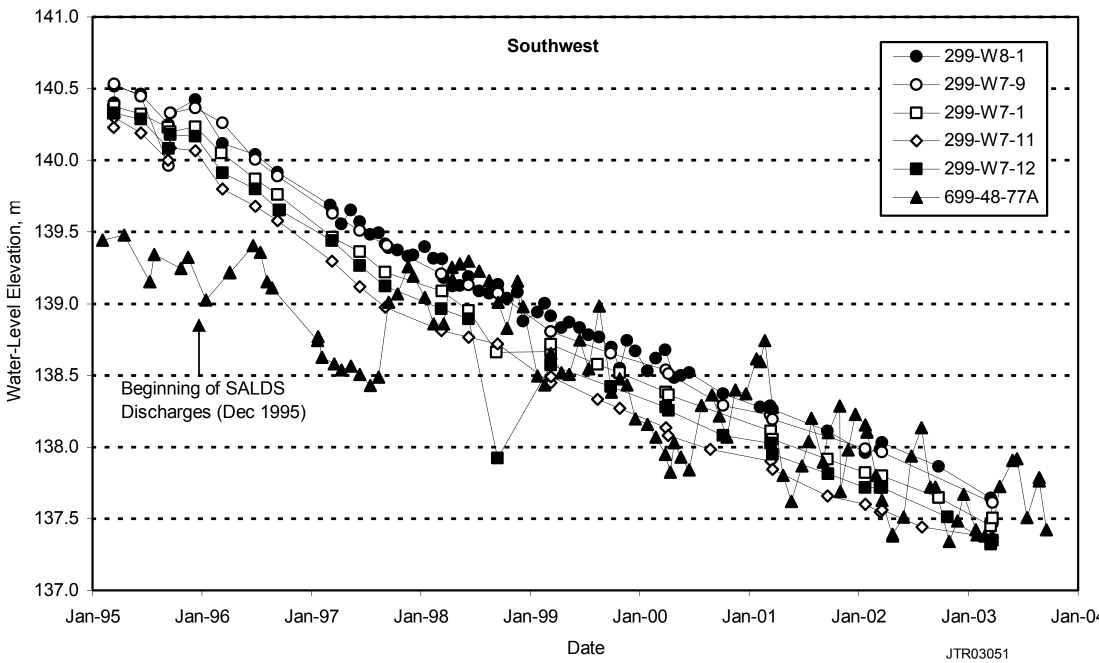
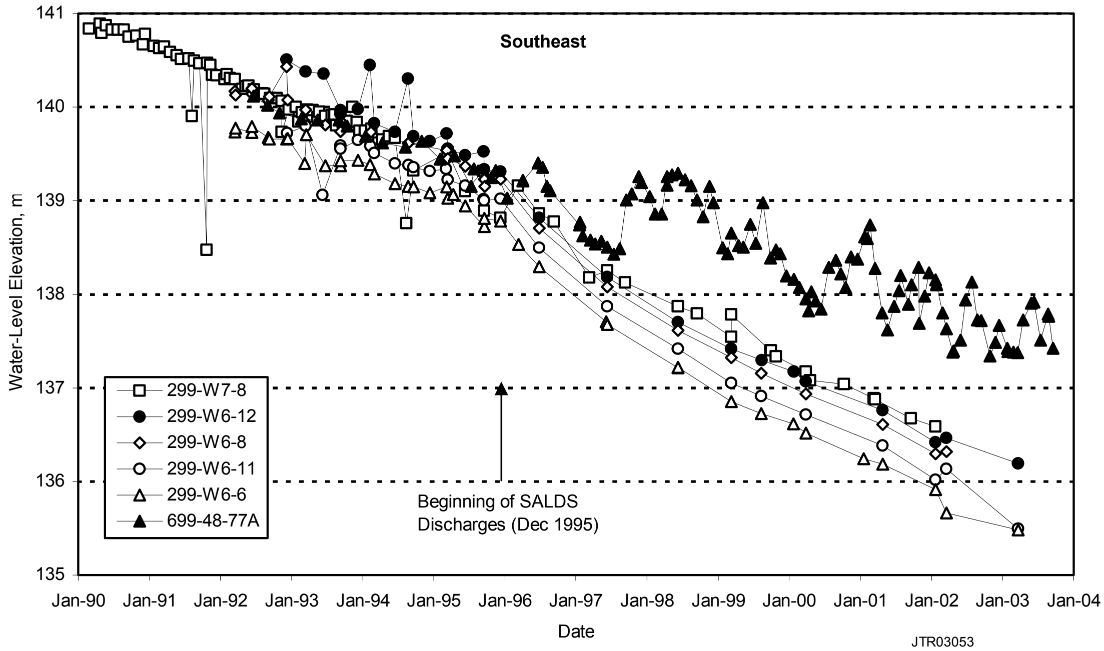


Figure 5. Hydrographs of Tritium-Tracking Wells South (top) and Southwest (bottom) of the SALDS Compared with Well 699-48-77A



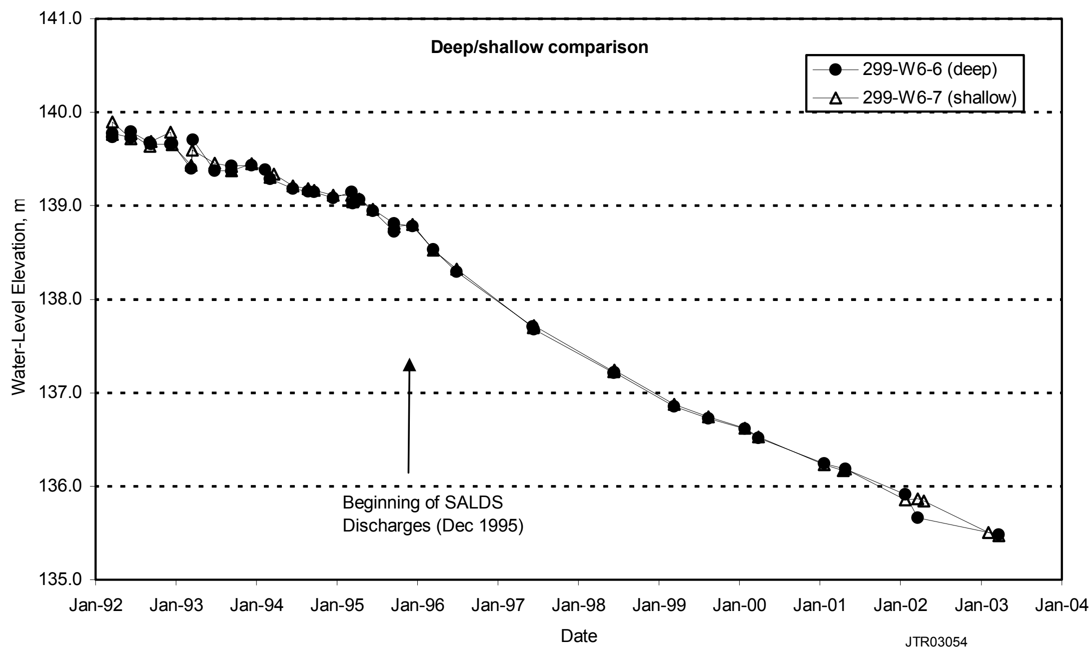


Figure 6. Hydrographs of Tritium-Tracking Wells Southeast of SALDS Compared with Well 699-48-77A (top) and Deep/Shallow Companion Wells (bottom). Well 299-W6-6 is completed approximately 49 meters deeper in the aquifer than Well 299-W6-7.

The water table in the vicinity of the SALDS for March 2003 is shown in Figure 7. The interpreted groundwater mound associated with the SALDS operation is shown near the facility based primarily on water levels measured in two of the SALDS proximal wells, 699-48-77A and 699-48-77D. The center of the mound is not necessarily located at well 699-48-77A; rather, this is an approximate location, with the actual center probably located somewhere between well 699-48-77A and the facility. Arrows denoting the interpreted flow paths (or the hydraulic potential for flow) of groundwater in the vicinity of the SALDS indicate that effluent from the SALDS could eventually affect wells to the south of the facility and may have already (see Section 3.2). Exactly how far south the effluent from SALDS could actually flow before turning east is not known. The interpretation of the flow potential in Figure 7, and hydrographs of Figures 4, 5, and 6, indicate that wells 699-51-75, 699-51-75P, and 699-48-71 northeast and east of the SALDS are regionally *downgradient* of the facility, and are in appropriate horizontal locations for intercepting SALDS effluent. The interpreted flow direction near SALDS has acquired a slightly more easterly component in the past few years (compare with Barnett 2000), perhaps as a result of the continuing regional decline in water levels combined with SALDS effects. Superimposed on Figures 4 through 6 is the obvious, general decline in head, as a result of discontinuation of operational discharges in the 1980s in the 200-West Area.

