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Water Monitoring Programs

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Lawrence Livermore National Laboratory monitors a multifaceted system of waters that includes wastewaters, storm water, and groundwater, as well as rainfall and local surface waters. Water systems can also operate differently between the Livermore site and Site 300. For example, Site 300 is not serviced by a publicly owned treatment works as is the Livermore site, so different methods of treating and disposing of sanitary waste are used at the two LLNL sites. As described below, many different drivers determine the appropriate methods and locations among the various water monitoring programs.

In general, water samples are collected according to written standardized procedures appropriate for the medium (see Woods 2005). Sampling plans are prepared in advance by each network analyst, who is the LLNL staff person responsible for developing and implementing the specific monitoring programs or networks. The network analyst decides what analytes are to be sampled (see Appendix A) and at what frequency, incorporating any permit-specified analyses. Except for certain sanitary sewer and retention tank analytes, the analyses were usually performed by off-site California-certified contract analytical laboratories.

SANITARY SEWER EFFLUENT MONITORING

In 2004, the Livermore site discharged an average of 1.25 million liters (ML) per day of wastewater to the City of Livermore sewer system, 4.7% of the total flow into the city's system. This volume includes wastewater generated by Sandia National Laboratories/California (Sandia/California), which is discharged to the LLNL collection system and combines with LLNL sewage before it is released at a single point to the municipal collection system (**Figure 4-1**). In 2004, Sandia/California generated approximately 11.3% of the total effluent discharged from the Livermore site. LLNL's wastewater contains both sanitary sewage and process wastewater and is discharged in accordance with permit requirements and the City of Livermore Municipal Code, as discussed below.

Livermore Site Sanitary Sewer Monitoring Complex

LLNL's sanitary sewer discharge permit (Permit 1250, 2003/2004 and 2004/2005) requires continuous monitoring of the effluent flow rate and pH. Samplers collect flow-proportional composite samples and instantaneous grab samples that are analyzed for metals, radioactivity, toxic chemicals, and water-quality parameters at the Sewer Monitoring Station (SMS). In addition, as a best management practice, the outflow to the municipal collection system is sampled continuously and analyzed in real time for conditions that might cause upset or pass through to the Livermore Water Reclamation Plant (LWRP) treatment process or otherwise impact the public welfare. The effluent is continuously analyzed for flow, pH, regulated metals, and gamma radioactivity. If

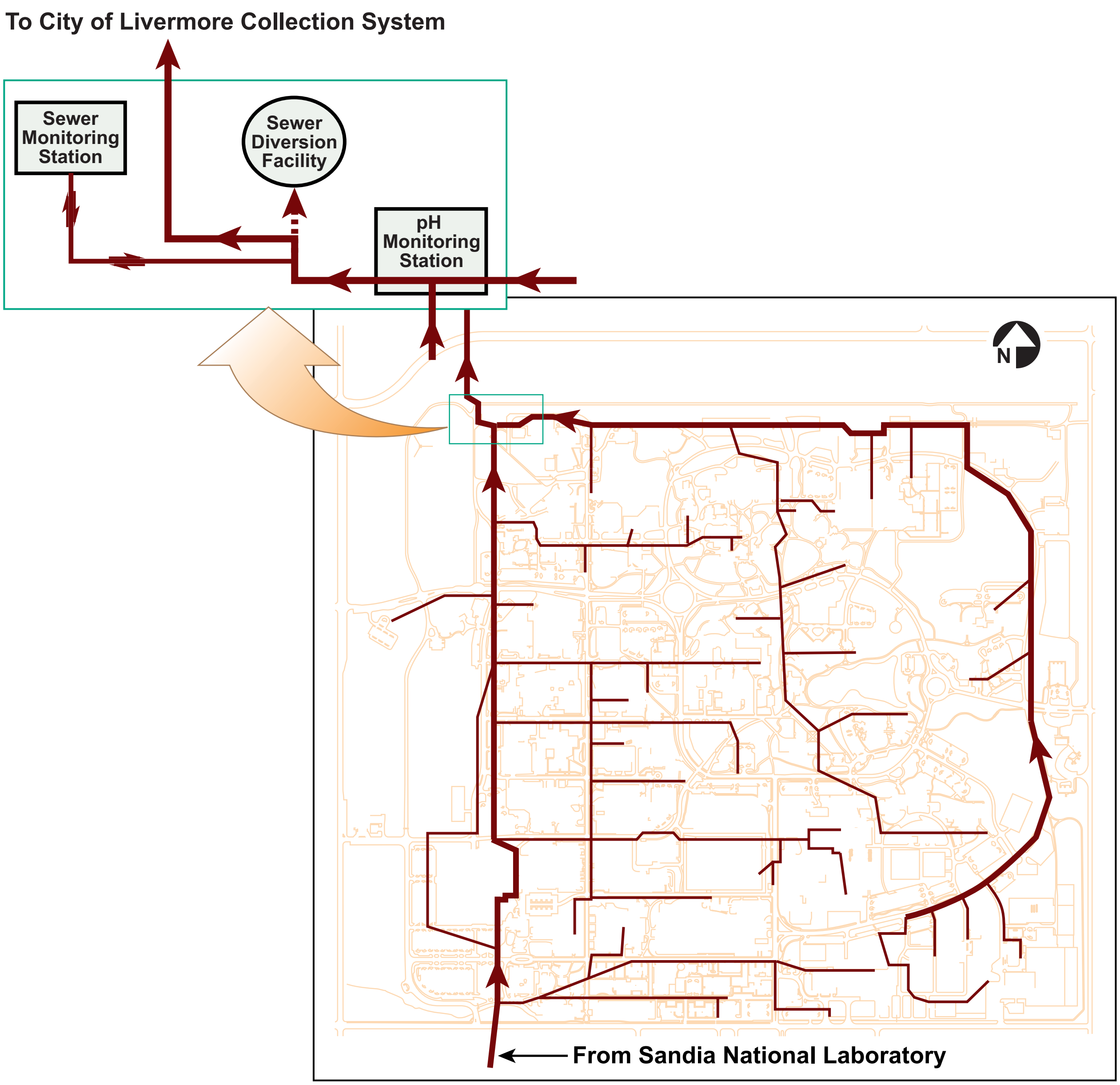


Figure 4-1. LLNL sanitary sewer system, monitoring stations, and diversion facility

concentrations above warning levels are detected the site effluent is automatically diverted to the Sewer Diversion Facility (SDF), and an alarm is registered at the LLNL Fire Dispatcher's Station, which is attended 24 hours a day. The monitoring system provides a continuous check on sewage control, and the LWRP is notified of contaminant alarms. Trained LLNL staff respond to all alarms to evaluate the cause and take appropriate action.

In addition to the continuous monitoring at the SMS, LLNL monitors pH at the upstream pH Monitoring Station (pHMS) (see **Figure 4-1**). The pHMS continuously monitors pH during peak flow hours between 7 a.m. and 7 p.m. during the workweek and diverts pH discharges outside the permit range of 5 to 10 to the SDF. The pHMS duplicates the pH monitoring and diversion capabilities of the SMS but is able to initiate diversion earlier because it is located upstream of the SDF.

LLNL maintains and operates a diversion system that activates automatically when either the SMS continuous monitoring system or the pHMS detects an anomalous condition. For SMS-activated alarms, the SDF ensures that all but the first few minutes of the potentially affected wastewater flow is retained at LLNL, thereby protecting the LWRP and minimizing any potential cleanup. When the SDF is activated by the pHMS for pH excursions, even the first few minutes of affected wastewater flow are retained. Up to 775,000 L of potentially contaminated sewage can be held, pending analysis to determine the appropriate handling method. The diverted effluent may be returned to the sanitary sewer (if it meets LLNL's wastewater discharge permit limits), shipped for off-site disposal, or treated at LLNL's Radioactive and Hazardous Waste Management (RHWM) facilities and then released to the sanitary sewer. All diverted sewage in 2004 was returned to the sanitary sewer.