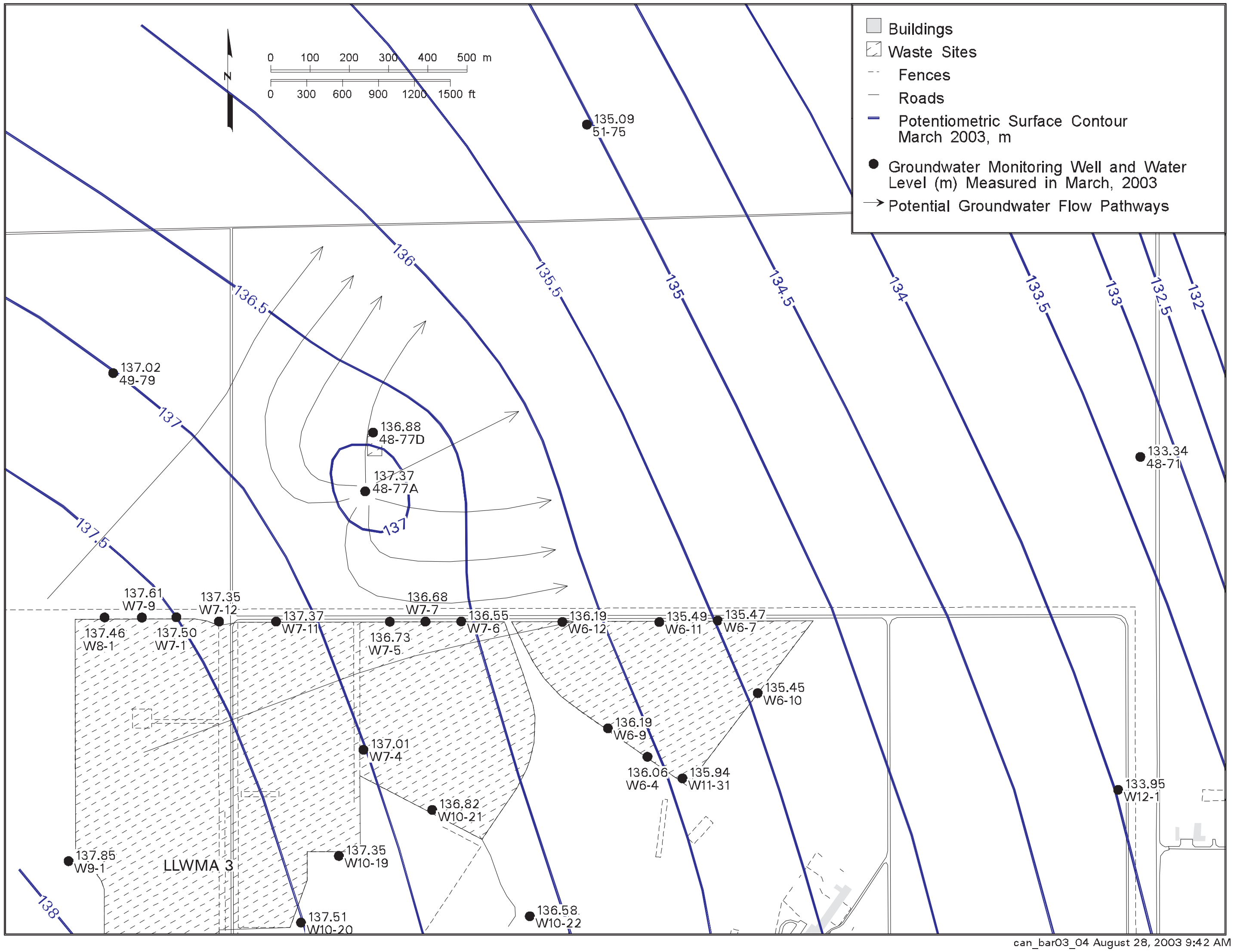


Figure 7. Water-Table Map and Interpreted Groundwater Flow Directions in the SALDS Area for March 2003

3.0 Results of FY 2003 Groundwater Analyses for SALDS

Tritium in groundwater is analyzed quarterly in the SALDS proximal wells (699-48-77A, 699-48-77C, and 699-48-77D) and annually to semiannually in 16 additional "tritium-tracking" wells in the vicinity of the facility. Tritium results from FY 2003 are discussed in Section 3.2 and listed in the Appendix.

In addition to tritium, groundwater from the SALDS proximal wells (699-48-77A, 699-48-77C, and 699-48-77D) is analyzed for a list of 15 constituents required by ST-4500 Special Condition S1 (A). Enforcement limits were set for most of these constituents: acetone, benzene, cadmium (total), chloroform, copper (total), lead (total), mercury (total), pH, sulfate, tetrahydrofuran, and total dissolved solids (TDS). Gross alpha, gross beta, strontium-90, and tritium are not assigned enforcement limits, but are monitored and reported. Analytical results for all parameters required by ST-4500 are also reported quarterly in Discharge Monitoring Reports. Additional parameters, such as alkalinity, dissolved oxygen, temperature, and turbidity, are sought for determination of general groundwater characteristics and verifying the quality of analytical results. Maximum concentrations for these constituents and the corresponding sample months for FY 2003 are discussed below and listed in Table 1.

3.1 Groundwater Sampling and Analysis for FY 2003

Samples for the three SALDS proximal wells were collected in October 2002, and January, February, April, and September of 2003. Tritium-tracking wells are sampled on an annual or semiannual basis for tritium only and were sampled in January, February, and September of 2003. Some of the tritium-tracking wells are also sampled for a broader range of constituents for the LLBGs facility and sitewide groundwater surveillance. Tritium results from these programs, in addition to those collected specifically for the SALDS, are included in the reported data in the Appendix. Semiannual results for four tritium-tracking wells (299-W7-3, 299-W7-5, 299-W7-7, and 699-51-75) had not been received at the time of this report due to fire restrictions near the wellheads and consequent late sampling. These results will be included in the FY 2004 report.

Declining regional water levels are causing some wells in the SALDS tritium-tracking network to go dry. In FY 2002, wells 299-W7-8, 299-W7-11, and 299-W6-8 became dry and were not sampled during FY 2003. Wells 299-W7-6 and 299-W7-9 were sampled by bailer during the January sampling event, but well 299-W7-6 was reported dry during a September 2003 sampling attempt. Likewise, well 299-W7-9 (on an annual schedule) may also have produced its final sample, based on the low water level reported in the January 2003 event.

Wells 699-51-75, 699-48-71, and 699-49-79 are older wells that are sampled with dedicated submersible electric pumps. Well 699-51-75P is a piezometer nested within well 699-51-75, but completed 135 ft deeper in the aquifer, and is sampled with an airlift hose. This method is acceptable where sampling for tritium only, as long as well recovery can be confirmed after purging. All other wells were sampled using dedicated *Hydrostar* pumps. The pump in well 699-48-77C was replaced in January 2003 when the existing pump failed to operate.

Table 1. Maximum or Range of Concentrations of Constituents in Groundwater and Corresponding Sample Month for SALDS Wells, FY 2003

Constituent (permit limit)	Well 699-48-77A	Well 699-48-77C	Well 699-48-77D
Acetone (160)	<4.4 (u); <1.0(u)	<4.4 (u); <1.0(u)	<4.4 (u); <1.0(u)
Benzene (5)	<0.5 (u); <1.0(u)	<0.5 (u); <1.0(u)	<0.5 (u); <1.0(u)
Cadmium, total (10)	<0.1(u); <0.125(u)	<0.1(u); <0.125(u)	<0.1(u)
Chloroform (6.2)	<0.40 (u); <1.0(u)	<0.40 (u); <1.0(u)	<0.40 (u); <1.0(u)
Copper, total (70)	3.98—Feb 2003	2.24—Apr 2003	0.88(J)—Oct 2002
Lead, total (50)	<1.2 (u)	<1.2 (u); <1.5(u)	<1.2 (u)
Mercury, total (2)	<0.1(u)	<0.1(u); <0.125(u)	<0.1(u)
Laboratory pH, pH units[b] (6.5 – 8.5)	8.03—8.67	7.98—8.12	7.91—8.16
Field pH, pH units[b] (6.5 – 8.5)	8.26--8.30	7.95—7.99	8.06—8.09
Sulfate (250,000)	1,630—Oct 2002	10,400—Oct 2002	9,420—Apr 2003
Tetrahydrofuran (100)	<4.6 (u); <2(u)	<4.6 (u); <2(u)	<4.6 (u); <2(u)
Total Dissolved Solids (500,000)	119,000—Apr 2003	194,000—Apr 2003	174,000—Sep 2003
Gross Alpha, pCi/L[c]	4.2—Apr 2003	2.1—Apr 2003	2.1—Oct 2002
Gross Beta, pCi/L[c]	3.6—Apr 2003	3.0—Sep 2003	3.6—Feb 2003
Strontium-90, pCi/L[c]	2.8—Feb 2003 [a]	1.0(u); 0.5(u); 0.6(u) 0.16(u); 0.06(u)	0.7—Apr 2003 [a] 0.01(u)
Tritium, pCi/L[c]	180,000—Oct 2002	430,000—Oct 2002	220,000—Oct 2002
Alkalinity, mg/L[b,d]	55—84	100—120	100—120
Field Conductivity, µS/cm[b,d]	115—136	233—245	236—248
Dissolved Oxygen, mg/L[b,d]	7.9—Oct 2002; Feb 2003	9.52—Oct 2002	9.2—Oct 2002
Field Temperature, °C[b,d]	22.8—23.2	16.9—18.0	17.0—17.9
Turbidity, NTU[d,e]	2.91—Apr 2003	2.58—Oct 2002	4.22—Apr 2003

Notes:
1. All concentrations in µg/L unless noted.
2. "(u)" = not detected; multiple MDLs or lower thresholds of detection are indicated where applicable; "(J)"= estimated quantity.