Radiological Monitoring Results

Work Smart Standards (WSS) establish the standards of operation at LLNL (see Chapter 2), and include the standards for sanitary sewer discharges. For radioactive material releases, complementary (rather than overlapping) sections from Department of Energy (DOE) Order 5400.5 and 10 CFR Part 20 are both part of the standards. From DOE Order 5400.5, the WSS for sanitary sewer discharges include the criteria DOE established for the application of best available technology to protect public health and minimize degradation of the environment. These criteria (the Derived Concentration Guides, or DCGs) limit the concentration of each radionuclide discharged to publicly owned treatment works. If a measurement of the monthly average concentration of a radioisotope exceeds its specific concentration limit, LLNL is required to improve discharge control measures until concentrations are again below the DOE limits. From 10 CFR Part 20, the numerical discharge limits for sanitary sewer discharges in the WSS include the annual discharge limits for radioactivity: 185 GBq (5 Ci) of tritium, 37 GBq (1 Ci) of carbon-14, and 37 GBq (1 Ci) of all other radionuclides combined. The 10 CFR Part 20 limit on total tritium activity dischargeable during a single year (185 GBq [5 Ci]) is primary over the DOE Order 5400.5 concentration-based limit for tritium for facilities such as LLNL that generate wastewater in large volumes. In addition to the DOE average concentration discharge limit for tritium and the 10 CFR Part 20 annual total discharge limit for tritium, the LWRP established in 1999 an effluent concentration discharge limit for LLNL governing daily releases of tritium. This limit is more stringent than the DOE discharge limit: it is a factor of 30 smaller and applies to a daily rather than an annualized concentration. The following discussion includes the specific radioisotopes with potential to be found in the sanitary sewer effluent at LLNL with respect to the appropriate discharge limit. (All analytical results are included in the file "Ch4 LV Wastewater" provided on the report CD.)

LLNL determines the total radioactivity released from tritium, gross alpha emitters, and gross beta emitters from the measured radioactivity in the monthly effluent samples. The 2004 combined release of alpha and beta sources was 0.54 GBq (0.15 Ci), which is 0.054% of the corresponding 10 CFR Part 20 limit (37 GBq [1.0 Ci]). The combined total is the sum of the alpha and beta results shown in **Table 4-1**. The tritium total was 1.3 GBq (0.35 Ci), which is 0.72% of the 10 CFR Part 20 limit (185 GBq [5 Ci]).

Table 4-1. Estimated total radioactivity in LLNL sanitary sewer effluent, 2004

Radioactive emitter	Estimate based on effluent activity (GBq)[a]	Limit of sensitivity (GBq)
Tritium	1.34	1.12
Gross alpha sources	0.03	0.112
Gross beta sources	0.51	0.239

a 37 GBq = 3.7×10^{10} Bq = 1 Ci

Summary results and statistics for tritium measured in the sanitary sewer effluent from LLNL and LWRP are presented in **Table 4-2**. The total monthly activity is calculated by multiplying each monthly concentration by the total flow volume over which the sample was collected. (Per DOE guidance, all total annual results presented in this chapter for radioactive emitters are calculated by using the analytical results regardless of whether they were above or below the detection limit. [U.S. DOE 1991])

As shown in **Table 4-2**, the median monthly concentration and the maximum monthly average concentration of tritium were a small fraction of the DOE annualized discharge limit (370 Bq/mL [0.01 µCi/mL]). The maximum daily concentration for tritium was far below the permit discharge limit (12 Bq/mL [333 pCi/mL]).

The historical trend in the monthly concentration of tritium is shown in **Figure 4-2** (before 2002, the figure shows the calculated monthly average). Also included in the figure are the limit of sensitivity (LOS) values for the tritium analysis and the DOE tritium limit (370 Bq/mL [0.01 µCi/mL]).

The concentrations of plutonium-239 and cesium-137 measured in the sanitary sewer effluent from LLNL and LWRP, and LWRP sludge are presented in **Tables 4-3** and **4-4**, respectively. The plutonium and cesium results are from monthly composite samples of LLNL and LWRP effluent, and quarterly composites of LWRP sludge. For 2004, the annual total discharge of cesium-137 and the annual total plutonium-239 were far below the DOE DCG. Plutonium discharged in LLNL effluent is ultimately concentrated in LWRP sludge. The median plutonium concentration observed in 2004 sludge (**Table 4-4**), is many times lower than the EPA preliminary remediation goal for residential soil (93 mBq/dry g [2.5 pCi/dry g]) and is 18,500 times lower than the remediation goal for industrial or commercial soil (370 mBq/dry g [10 pCi/dry g]).

Table 4-2. Summary statistics of tritium in sanitary sewer effluents, LLNL and LWRP, 2004

Monitoring results			
	LLNL		LWRP
	Daily	Monthly	Monthly
Maximum (Bq/mL)	0.04[(a)]	0.006[(b)]	0.004[(c)]
Median (Bq/mL)	0.002	0.003	0.0006
LLNL annual total (GBq)	1.34		
Discharge limits for LLNL effluent			
	Discharge limit	Monitoring results as percentage of limit	
		Maximum	Median
LWRP permit daily (Bq/mL)	12	0.33%	0.02%
DOE annualized discharge limit for application of BAT[(d)] (Bq/mL)	370	0.002%[(e)]	0.0008%[(e)]
10 CFR 20 annual total (GBq)	185	0.7%	

a This daily result is for an August sample.

b This is the monthly value for May. All monthly values above limit of sensitivity are plotted in **Figure 4-2.**

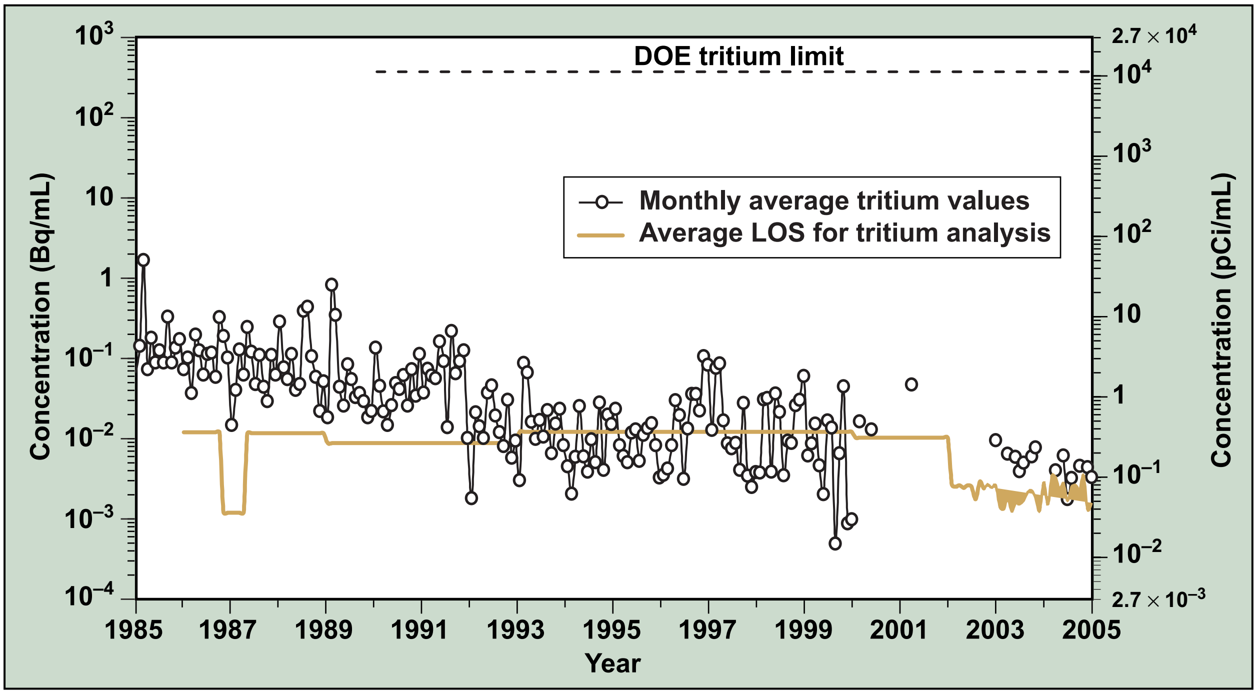
c This is the monthly result for March.