(a) Anomalous or suspect reading—see text for discussion.
(b) Range of quarterly averages (pH, conductivity, DO, temperature) or values (alkalinity) for FY 2003 (October 1, 2002 through September 2, 2003).
(c) Constituent is not assigned an enforcement limit, but is subject to routine monitoring and reporting.
(d) Constituent is sought for evaluation of groundwater character and analytical quality, and is not subject to permit conditions.
(e) Maximum value at time of sampling.

3.2 Results of Tritium Analyses (Tritium Tracking)

Results of tritium analyses in the SALDS tritium-tracking well network for FY 2003 are shown on Figure 8 and listed in the Appendix. Wells in the SALDS proximal network (699-48-77A, 699-48-77C, and 699-48-77D) have been affected by SALDS tritium discharges since 1996. Figure 9 illustrates the trends in tritium activities in the three SALDS proximal wells since groundwater monitoring began at the SALDS.

Maximum FY 2003 tritium activities for SALDS proximal wells were 189,000 pCi/L in well 699-48-77A (February 2003), 430,000 pCi/L in well 699-48-77C (October 2002), and 220,000 pCi/L in well 699-48-77D (October 2002). As the data in Figure 8 illustrate, tritium activities were either down or unchanged in FY 2003 compared with FY 2002. Peak tritium activities in groundwater occurred in late 1997 and early 1998 in wells 699-48-77A and 699-48-77D, respectively (Figure 9). Since the time of peak activities, the general trends are down for all three wells. However, note that the curve for well 699-48-77A in Figure 9 is irregular, with what appears roughly to be annual highs and lows of significant amplitude (more than two orders of magnitude) in tritium activity during the past 3+ years. This periodicity probably reflects the annual campaigns of the 242-A Evaporator. Well 699-48-77D is nearest the SALDS, and showed tritium incursion about 18 months later than the more distant well 699-48-77A. The reason for this delay is related to the fact that the SALDS drainfield fills from the end of the facility (south end) farthest away from well 699-48-77D and the effects of the aforementioned geologic features beneath the SALDS. These two conditions shunt the subsurface flow of effluent away from well 699-48-77D before it reaches groundwater. Some hint of quasi-annual fluctuation is suggested by the curve for well 699-48-77D, but the amplitude is significantly less, compared with 699-48-77A.

Well 699-48-77C is screened ~20 meters deeper in the aquifer than wells 699-48-77A and 699-48-77D, and did not detect a peak tritium activity until late 2000. Because of its deeper position in the aquifer, tritium incursions from the SALDS operation have been historically lower in activity. During times of high discharge, the hydraulic head beneath the SALDS is increased, and effluent is forced deeper into the aquifer. Figure 9 shows that historical, maximum tritium activities are slightly less in this well compared with 699-48-77A and 699-48-77C, and cyclical variations are absent. This difference is undoubtedly due to the dilution of the effluent in reaching groundwater at this depth.

Wells generally southeast of the SALDS have produced elevated values for tritium as a result of historical disposal practices in the 200-West Area. As shown in Figure 10, tritium activities in these wells have generally decreased or remained unchanged over the past several years. Well 299-W6-7 has experienced a steady decline in activity since FY 1995, reflecting the diminished effect of the plume originating in the northeast part of the 200-West Area, and may be leveling off around 10,000 pCi/L. Well 299-W7-1 has produced very infrequent detections of tritium, but those have all been near the minimum detectable activities (MDAs). Results in FY 2003 in this well produced one non-detect and one barely above detection (334 pCi/L in March 2003). Scattered results barely above MDAs are observed in other wells near well 299-W7-1 (e.g., see Hartman et al. 2003), but there are no known plumes affecting the immediate area of this well.

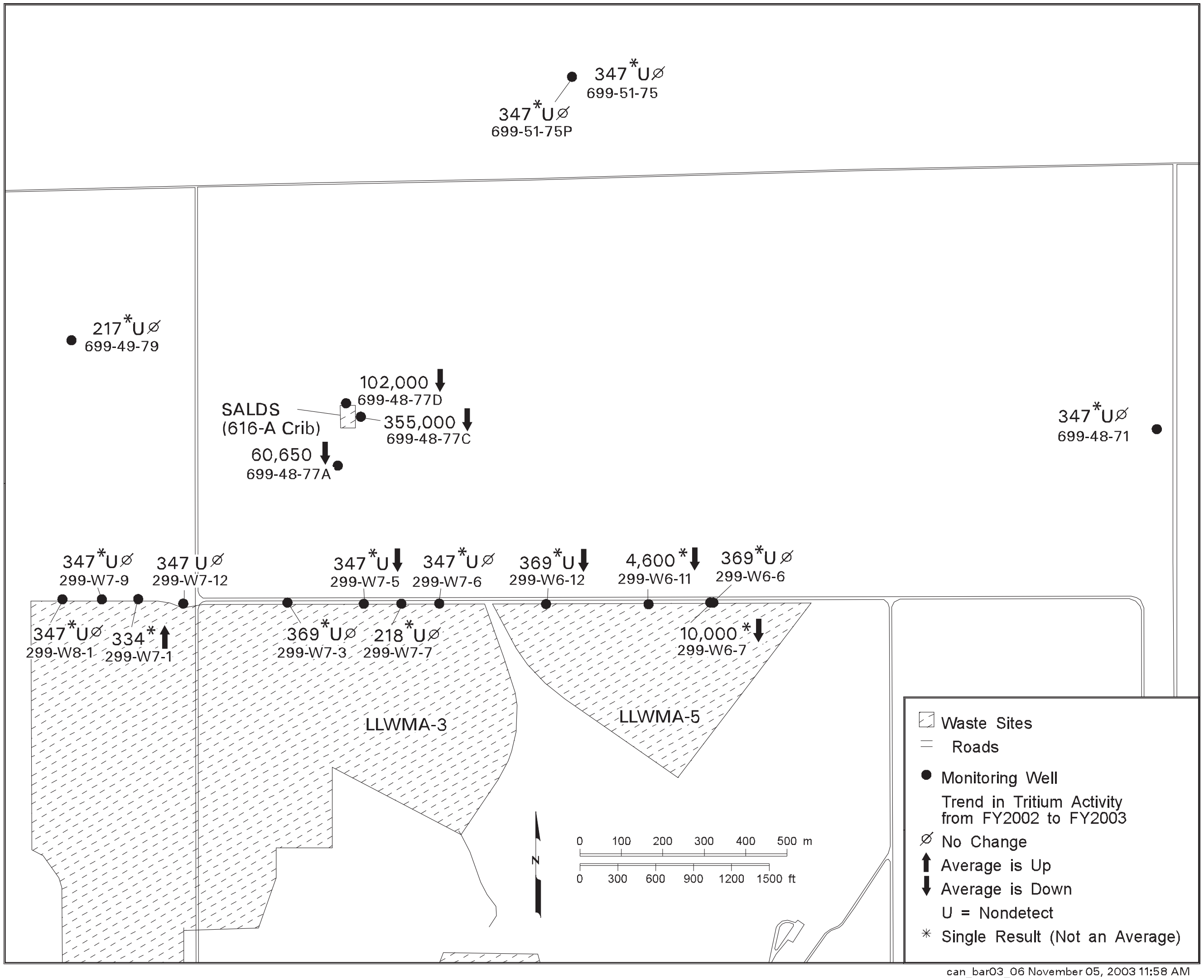


Figure 8. Tritium Activities in Groundwater for the SALDS Tritium-Tracking Network for FY 2003, Indicating Change from FY 2002 Results. As indicated in the legend, these results are either averages for FY 2003 or single results (sampled only once).