d The DOE annualized discharge limit for application of best available technology (BAT) is five times the derived concentration guide (DCG: ingested water) for each radionuclide released.

e Monitoring results as a percentage of limit are calculated using the LLNL monthly sample and the DOE annualized discharge limit.

Figure 4-3 summarizes the cesium-137 and plutonium-239 monitoring data over the past 10 years. The historical levels for plutonium-239 observed since 1995 average approximately 1 µBq/mL (3×10^{-5} pCi/mL). These historical levels generally are 0.0003% of the DOE DCG for plutonium-239. The cyclic nature of the data in **Figure 4-3** suggests a potential frequency relationship in LLNL sewer lines for radionuclide buildup and subsequent liberation by line cleaning. Regardless, the higher plutonium and cesium concentrations are all well below applicable DOE DCGs.

LLNL also compares annual discharges with historical values to evaluate the effectiveness of ongoing discharge control programs. **Table 4-5** summarizes the radioactivity in sanitary sewer effluent over the past 10 years. During 2004, a total of 1.3 GBq (0.35 Ci) of tritium was discharged to the sanitary sewer, an amount that is well within environmental protection standards and is comparable to the amounts discharged during the past 10 years.



Note: Only values above the limit of sensitivity (LOS) of the analytical method used are plotted.

Figure 4-2. Historical tritium concentrations in the Livermore site sanitary sewer effluent

Nonradiological Monitoring Results

LLNL monitors sanitary sewer effluent for chemical and physical parameters at different frequencies depending on the intended use of the result. For example, LLNL's wastewater discharge permit requires LLNL to collect monthly 24-hour composites, weekly composites, and daily composites. Once a month, a 24-hour, flow-proportional composite is collected and analyzed; this is referred to as the monthly 24-hour composite in the discussion below. The weekly composite refers to the flow-proportional samples collected over a 7-day period continuously throughout the year. The daily composite refers to the flow-proportional sample collected over a 24-hour period, also collected continuously throughout the year. LLNL's wastewater discharge permit specifies that the effluent pollutant limit (EPL) is equal to the maximum pollutant concentration allowed per 24-hour composite sample. Only when a weekly composite sample concentration is at or above 50% of its EPL are daily samples collected during the corresponding period analyzed to determine if any of their concentrations are above the EPL.

To better understand the characteristics of the Livermore site sanitary sewer effluent, LLNL also tracks flow-weighted monthly concentrations for all regulated metals in LLNL's sanitary sewer effluent; Table 4-6 presents the flow-weighted monthly concentrations for 2004. To obtain these concentrations, each weekly composite is weighted by the total flow volume for the period during which the sample was collected. This flow-weighted monthly concentration represents the characteristic concentration for that

Table 4-3. Cesium and plutonium in LLNL and LWRP sanitary sewer effluents, 2004

Month	Cesium-137 (μBq/mL)				Plutonium-239 (nBq/mL)			
	LLNL		LWRP		LLNL		LWRP	
	Radioactivity	MDC[a]	Radioactivity	MDC[a]	Radioactivity	MDC[a]	Radioactivity	MDC[a]
Jan	0.80 ± 2.8	3.5	–1.03 ± 4.4	3.9	5.291 ± 5.4	6.7	2.72 ± 3.7	5.1
Feb	9.07 ± 37	37	—[b] ± —[b]	—[b]	60.31 ± 16	6.9	–1.40 ± 3.7	7.5
Mar	0.00 ± 0.0	53	18.7 ± 60	52	38.85 ± 14	7.7	11.8 ± 17	19
Apr	2.68 ± 24	21	–0.07 ± 21	19	19.72 ± 9.0	5.8	–1.90 ± 5.0	10
May	–3.23 ± 21	19	–1.57 ± 22	19	40.33 ± 14	6.4	4.88 ± 4.4	3.2
Jun	0.68 ± 3.8	3.4	0.68 ± 3.8	3.5	22.72 ± 9.1	5.5	–2.10 ± 24	32
Jul	1.54 ± 3.6	3.3	0.39 ± 4.0	3.6	13.47 ± 7.4	6.3	0.00 ± 0.0	82
Aug	5.00 ± 4.3	4.0	1.38 ± 3.6	3.3	23.13 ± 9.1	5.8	1.62 ± 4.1	6.5
Sep	0.79 ± 3.4	3.1	–2.98 ± 4.2	3.5	16.50 ± 7.4	4.6	10.4 ± 6.3	5.4
Oct	0.64 ± 3.8	3.4	1.53 ± 5.4	5.0	14.80 ± 7.3	5.3	–3.36 ± 2.8	10
Nov	1.46 ± 7.0	6.1	3.36 ± 5.9	5.4	14.62 ± 12	16	5.40 ± 7.2	9.9
Dec	1.33 ± 6.9	6.1	0.68 ± 6.0	5.3	46.62 ± 11	4.0	0.24 ± 2.2	4.2
Median	1.06		0.68		21.22		0.93	
	Annual LLNL total discharge by radioisotope							
	Cesium-137				**Plutonium-239**			
Bq/y[c]	8.3×10^{5}				1.16×10^{4}			
Ci/y	2.3×10^{-5}				3.1×10^{-7}			
	Fraction of limit [d]							
DOE 5400.5 DCG[e]	3.2×10^{-6}				6.9×10^{-8}			

Note: Results in this table are reported as radioactivity (the measured concentration and a ± 2σ counting uncertainty) along with the detection limit or minimum detectable concentration (MDC). A measured concentration exhibiting a 2σ counting uncertainty greater than or equal to the measured concentration is considered a nondetection (see Chapter 8).

a MDC = minimum detectable concentration

b The sample could not be analyzed due to an inadvertent error at the analytical laboratory.

c 1 Ci = 3.7×10^{10} Bq

d Fraction of limit calculations are based on the annual total discharge for a given isotope and the corresponding concentration-based limit (0.56 and 0.37 Bq/mL for cesium-137 and plutonium-239, respectively) multiplied by the annual volume of Livermore site effluent.

e DCG = Derived Concentration Guide

Table 4-4. Radioactivity of cesium and plutonium in LWRP sludge, 2004

Month	Cesium-137 (mBq/dry g)[(a)]	Plutonium-239 (mBq/dry g)[(a)]
Mar	<1.01	0.126 ± 0.033
Jun	<0.98	0.101 ± 0.051
Sep	<0.99	0.132 ± 0.029
Dec	<1.01	0.141 ± 0.024
Median	1.00	0.129

Note: Sludge from LWRP digesters is dried before analysis. The resulting data indicate the cesium and plutonium concentration of the sludge prepared by LWRP for disposal at the Vasco Road Landfill in Alameda County.

a Results are reported as radioactivity (the measured concentration and ± 2σ counting uncertainty). A measured concentration exhibiting a 2σ counting uncertainty greater than or equal to 100% is considered to be a nondetection and is reported with a less than (<) symbol. See Chapter 8.