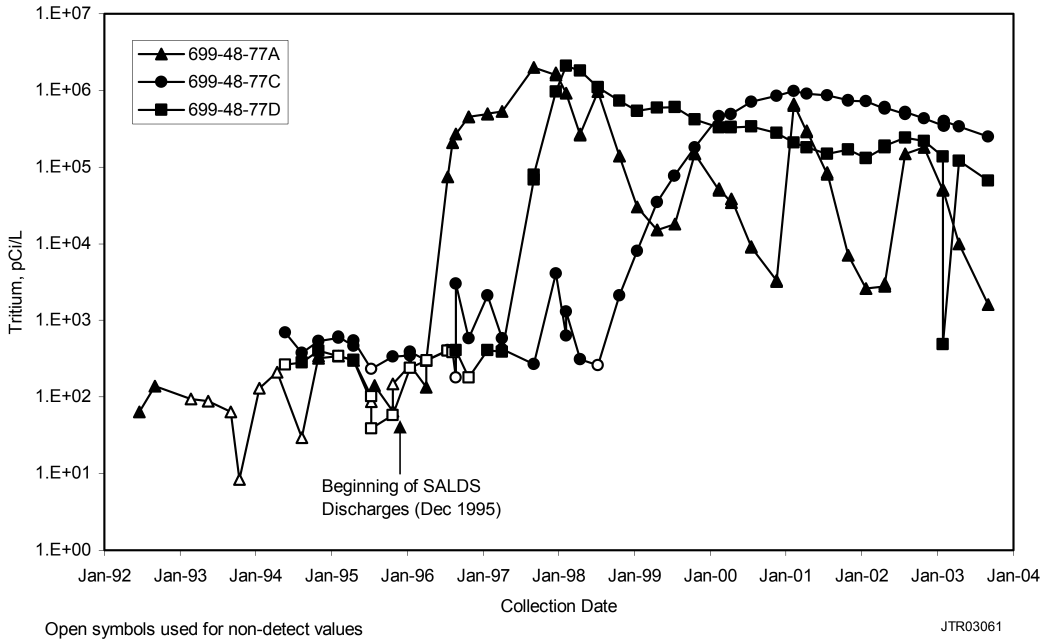
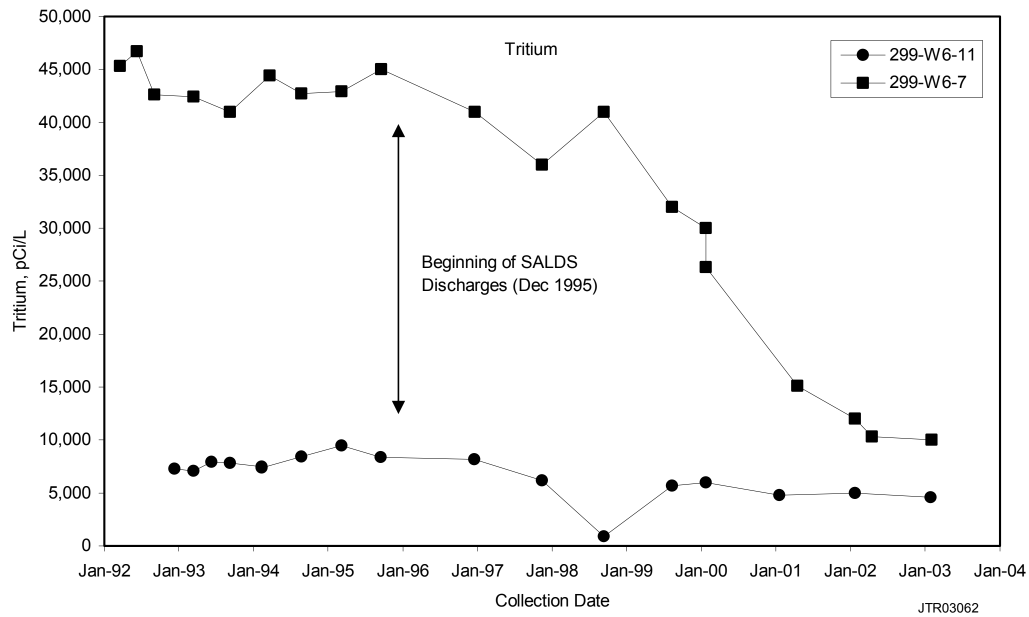


Figure 9. Tritium Activity Trends in SALDS Proximal Wells through September 2, 2003. Well 699-48-77C is completed ~20 meters deeper in the aquifer than wells 699-48-77A and 699-48-77D.

Well 299-W7-5 has produced detectable tritium results sporadically since 1988. Some of the detections from this well may be false because of large counting errors, or they may be actual detections of the decaying plume originating from the 200-West Area. The results from this well in the February 2003 sampling event were above detection, but below the maximum results for FY 2002. Because of its location and history, it is premature to conclude that tritium in this well is from SALDS or the existing plume in the 200-West Area.

3.3 Results of Other Constituent Analyses

Groundwater from the SALDS proximal wells (699-48-77A, 699-48-77C, and 699-48-77D) is analyzed for a list of 15 constituents (including tritium) required by the State Waste Discharge Permit ST-4500 Special Condition S1 (A). Permit limits are set for most of these constituents: acetone, benzene, cadmium (total), chloroform, copper (total), lead (total), mercury (total), pH, sulfate, tetrahydrofuran, and TDS. Gross alpha, gross beta, strontium-90, and tritium are not assigned enforcement limits, but are monitored and reported. Additional parameters, such as alkalinity, dissolved oxygen, temperature, and turbidity are monitored for determination of general groundwater characteristics and verifying the quality of analytical results. Maximum concentrations for these constituents, and the corresponding sample months for FY 2003, are listed in Table 1.



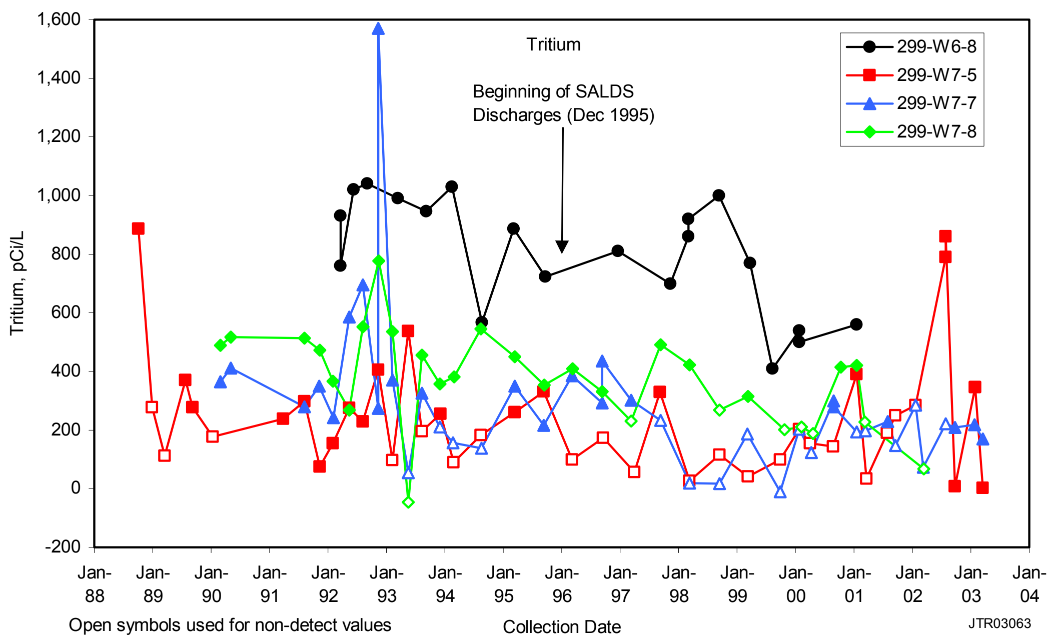


Figure 10. Tritium Activity Trends in Wells Southeast of the SALDS Showing Remnant Effects of the Tritium Plume from the 200-West Area. The high value for Well 299-W7-7 is suspected to be erroneous, with a duplicate on this date producing a result in line with the historic range. The spike in well 299-W7-5 appears to be a legitimate result, and may indicate that the SALDS tritium plume and/or the plume from the northeast corner of the 200-West Area are peripherally influencing this well.

All 11 constituents with ST-4500 permit limits were below these limits in groundwater during FY 2003[1]. Acetone, benzene, cadmium, chloroform, lead, mercury, and tetrahydrofuran results were reported below detection limits in all three wells for all of FY 2003. Method detection limits (MDLs) varied slightly between sample dates for some constituents. The various MDLs associated with each constituent are indicated in Table 1. Copper is the only metal on the list that produced detectable concentrations (maximum = 3.98 μg/L in February 2003 in well 699-48-77A).

Laboratory measurement of pH slightly exceeded the 8.5 criterion in well 699-48-77A in the September sample. However, field measurements of pH for the same sample remained well within permit criteria and on trend with historical values. Laboratory pH can be spurious depending on sampling handling and storage details. A loss of CO_2 during sampling or handling may result in slightly elevated pH.

The highest gross alpha result for FY 2003 of 4.2 pCi/L was recorded for well 699-48-77 in April. The highest gross beta value of 3.6 pCi/L was shared by wells 699-48-77A and 699-48-77C, in April and February, respectively. All gross alpha and gross beta activities remained well below groundwater quality standards, and no definite trends are apparent for either of these indicators.

Results for strontium-90 for FY 2003 in wells 699-48-77A and 699-48-77D are suspect. Independent analyses by Pacific Northwest National Laboratory sitewide surveillance in well 699-48-77A in 2002 and wells 699-48-77C and 699-48-77D in FY 2002 and FY 2003 produced no detectable results. The independent analyses produced lower MDAs and lower counting errors than the routine measurements. Therefore, it remains doubtful whether actual detections occurred in the routine analyses for this radionuclide.

Along with detection of the first elevated tritium in late 1996, concentrations of anions, metals, and other parameters were also found to have increased in groundwater from well 699-48-77A. This is interpreted to be a result of the dilute (clean water) effluent from SALDS dissolving soluble mineral species (such as gypsum in the case of sulfate) in the vadose zone during infiltration (Thornton 1997; Barnett et al. 1997). This hypothesis is discussed in greater detail in Section 4. More recently, wells 699 48-77C and 699-48-77D have shown similar, but more subtle, incursions of these constituents. Figures 11 through 13 show the trends for some of the parameters in the SALDS wells that best reflect this phenomenon, e.g., sulfate and conductivity. Other species, such as calcium and sodium, show a more subdued response during the same time period. Results for the September 2003 analyses for sodium and calcium were unavailable as of this writing, and will be included in subsequent reports. The initial rise in these constituents can be traced to the leaching of minerals in the vadose zone (see discussion in Section 4). Several other metals show similar trends of increase with subsequent decreases. The trends are most pronounced in wells 699-48-77A and 699-48-77D because these wells are screened at the water table. The ions and indicators (e.g., conductivity) have trended downward for the past few years in wells 699-48-77A and 699-48-77D, and appear now to be stabilizing below initial background (before 1995) concentrations in these two wells.

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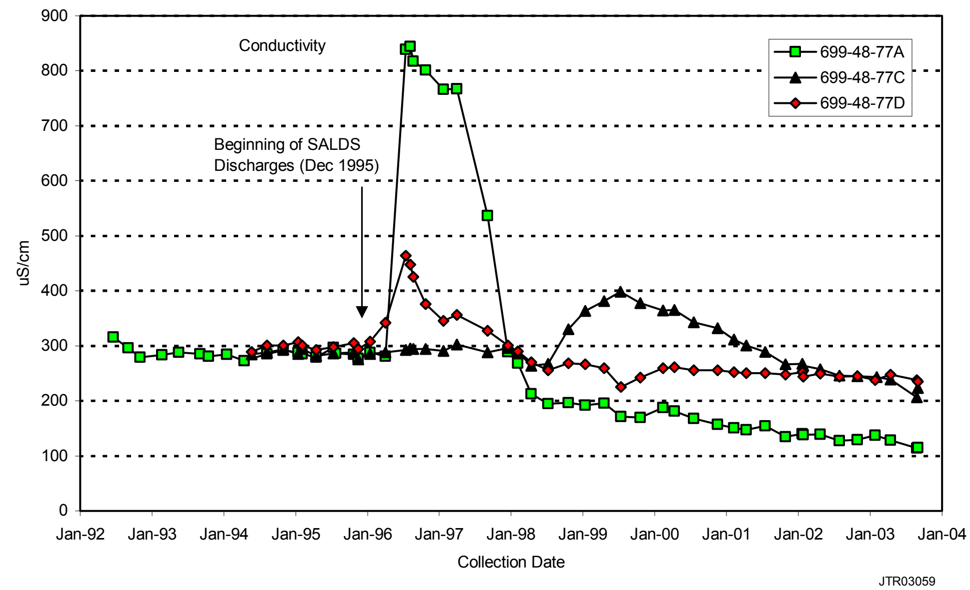
[1] Period reported is October 1, 2002, through September 2, 2003.



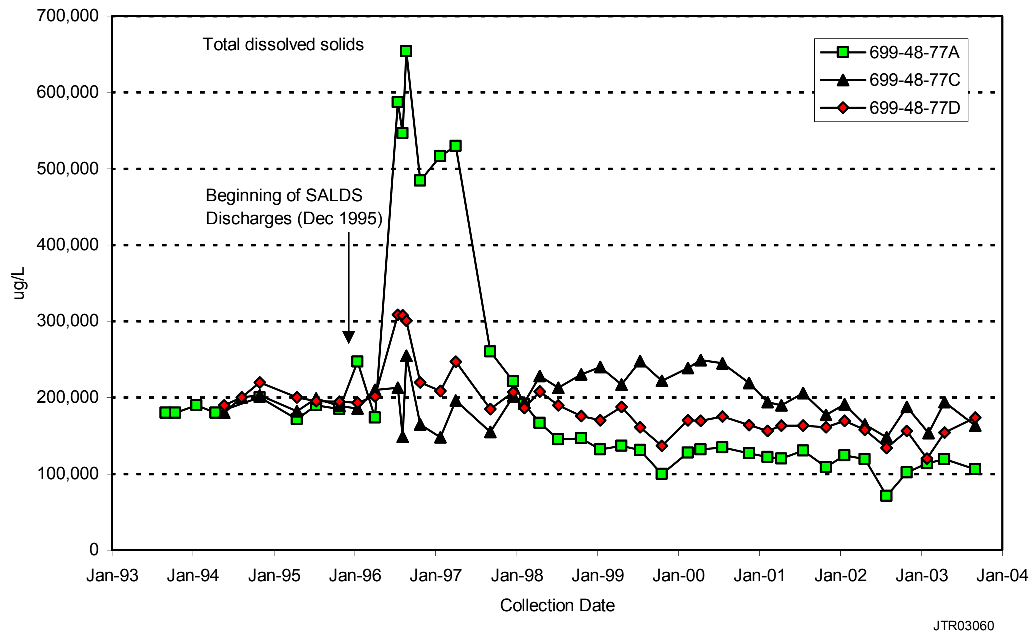
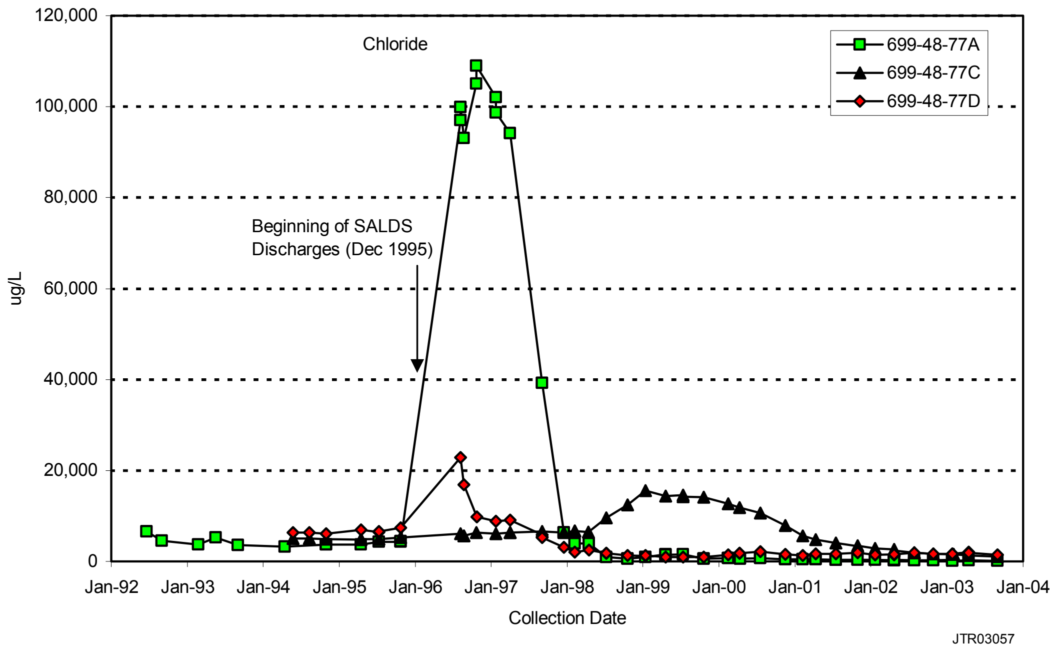


Figure 11. Trend Plots for Conductivity and Total Dissolved Solids in SALDS Proximal Wells

Well 699-48-77C is screened ~20 meters below the water table, so the effects of SALDS discharges in this well are significantly delayed and subdued with respect to the two shallow wells. The peak concentrations of the parameters represented in Figures 11 to 13 occurred in this well in late 1999 to early 2000, approximately 3 years later than in wells 699-48-77A and 699-48-77D. Concentrations in all three wells now reflect the dilute effluent from the SALDS that have replaced the natural concentrations to a minor degree in well 699-48-77C and more so in wells 699-48-77A and 699-48-77D.