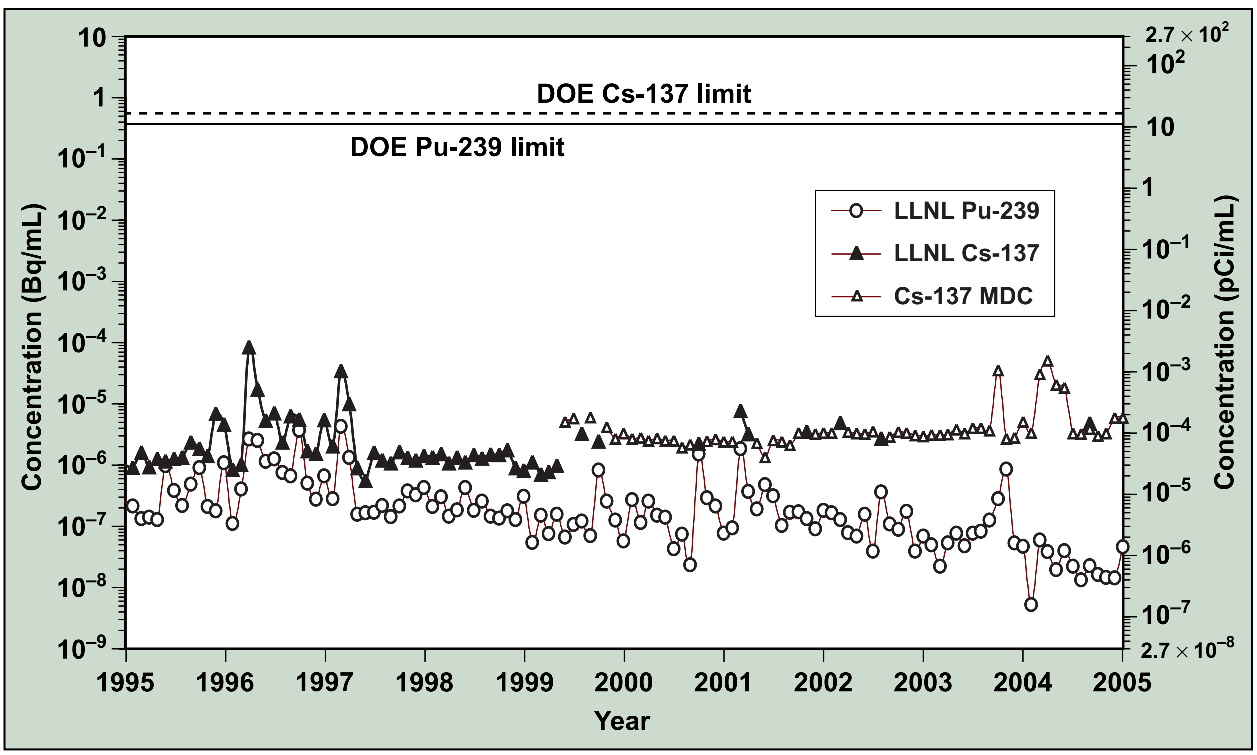


Figure 4-3. Average monthly plutonium and cesium concentrations in LLNL sanitary sewer effluent

Table 4-5. Historical radioactive liquid effluent releases from the Livermore site, 1994–2004

Year	Liquid effluent (GBq)	
	Tritium	Plutonium-239
1994	6.9	1.9×10^{-4}
1995	6.0	1.2×10^{-4}
1996	12[(a)]	4.2×10^{-4}
1997	9.1	2.1×10^{-4}
1998	10	0.77×10^{-4}
1999	7.1	0.68×10^{-4}
2000	5.0	0.96×10^{-4}
2001	4.9	1.1×10^{-4}
2002[(b)]	0.74	0.42×10^{-4}
2003[(b)]	1.11	0.51×10^{-4}
2004[(b)]	1.34	1.16×10^{-5}

a In 1995, Sandia/California ceased all tritium facility operations. Therefore, the annual tritium totals beginning with the 1996 value do not include contributions from Sandia/California.

b Starting in 2002, following DOE guidance, actual analytical values were used to calculate total instead of LOS values.

month. In 2004, the flow-weighted monthly concentrations were generally typical of the values seen in recent years. In **Table 4-6**, the 2004 median flow-weighted concentration for each metal is shown and compared with the EPL. The median flow-weighted monthly concentrations for the nine regulated metals remained essentially unchanged, less than 10% variation, from the corresponding 2003 values for all nine regulated metals. These flow-weighted monthly concentration median values were less than 10% of the EPLs for all but copper, lead, and zinc, which were at 18%, 11%, and 15% of the wastewater discharge permit limit, respectively.

Figure 4-4 presents historical trends for the monthly 24-hour composite sample results from 2000 through 2004 for eight of the nine regulated metals; cadmium is not presented because this metal was not detected above the practical quantitation limit (PQL) of 0.005 mg/L. (Typical PQLs for the regulated metals in LLNL sanitary effluent are shown in **Table 4-6**. Sample results for the 2004 monthly 24-hour composites are included in the file "Ch4 LV Wastewater" provided on the report CD.) All of the monthly 24-hour composite samples were in compliance with LLNL's wastewater discharge permit limits. As noted in recent years, the concentrations of silver, arsenic, chromium, mercury (other than the August value of 0.002 mg/L, an analytical artifact resulting from matrix interference), and nickel remain very close to their respective

Table 4-6. Flow-weighted monthly concentrations for regulated metals in LLNL sanitary sewer effluent (mg/L), 2004

Month	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Jan	0.012	0.0026	<0.0050	0.020	0.17	0.00033	0.0095	0.014	0.48
Feb	<0.010	0.0027	<0.0050	0.020	0.15	0.00037	0.0081	0.013	0.42
Mar	<0.010	0.0042	<0.0050	0.023	0.16	0.00055	0.0088	0.019	0.46
Apr	<0.010	0.0038	<0.0050	0.027	0.16	0.00038	0.0093	0.067	0.46
May	<0.010	0.0040	<0.0050	0.027	0.15	0.00042	0.0088	0.038	0.39
Jun	0.013	0.0063	<0.0050	0.030	0.20	0.00073	0.012	0.025	0.48
Jul	<0.010	0.0055	<0.0050	0.020	0.25	0.00034	0.011	0.035	0.38
Aug	0.010	0.0051	<0.0050	0.018	0.23	0.00051	0.010	0.028	0.34
Sep	<0.010	0.0057	<0.0050	0.021	0.30	0.00033	0.012	0.024	0.39
Oct	<0.010	0.0042	<0.0050	0.018	0.18	0.00031	0.010	0.018	0.43
Nov	<0.010	0.0034	<0.0050	0.020	0.18	0.00026	0.0093	0.012	1.88
Dec	<0.010	0.0044	<0.0050	0.018	0.23	0.00029	0.012	0.019	0.44
Median	<0.010	0.0042	<0.0050	0.020	0.18	0.00035	0.0097	0.021	0.44
IQR[a]	—[b]	0.0015	—[b]	0.0045	0.064	0.00012	0.0017	0.012	0.075
EPL[c]	0.20	0.06	0.14	0.62	1.0	0.01	0.61	0.20	3.00
Median fraction of EPL	<0.05	0.07	<0.04	0.03	0.18	0.04	0.02	0.11	0.15
PQL[d]	0.010	0.0020	0.0050	0.010	0.010	0.00020	0.0050	0.0020	0.020

Note: Monthly values are presented with less-than signs when all weekly composite sample results for the month are below the detectable concentration.

a IQR = Interquartile range

b Because of the large number of nondetects, the interquartile range cannot be calculated. See Chapter 8.

c EPL = Effluent pollutant limit (LLNL Wastewater Discharge Permit 1250, 2003/2004, and 2004/2005)

d PQL = practical quantitation limit (These limits are typical values for sanitary sewer effluent samples.)

PQLs. The other metals (copper, lead, and zinc) are regularly detected above their PQLs and continue to show an occasional elevated concentration. Even these elevated values, however, never exceeded 30% of their EPLs in 2004; copper, lead, and zinc peaked at 28%, 21%, and 16% of their respective EPLs.

The monthly 24-hour composite and weekly composite concentrations for 2004 are presented in **Figure 4-5** for eight of nine regulated metals as a percentage of the corresponding EPL; cadmium results are not presented because the metal was not detected above the practical quantitation limit of 0.005 mg/L in any of the weekly or monthly samples. As previously mentioned, all of the monthly 24-hour composite samples are

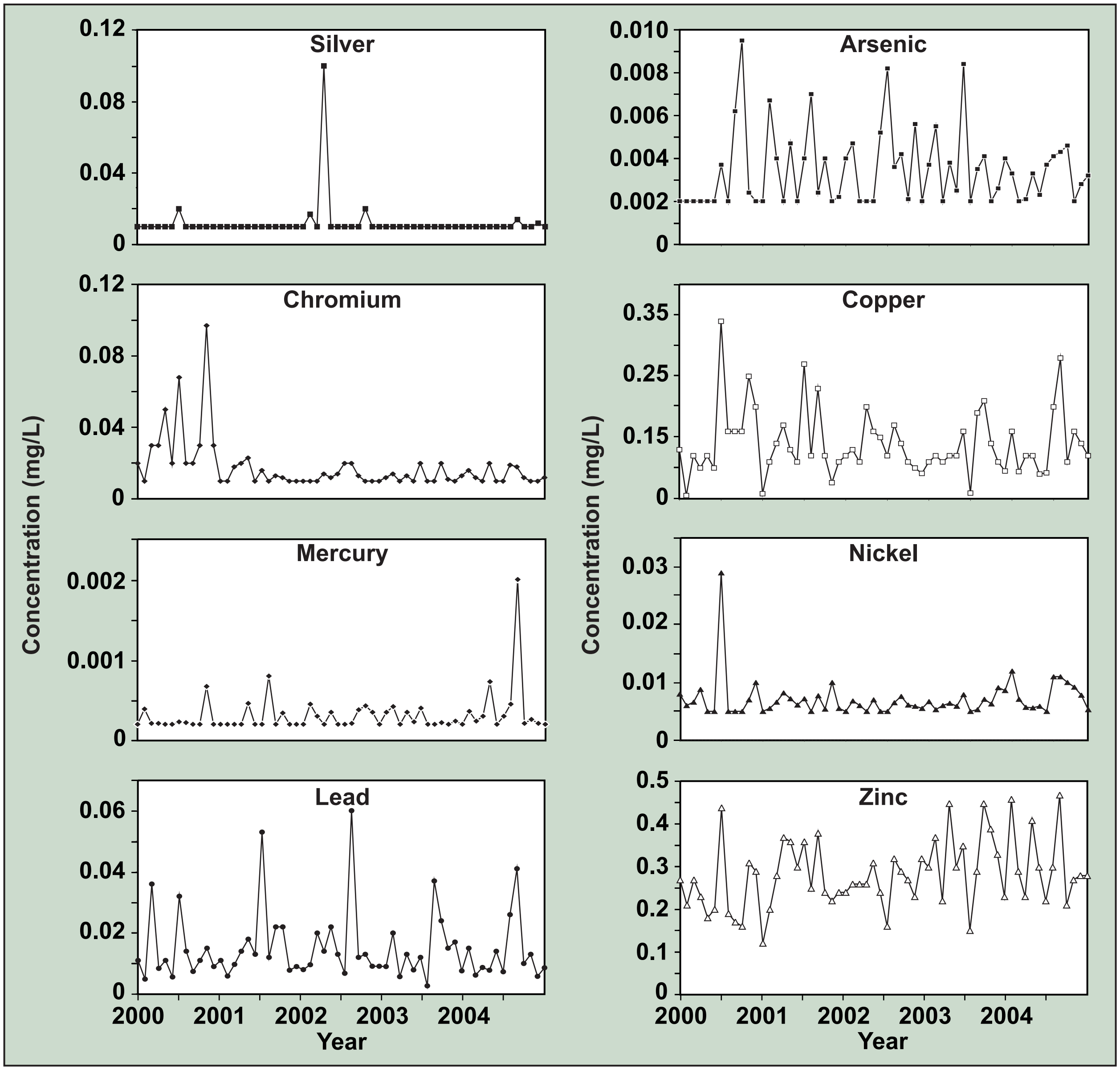


Figure 4-4. Monthly 24-hour composite sample concentrations for eight of the nine regulated metals in LLNL sanitary sewer effluent showing historical trends

well below 50% of their respective EPLs. Of the weekly composites, a total of four samples were identified for additional analyses based on concentrations above the permit-specified action limit.

These investigations examined two weekly samples for lead (from April and May at 126% and 59% of the EPL, respectively), one weekly sample for copper (from September at 68% of the EPL), and one weekly sample for zinc (from November at 193% of the EPL).