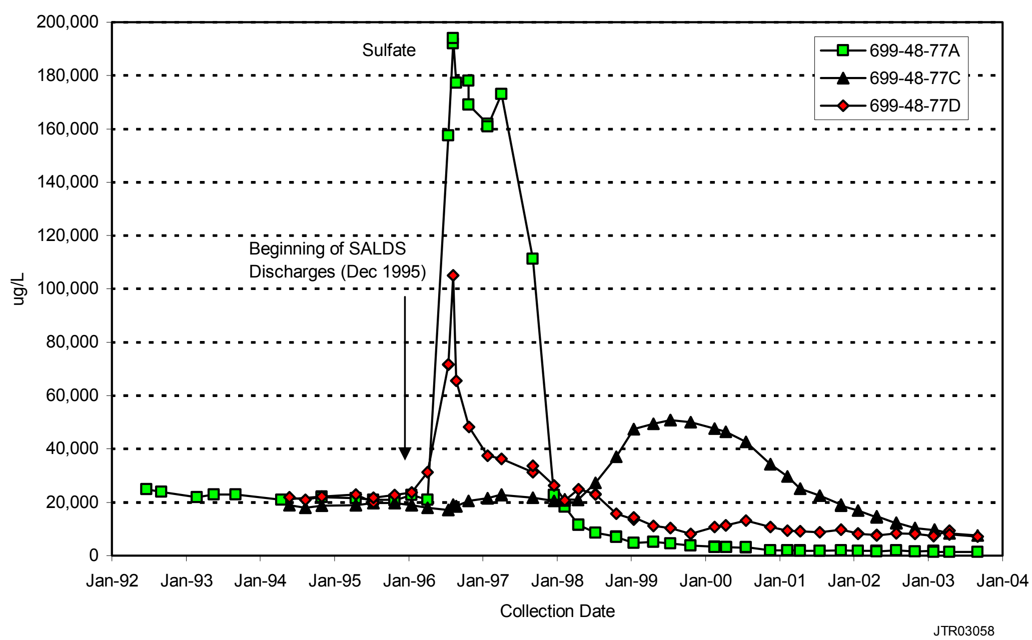
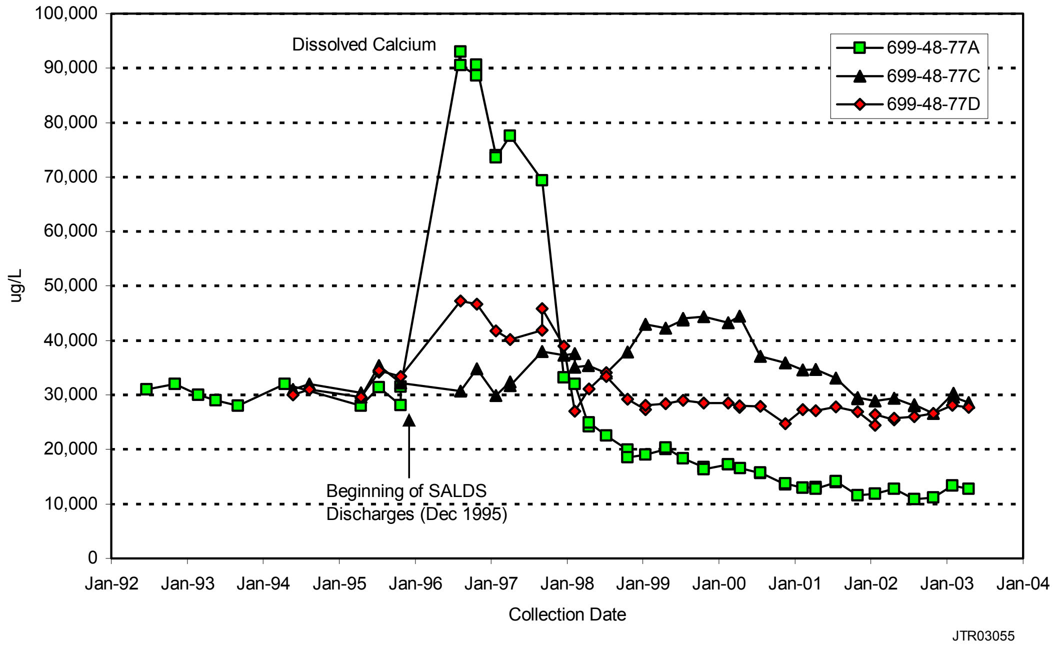


Figure 12. Trend Plots for Chloride and Sulfate in SALDS Proximal Wells



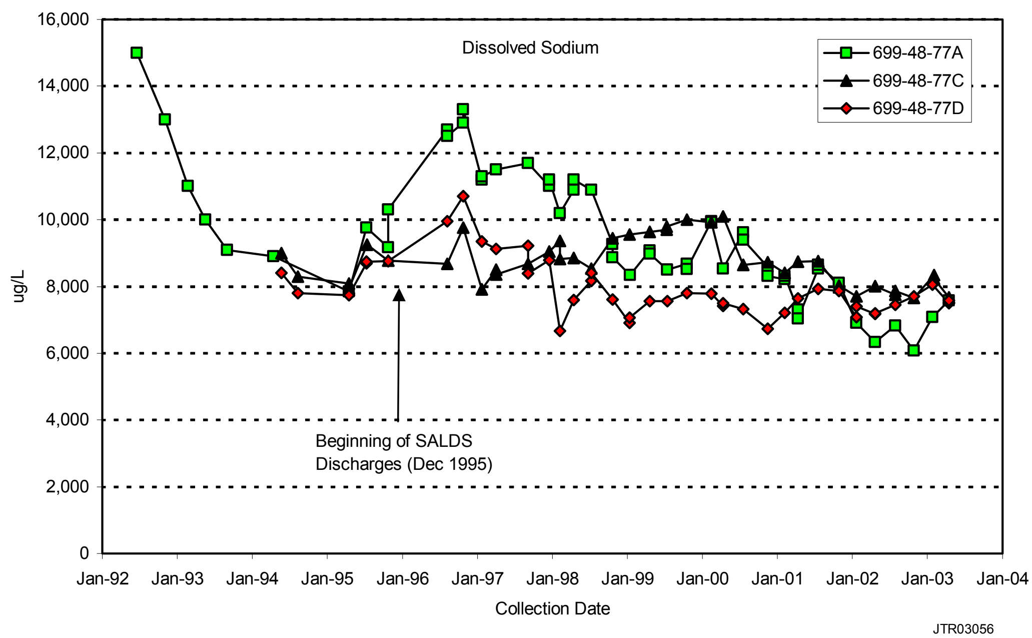


Figure 13. Trend Plots for Dissolved Calcium and Dissolved Sodium for SALDS Proximal Wells

4.0 Site Analysis and Conclusions

Water levels have fallen critically low in several of the tritium-tracking wells to the south of the SALDS, such that sampling has become infeasible in these wells. During the past 18 months, four wells in the tritium-tracking network have gone dry (299-W6-8, 299W7-6, 299-W7-8, and 299-W7-11), and three more (299-W6-7, 299-W7-9, and 299-W7-12) may be dry within the next 1 year (see Table 2 of Barnett and Rieger 2002). These wells are all located along the northern edge of the 200-West Area south of the SALDS. Because of the close spacing of wells in this area, the loss of the six wells mentioned above is not yet critical to tracking tritium originating from the SALDS, but it could affect modeling calibration or verification. The discussions presented below focus on additional topics that may have the greatest effects on SALDS operation.

4.1 Numerical Model Comparisons

Both numerical model snapshots for years 2000 and 2005 (Figure 14) (Barnett et al. 1997) show an incursion of tritium into wells along the southern portion of the tritium-tracking network (>500 pCi/L by year 2000 and nearly 2,000 pCi/L by year 2005). Although well 299-W7-5 is projected to be one of the first wells affected in this area, actual detection of tritium is sporadic during the past few years (see Figure 10). In FY 2002, this well produced a historically high result of 860 pCi/L, but the result fell below detection (347 pCi/L) in the January 2003 sample.

Three other wells south of SALDS predicted to detect tritium from the facility by 2000 are as yet unaffected. Models of vertical distribution of tritium beneath SALDS predict activities of tritium of >200,000 pCi/L reaching to depths monitored by well 699-48-77C. Thus far, the maximum is 980,000 pCi/L in this well. It should be noted that although discharge volumes to date are in line with model assumptions, the model assumed that a total of ~745 curies would be discharged to the SALDS by the end of calendar year 2002. This is more than double the actual amount (333+ curies) discharged thus far, and may eventually result in a disparity between the activities observed in the tritium-tracking wells versus the predicted activities.

Predicted hydraulic potential distribution in the area of SALDS for 2000 and 2005 (Figure 15) is similar to current interpretations of potential (see Figure 7). The main departures are that the actual March 2003 potential at SALDS well 699-48-77A is approximately 2 meters lower than that predicted for 2000 and 2005. Also, the March 2003 water table indicates a slightly more easterly component of flow potential in the vicinity of the SALDS than model predictions for 2000 and 2005 or the March 2003 water-table map.

Despite some discrepancy between the predicted hydraulic potential distribution in the model predictions and the observed water levels in March 2003, the 1997 model continues to be a reasonable estimate of hydraulic head and tritium dispersal in the SALDS area. However, new hydrostratigraphic information (Williams et al. 2002) and recent numerical and conceptual modeling efforts (e.g., Cole et al. 2001; Vermeul et al. 2001) will need to be applied to future estimates of tritium migration from the SALDS. A revised flow/transport model of the SALDS is planned for FY 2004 and will incorporate parameters from this new body of information and actual operational parameters (e.g., actual tritium inventories and future projections) for the SALDS.