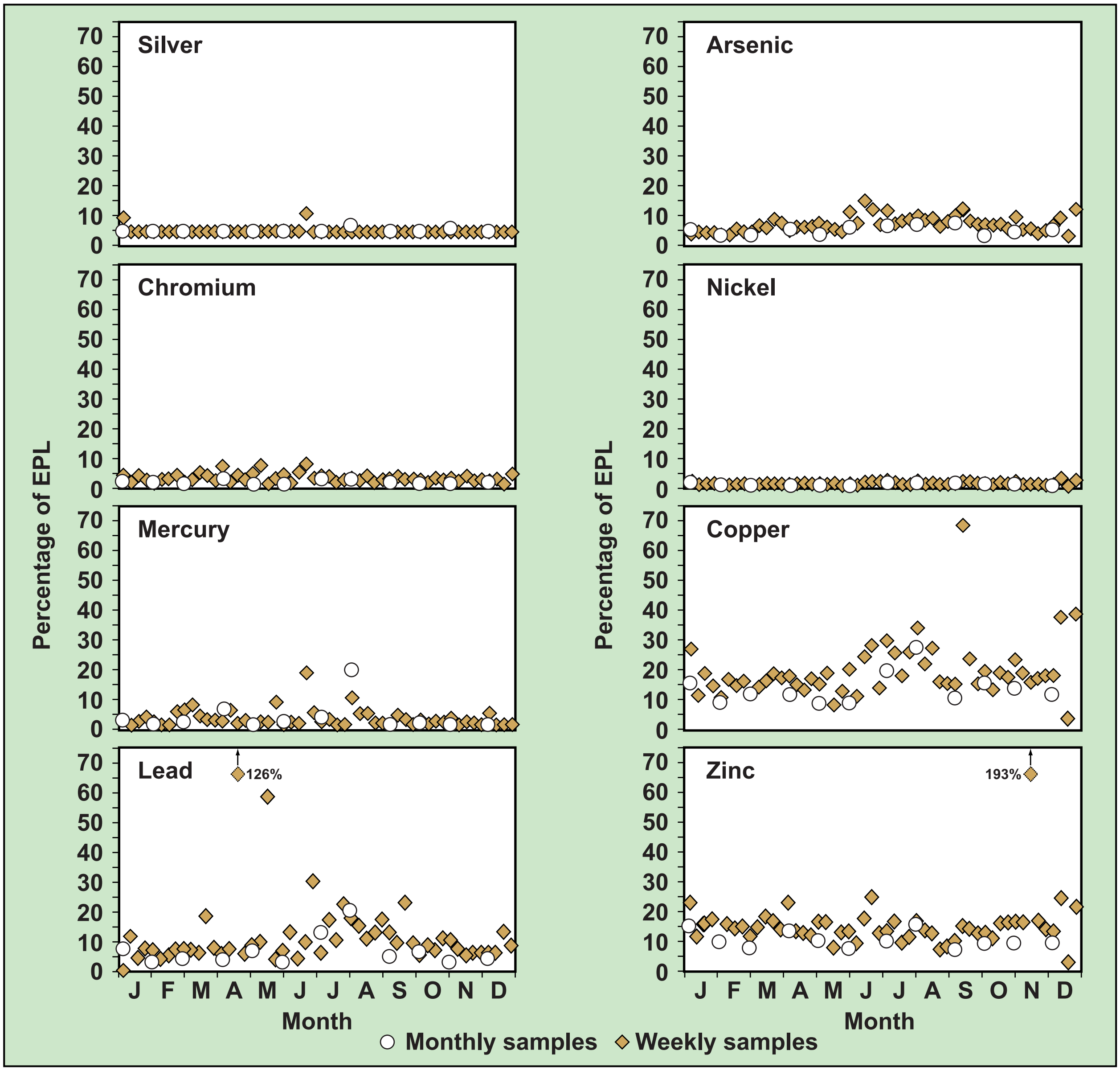


Figure 4-5. Results as percentages of effluent pollutant limits (EPLs) for eight of the nine regulated metals in LLNL sanitary sewer effluent, 2004

As required by the permit, the daily samples that correspond to the appropriate 7-day composite sampling periods were submitted to an off-site contract analytical laboratory for analysis. In each of these four cases, results from the 24-hour composite daily samples demonstrated that no metal concentration exceeded the wastewater discharge limits. Although the LWRP was advised of these elevated metal concentrations (initially detected in weekly composite samples), the results from the follow-up analyses of daily samples were also reported; confirming that there was no threat to the integrity of the

LWRP operations. (Note: Experience has demonstrated a number of limitations associated with the weekly composite sampling location used through 2004, impacting the homogeneity of effluent samples and resulting in anomalous concentration values for the permitted metals. To improve the quality of the weekly samples, the LWRP approved relocating LLNL's weekly composite sampler into the SMS facility alongside the existing daily composite sampling system. This location change became effective on December 30, 2004, and will apply to all the weekly composite samples reported for 2005.)

Detections of anions, metals, and organic compounds and summary data concerning other physical and chemical characteristics of the sanitary sewer effluent are provided in **Table 4-7**. (**Table 4-7** does not include the monthly metals results, which are plotted in **Figure 4-5**, or monthly monitoring results for analytes not detected in any of the 24-hour composite or grab samples. All analytical results are included in the file "Ch4 LV Wastewater" provided on the report CD.) The 2004 results are similar to typical values seen in previous years for the two regulated parameters, cyanide and total toxic organics (TTO; see chemicals with a "(g)" superscript in **Table 4-7**), and all other nonregulated parameters. Cyanide (permit limit 0.04 mg/L) was below analytical detection limits (0.02 mg/L) in both the April and September semiannual samples. The monthly TTO values ranged from <0.010 mg/L to 0.065 mg/L (with a TTO median value of 0.036 mg/L), well below the TTO permit limit of 1.0 mg/L. In addition to the organic compounds regulated under the TTO standard, six nonregulated organics were also detected in LLNL's sanitary sewer effluent: three volatile organic compounds (acetone, ethanol, and Freon 113) and three semivolatile organic compounds (benzoic acid, benzyl alcohol, and 3- & 4-methylphenol [m- and p-Cresol]).

In 2004, the SMS continuous monitoring system detected one inadvertent discharge outside the permitted pH range of 5 to 10. This event, with a pH slightly below 5, occurred off-hours (Sunday, March 7, 2004) when the upstream pHMS was off-line. As a result, a small front-end volume of low pH sanitary effluent was released to the LWRP system before the SMS initiated a diversion to the SDF. The LWRP was immediately notified of this low pH discharge; however, this incident did not represent a threat to the integrity of the operations of the LWRP. The lowest pH recorded for effluent contained in the March 7 release was 4.6.

Table 4-7. Monthly monitoring summary for physical and chemical characteristics of the LLNL sanitary sewer effluent, 2004[(a)]

Parameter	Detection frequency[(b)]	Minimum	Maximum	Median	IQR[(c)]
24-hour composite sample parameter (mg/L)					
Alkalinity					
Bicarbonate alkalinity (as $CaCO_3$)	12 of 12	190	330	230	42.5
Carbonate alkalinity (as $CaCO_3$)	7 of 12	<5	68	10.5	—[(d)]
Total alkalinity (as $CaCO_3$)	12 of 12	210	360	245	62.5
Anions					
Bromide	11 of 12	<0.1	0.6	0.25	0.25
Chloride	12 of 12	41	350	100	200
Fluoride	11 of 12	<0.05	0.39	0.19	0.1

Table 4-7. Monthly monitoring summary for physical and chemical characteristics of the LLNL sanitary sewer effluent, 2004[(a)] (continued)

Parameter	Detection frequency[(b)]	Minimum	Maximum	Median	IQR[(c)]
Nitrate (as N)	10 of 12	<0.1	0.83	0.20	0.38
Nitrate (as NO_3)	10 of 12	<0.5	3.7	0.86	1.6
Nitrate plus Nitrite (as N)	2 of 3[(e)]	<0.1	1.1	—[(e)]	—[(d)]
Nitrite (as NO_2)	4 of 12	<0.5	0.96	<0.5	—[(d)]
Orthophosphate	11 of 11[(f)]	9.3	20	16	5.5
Sulfate	12 of 12	<0.1	0.6	0.25	0.25
Nutrients					
Ammonia nitrogen (as N)	12 of 12	23	53	42	8.8
Total Kjeldahl nitrogen	12 of 12	35	74	57	13
Total phosphorus (as P)	12 of 12	5.4	11	8.5	1.7
Oxygen demand					
Biochemical oxygen demand	12 of 12	154	349	262	49.8
Chemical oxygen demand	12 of 12	404	712	522	150
Solids					
Settleable solids	12 of 12	5	40	27	11
Total dissolved solids (TDS)	12 of 12	208	970	379	441
Total suspended solids (TSS)	12 of 12	240	650	320	105
Volatile solids	12 of 12	320	820	405	143
Total metals					
Aluminum	12 of 12	0.3	0.74	0.42	0.18
Calcium	12 of 12	14	61	27	27
Iron	12 of 12	1.4	3.4	1.9	0.85
Magnesium	12 of 12	3.1	36	9.5	18
Potassium	12 of 12	17	27	20	4.3
Selenium	3 of 12	<0.002	0.0023	<0.002	—[(d)]
Sodium	12 of 12	34	240	71	110
Total organic carbon (TOC)	12 of 12	32	62	51	11
Grab sample parameter					
Semivolatile organic compounds (µg/L)					
Benzoic acid	8 of 12	<10	110	<22	—[(d)]
Benzyl alcohol	11 of 12	<10	650	12	—[(d)]
Bis(2-ethylhexyl)phthalate[(g)]	4 of 12	<5	<30	<5.4	—[(d)]
Butylbenzylphthalate[(g)]	2 of 12	<2	12	<2	—[(d)]
Dibutylphthalate[(g)]	3 of 12	<2	32	<3	—[(d)]
Diethylphthalate[(g)]	11 of 12	<10	29	21	—[(d)]
Phenol[(g)]	7 of 12	<2	41	<8.5	—[(d)]
m- and p-Cresol	7 of 12	<2	54	<9.9	—[(d)]
Total oil and grease (mg/L)[(h)]	8 of 8	9.5	38	24.5	8.8
Volatile organic compounds (µg/L)					
1,4-Dichlorobenzene[(g)]	5 of 12	<0.5	2.2	<0.5	—[(d)]
Acetone	12 of 12	110	520	290	180
Bromodichloromethane[(g)]	8 of 12	<0.5	3	1.5	—[(d)]
Bromoform[(g)]	7 of 12	<0.5	3	0.55	—[(d)]