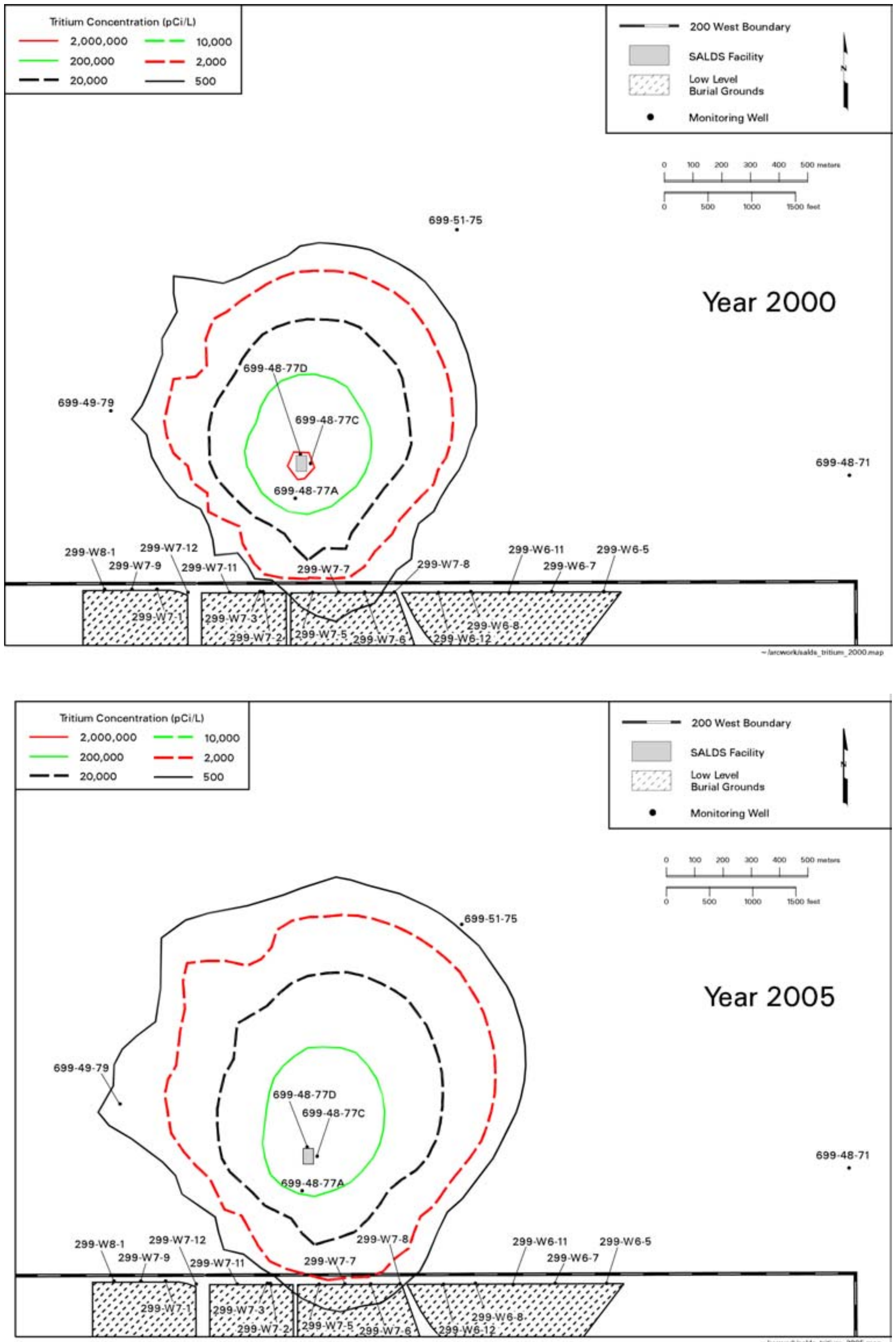
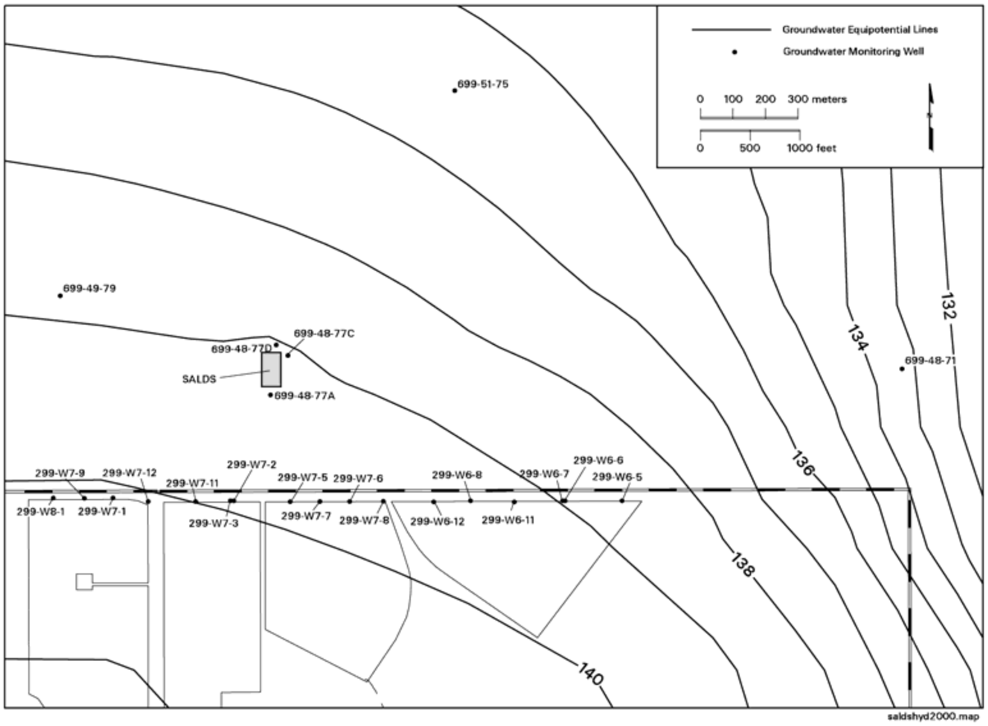


Figure 14. Predicted Tritium Distribution as a Result of SALDS Operation in Years 2000 (top) and 2005 (bottom) (after Barnett et al. 1997)



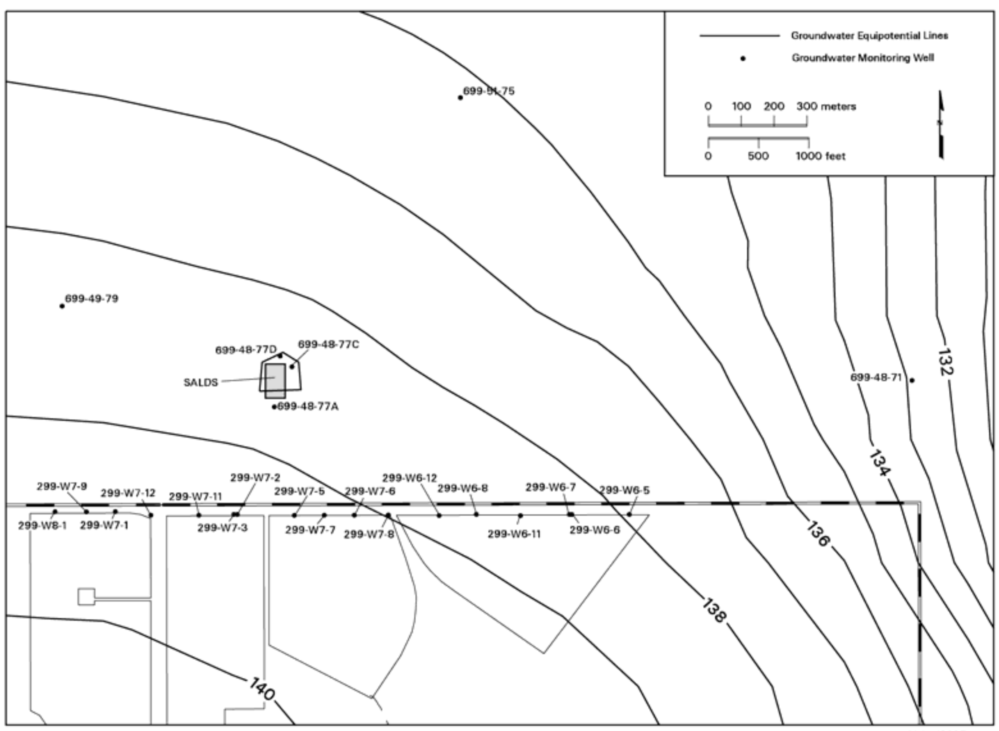


Figure 15. Hydraulic Head Distribution Predicted for SALDS in Years 2000 (top) and 2005 (bottom) (after Barnett et al. 1997)

4.2 Conceptual Model of SALDS

Two of the SALDS monitoring wells were less affected by the effluent, and at a delayed time compared with well 699-48-77A. It was at first perplexing that the incursion of elevated ions in well 699-48-77D, directly adjacent to the SALDS, occurred at a later date than in well 77A, but *without* elevated tritium activities. Site characterization efforts revealed that the Cold Creek unit (Figure 16) dips slightly to the south and forms a discontinuous, but locally impermeable barrier to downward infiltration. It was surmised that this feature intercepted and directed the small, initial test discharges (before December 1995) southward an indeterminate distance before infiltrating to the water table. The effluent then moved with the regional groundwater flow toward well 699-48-77D, but the discharges were of insufficient volume to reach well 699-48-77A. Shortly afterward, the first major discharges containing tritium followed roughly the same pathways to groundwater, but were voluminous enough to create a hydraulic reversal in gradient locally, and thus reached well 699-48-77A before the effects of the small test discharges could reach the next nearest well at the water table (699-48-77D) or the deep-completion well (699-48-77C).

During the initial characterization of the site, laboratory analysis and leaching tests (Table 2) were conducted on vadose-zone sediment samples from the SALDS (Riedel and Thornton 1993). Sediment chemistry, together with aqueous-speciation and mineral-saturation modeling results, was used to predict the groundwater chemical changes at the SALDS as the result of water disposal activities. Insight into the transport of solutes from the vadose zone to the aquifer was obtained by examining the results of the tests. In particular, these data indicate that sulfate and other anions and cations are present in the vadose zone in sufficient quantities to account for the observed increases in constituent levels in the groundwater that occurred in 1996 and afterward.

Soil sulfate concentrations obtained from soil analyses and leach tests performed during the characterization study suggest that an average value of about 10.6 mg/kg sulfate is present in the vadose zone. The observed maximum groundwater concentration of 190 mg/L sulfate could be achieved if 0.3 pore volumes of vadose zone water were to dissolve all of the gypsum present in vadose zone soils. This sulfate level was maintained for roughly a year before declining. A maximum sulfate concentration of about 879 mg/L potentially could be achieved if water infiltrating the vadose zone were saturated with respect to gypsum and calcite. It would be necessary for all of the sulfate in the vadose zone to be dissolved in only about 0.07 pore volumes of water for saturation to be maintained with respect to gypsum, however, and this level could be maintained for only a month or two. It is thus inferred that maximum groundwater sulfate levels were constrained by the dissolution rate of gypsum in the vadose zone.

4.3 Conclusions

Drying wells in the SALDS tritium-tracking network have reduced the number to 16 wells (excluding the 3 proximal SALDS wells). Thus far, the remainder of the network is adequate to track tritium from the facility, but the continued loss of wells could have a deleterious effect on numerical groundwater model verification.

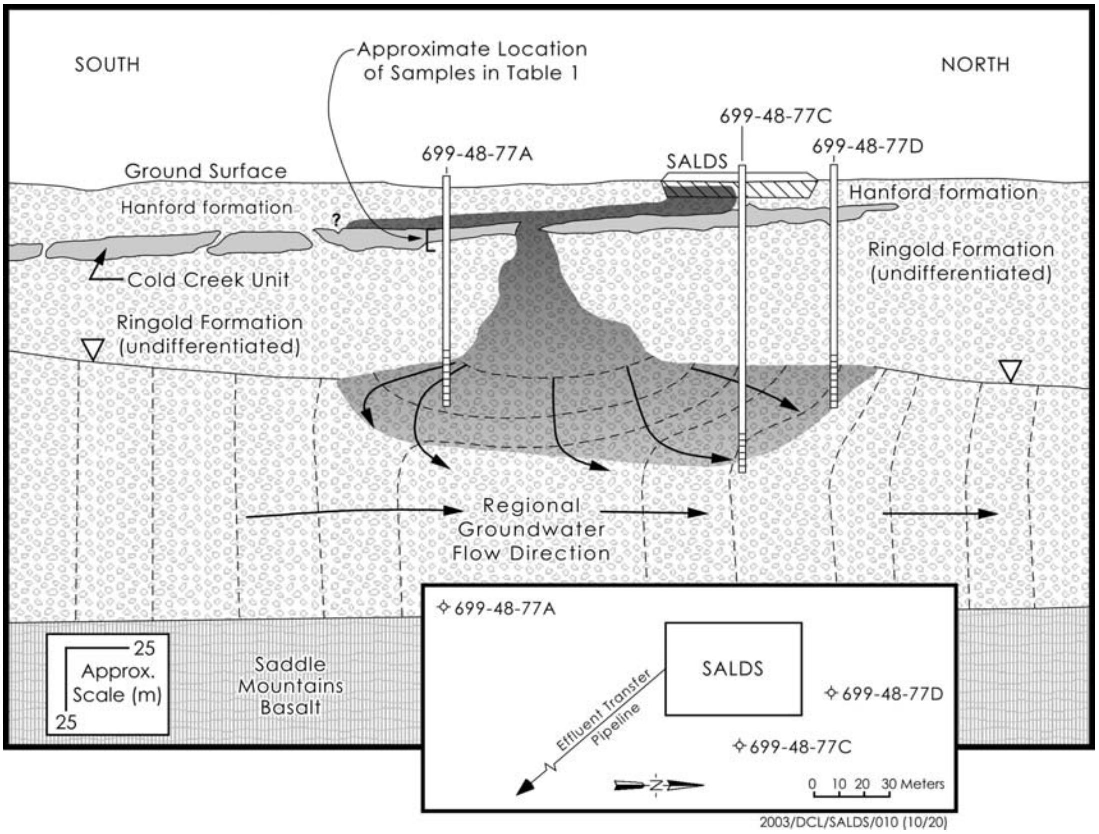


Figure 16. Conceptual Diagram of SALDS Operational Effects

Table 2. Soil Sample Analytical Results from SALDS Site Characterization

Sample Depth, ft	Soil Analysis or Leach Test Result	Soil Sulfate Concentration, ppm
0.5 to 1.0	Leach Test	12.9
1.5 to 2.0	Leach Test	5.9
1.5 to 2.5	Soil Analysis	<20
26.0 to 26.5	Leach Test	8.5
26.5 to 27.5	Soil Analysis	<20
29.7 to 30.7	Soil Analysis	37
34.8 to 35.3	Leach Test	4.3
43.1 to 43.6	Leach Test	11.7
57.2 to 57.7	Leach Test	6.5
57.7 to 58.2	Leach Test	4.8
68.0 to 68.5	Leach Test	3.4
68.5 to 70.0	Soil Analysis	<20
68.5 to 70.0	Soil Analysis (duplicate)	<20
84.7 to 86.2	Soil Analysis	<20
229.5 to 231.5	Soil Analysis	<20

A consistently downward potential, as indicated by the head differences between the shallow proximal wells 699-48-77A and 699-48-77D, and deep proximal well 699-48-77C (see Figure 4), results in tritium from SALDS being gradually forced to lower levels in the aquifer in the immediate vicinity of the facility. Away from the SALDS hydraulic mound, the vertical hydraulic gradient appears to be negligible.

In general, tritium activities in all wells near the SALDS either show a long-term decline or are unchanging. Based on observed fluctuations in tritium activity in well 699-48-77A, there is an "quasi-annual" periodicity between highs and lows in tritium over time. This probably reflects the campaigns of the 242-A Evaporator. It is still uncertain whether the SALDS tritium has affected groundwater near the border of the 200-West Area.

The origin of observed increases in sulfate concentration levels of groundwater in the vicinity of the SALDS disposal site during the first few years of operation can be attributed to dissolution of a sulfate mineral by water flowing through the vadose zone. This is supported by the observation that sulfate was found to be present in soils collected from the vadose zone during initial site characterization studies and analyses from nearby subsurface studies in the same strata. Based on the common occurrence of gypsum in typical terrestrial evaporite accumulations, this mineral species was always assumed to be the source of the sulfate. However, nearby saline lake deposits (Bennett 1962) suggest that other sulfate mineral species are common to the region. These minerals have much higher solubilities than gypsum (under normal arid soil conditions), and hence, may have a much greater leaching potential by infiltrating effluent. Identification of soluble minerals in the Hanford vadose zone, may provide a key to predicting or explaining elevated concentrations of major ionic species in groundwater.

During the past few years, concentrations of sulfate and other major dissolved ions have fallen, and are now below background levels in the three SALDS proximal wells. This is because dilution of the groundwater in the vicinity of the SALDS has now replaced the earlier "plume" of soil-derived dissolved solids. A return to higher ionic concentrations in groundwater after the recent descent to below background is unlikely, but could occur again briefly if discharges were stopped for a long period, then resumed.

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Appendix

SALDS Tritium Results for FY 2003

Table A.1. SALDS Tritium Results, FY 2003

Well Number	Date Sampled	Result, pCi/L	Qualifier	Comments (change in maximum result from maximum FY 2002 result)
299-W6-11	01/30/03	4,600		(down slightly)
299-W6-12	01/30/03	369	U	(no change)
299-W6-6	01/30/03	369	U	(no change)
299-W6-7	02/04/03	10,000		(down)
299-W6-7				
299-W7-1	02/03/03	208	U	
299-W7-1	03/17/03	334		I (up from non-detect in FY02)
299-W7-12	01/29/03	347	U	(no change)
299-W7-12	03/17/03	15.60	U	I
299-W7-12	03/17/03	114.00	U	I
299-W7-3	01/30/03	369	U	(no change)
299-W7-3	03/17/03	123	U	I
299-W7-5	01/29/03	347	U	(down)
299-W7-5	01/29/03	347	U	Duplicate
299-W7-5	03/18/03	1.84	U	I
299-W7-6	01/29/03	347	U	(down)
299-W7-7	01/27/03	218	U	(no change)
299-W7-7	03/17/03	169	U	I
299-W7-9	01/29/03	347	U	(no change)
299-W8-1	01/29/03	347	U	(no change)
299-W8-1	03/18/03	0.00	U	I
699-48-71	01/28/03	212.00	U	
699-48-71	01/28/03	347.00	U	(no change)
699-48-71	07/09/03	164	U	I
699-48-77A	10/28/02	180,000		(up)
699-48-77A	01/27/03	49,900		I
699-48-77A	02/04/03	51,000		
699-48-77A	04/17/03	10,000		
699-48-77A	09/02/03	1,600		
I = Independent sample collected for Low-Level Burial Grounds or surveillance.				

Table A.1. (contd)

Well Number	Date Sampled	Result, pCi/L	Qualifier	Comments (change in maximum result from maximum FY 2002 result)
699-48-77C	10/28/02	430,000		(down)
699-48-77C	01/27/03	400,000		
699-48-77C	01/27/03	400,000		Duplicate
699-48-77C	02/03/03	344,000		I
699-48-77C	04/17/03	340,000		
699-48-77C	09/02/03	250,000		
699-48-77D	10/28/02	220,000		(down)
699-48-77D	01/27/03	137,000		I
699-48-77D	02/04/03	490		Suspect result
699-48-77D	04/17/03	120,000		
699-48-77D	04/17/03	120,000		Duplicate
699-48-77D	09/02/03	67,000		
699-49-79	01/27/03	28.20	U	I
699-49-79	02/19/03	217	U	(no change)
699-51-75	01/28/03	347	U	(no change)
699-51-75	01/28/03	0.00	U	I
699-51-75P	01/28/03	347	U	(no change)
I = Independent sample collected for Low-Level Burial Grounds or surveillance.				

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