Table 4-7. Monthly monitoring summary for physical and chemical characteristics of the LLNL sanitary sewer effluent, 2004[a] (continued)

Parameter	Detection frequency[b]	Minimum	Maximum	Median	IQR[c]
Bromomethane[g]	1 of 12	<1	5.6	<1	—[d]
Chloroform[g]	12 of 12	1.5	17	3.9	7.6
Dibromochloromethane[g]	7 of 12	<0.5	4.5	1.4	—[d]
Dibromomethane[g]	2 of 12	<0.5	0.78	<0.5	—[d]
Ethanol	2 of 12	<800	8300	<800	—[d]
Freon 113	2 of 12	<0.5	61	<0.5	—[d]
Toluene[g]	5 of 12	<0.5	1.3	<0.5	—[d]

a The monthly sample results plotted in **Figure 4-5** and nondetected values are not included in this table.

b The number of times an analyte was positively identified, followed by the number of samples that were analyzed (generally 12, one sample for each month of the year).

c IQR = Interquartile range

d When the detection frequency is less than or equal to 50%, or there is no range, or there are fewer than six results for a sample parameter, the interquartile range is omitted.

e Due to a change in analytical methods, the contract laboratory reported this parameter in only 3 of 12 months. With so few data points, the median value is omitted.

f Analytical laboratory error (one sample was not analyzed within hold time)

g Priority toxic pollutant parameter used in assessing compliance with the total toxic organic (TTO) permit limit of 1 mg/L (1000 µg/L), LLNL Wastewater Discharge Permit 1250, 2003/2004, and 2004/2005

h The requirement to sample for oil and grease has been suspended until further notice per LWRP letter of April 1, 1999, nevertheless, LLNL collects these samples (four per day) semiannually as part of the source control program.

Categorical Processes

The U.S. Environmental Protection Agency (EPA) publishes Categorical standards for broad categories of specific industrial processes determined to be the most significant contributors to point-source water pollution. These standards contain specific numerical limits for the discharge of industry-specific pollutants from individual processes. At LLNL, the federal Categorical requirements are incorporated into the wastewater discharge permit (1250 (04-05)), which is administered by the LWRP. The number of processes at LLNL under these standards is subject to periodic change as programmatic requirements dictate. During 2004, the LWRP identified 15 specific LLNL wastewater-generating processes that fall under the definition of two categorical standards: Electrical and Electronic Components (40 CFR 469), and Metal Finishing (40 CFR 433). Only those processes that discharge to the sanitary sewer require sampling, inspection, and reporting. Three of the 15 processes meet these criteria. In 2004, LLNL analyzed compliance samples for all regulated parameters from these three processes and demonstrated compliance with all federal Categorical discharge limits. Other processes that do not discharge to the sanitary sewer but would otherwise be regulated under the Metal-Finishing Point Source Category include printed circuit board manufacturing, electrolysis plating, chemical etching, electroplating, anodizing, coating, electrical discharge machining, and abrasive jet machining. These 12 nondischarging processes are evaluated semiannually. Wastewater from these nondischarging processes is either recycled or contained for eventual removal and appropriate disposal by LLNL’s RHWM Division. Because these processes do not discharge directly or indirectly to the sanitary sewer, they are not subject to the monitoring and reporting requirements contained in the applicable standard.

As required in LLNL's Wastewater Discharge Permit, compliance with Permit requirements is demonstrated by semiannual sampling and reporting. LWRP Source Control staff performed the required annual inspection and sampling of the three discharging categorical processes in 2004. LLNL Environmental staff sample the same processes semiannually. These compliance samples were analyzed for all regulated parameters and the resulting data collected demonstrate compliance with all federal and local pretreatment limits. Of the three discharging categorical processes, the Building 153 microfabrication facility released the largest volume of water to the sanitary sewer. As a further environmental safeguard, LLNL sampled each volume retained at Building 153 prior to discharge to the sanitary sewer. These monitoring data were reported to the LWRP in July 2004 and January 2005 semiannual wastewater reports (Grayson 2004, 2005).

Discharges of Treated Groundwater

LLNL’s groundwater discharge permit (1510G, 2002-2004) allows treated groundwater from the Livermore site Ground Water Project (GWP) to be discharged in the City of Livermore sanitary sewer system. (See Chapter 7 for more information on the GWP.) During 2004, there were six discharges to the sanitary sewer from the GWP. The total volume of treated groundwater discharged to sanitary sewer was 18,645 liters. In each of these discharge events, the groundwater released to the sanitary sewer originated from the lower zone, beneath the LLNL site. These volumes of groundwater were acquired at one of the on-site treatment facilities and used to condition new ion exchange resin columns. These six events were separately sampled and discharged to the sanitary sewer during 2004, all in compliance with self-monitoring permit provisions and discharge limits of the permit. Complete monitoring data are presented in the *Ground Water Discharge Annual Self-Monitoring Report for 2004* (Revelli 2005a).

Environmental Impact of Sanitary Sewer Effluent

During 2004, no discharges exceeded any discharge limits for release of radioactive materials to the sanitary sewer. The data are comparable to the lowest historical values. All the values reported for radiological releases are a fraction of their corresponding limits. Overall, LLNL achieved near perfect compliance with the provisions of its wastewater discharge permit for nonradioactive materials; only one release of nonradiological constituents outside permissible limits (a short pH discharge of 4.6, which was slightly below the 5.0 pH limit) was detected.

The data demonstrate that LLNL has continued the trend of excellent control of radiological and nonradiological discharges to the sanitary sewer. Monitoring results for 2004 reflect an extremely effective year for LLNL's wastewater discharge control program and indicate no adverse impact to the LWRP or the environment from LLNL sanitary sewer discharges.

Site 300 Sewage Ponds and Surface Impoundments

Wastewater samples collected from the influent to the sewage evaporation pond, within the sewage evaporation pond, and flow to the sewage percolation pond; and wastewater samples collected from discharges to the Class II surface impoundments (surface impoundments) from photographic processes, Chemistry Area processes, and Explosives processes were obtained in accordance with the written standardized procedures summarized in the *Environmental Monitoring Plan* (Woods 2005).

Sewage Evaporation and Percolation Ponds

Sewage generated at buildings in the General Services Area at Site 300 is discharged into a lined evaporation pond. The wastewater is disposed of through evaporation from the pond. However, during rare periods of high rainfall, treated wastewater may overflow into an unlined percolation pond, where it enters the ground and the shallow groundwater.

The environmental monitoring requirements for the sewage evaporation and percolation ponds (hereafter collectively referred to as sewage ponds) are specified in the Monitoring and Reporting Program (MRP) for Waste Discharge Requirements Order No. 96-248 (WDR 96-248). The monitoring requirements include both wastewater monitoring and groundwater monitoring to detect potential impacts of the sewage on groundwater quality. Wastewater is sampled quarterly at a sampling point (ISWP) in the line running into the sewage pond and within the sewage evaporation pond (ESWP). Overflows into the adjacent percolation pond are also permitted under WDR 96-248 and are sampled as needed in the discharge line (DSWP) from the sewage pond to the percolation pond. Nine groundwater monitoring wells are sampled semiannually to provide information on the groundwater quality in the vicinity of the sewage ponds. All sampling locations are shown in **Figure 4-6**. The wells are screened in three different geological formations: Qal, $Tnbs_1$, and $Tnsc_1$ (see Chapter 7). $Tnbs_1$ (Neroly Formation lower blue sandstone unit) is the regional aquifer.

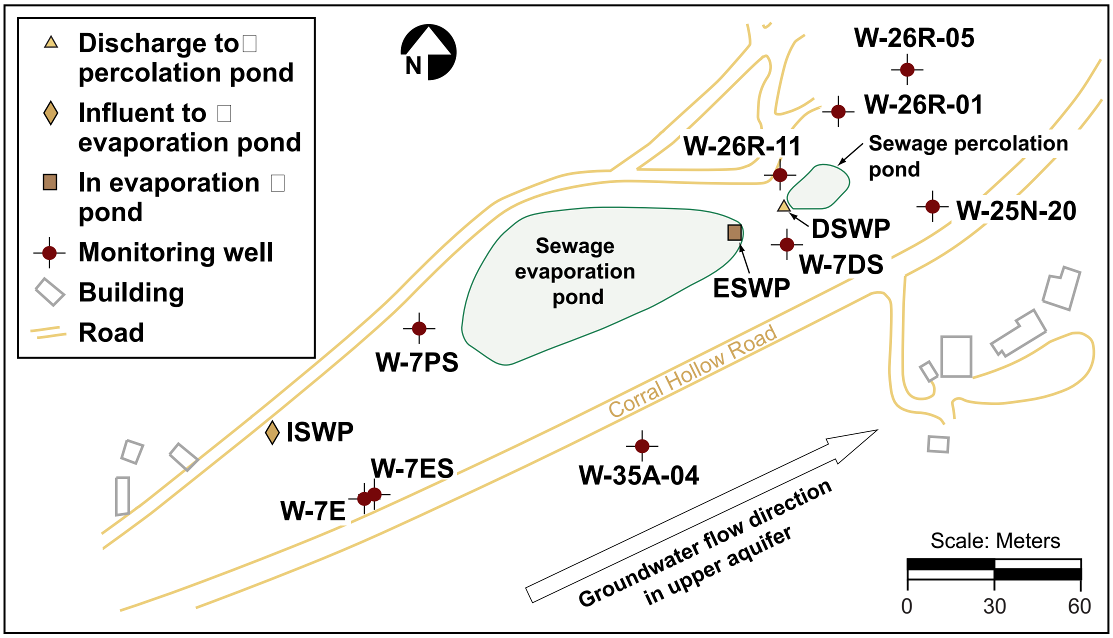


Figure 4-6. Sewage evaporation and percolation ponds, compliance groundwater monitoring wells, and wastewater monitoring locations, 2004

All wastewater parameters for the sewage evaporation and percolation ponds complied with permit provisions and specifications throughout 2004. There was one continuous overflow from the sewage evaporation pond to the percolation pond that began in late December 2003 and continued into the first quarter of 2004. This permitted discharge was sampled twice and reported to the Central Valley Regional Water Quality Control Board (CVRWQCB). For details, see *LLNL Experimental Test Site 300 Compliance Monitoring Report for Waste Discharge Requirements 96-248, Annual/Fourth Quarter Report 2004* (Brown 2005b). All of the monitored groundwater constituents were also in compliance with permit limits.

Surface Impoundments

WDR 96-248 also establishes the basis for compliance monitoring of two connected surface impoundments at Site 300 that receive wastewater and rinsewater discharges from the Explosives Process Area, chemistry buildings, and photographic processes. This includes monitoring of various influent waste streams to the surface impoundments. Influent monitoring complements administrative control of chemicals that could degrade the polyethylene liners of the impoundments. A two-tiered monitoring program comprising weekly visual inspections of the leachate collection and removal systems, and quarterly sampling of monitoring wells is in place to detect any release of chemicals from the surface impoundments.

Wastewater discharges from each of these three processes (explosives, chemistry, and photography) to the surface impoundments are analyzed for constituents of concern (COCs) that have been found, or are likely to be found, in the process water from each specified process area. The monitoring program contained in WDR 96-248 establishes limits for discharges of COCs into the surface impoundments. In addition, no hazardous or radioactive waste is allowed in the surface impoundments.

Influent waste streams are monitored at a prescribed frequency for area-specific COCs. Annual monitoring was performed on discharges from the Explosives Process Area: Buildings 806/807 and 817. (Building 809 is also included in this area but was inactive in 2004.) Discharges from this area were discharged automatically into the surface impoundments. Wastewater from the Chemistry Area (Buildings 825 and 826, and the Building 827 Complex) is held in retention tanks until analytical results indicate that all COCs are within discharge limits. No discharges occurred from the retention tanks at Buildings 825, 826, or 827A; several discharges from Buildings 827C, 827D, and 827E to the surface impoundments occurred in 2004. Photographic process rinsewaters from Buildings 801 and 851 were sampled before being discharged, but were released to the surface impoundments prior to obtaining sample results. Discharges to the surface impoundments from retention tanks at Buildings 801 and 851 were discontinued during the second quarter of 2004. Rinsewater from photographic processes at Building 823 was discharged automatically to the surface impoundments. Quarterly samples were collected and analyzed of those discharges from Building 823 to satisfy the requirements of WDR 96-248.

No release of water to ground from the surface impoundments occurred during 2004. For a detailed account of compliance monitoring of the Site 300 surface impoundments, see *LLNL Experimental Test Site 300 Compliance Monitoring Report for Waste Discharge Requirements 96-248, Annual/Fourth Quarter Report 2004* (Brown 2005b).

The two leachate collection and removal systems were monitored weekly for the presence of liquids to identify potential leaks. None were observed during 2004. No water has been observed in the leachate collection and removal system since liner repairs were made in 1997.

LLNL is required to obtain groundwater samples quarterly from four monitoring wells (see **Figure 4-7**) and has established statistical concentration limits for COCs in groundwater beneath the surface impoundments. These requirements are part of the MRP for the surface impoundments detailed in WDR 96-248. Sporadic detections of ammonia and of the plasticizer compound bis(2-ethylhexyl)phthalate have occurred since 2000. However, because these chemicals have also been detected in method blank samples, LLNL has determined that these COCs were not present in the groundwater samples but were due to laboratory contamination of the samples.

Explosive compounds (HMX, RDX, and breakdown products) and perchlorate are the compounds most indicative of discharges to groundwater from the Explosives Process Area surface impoundments. However, prior to 1985, explosives wastewater was discharged into unlined ponds in the vicinity of the present surface impoundments where it infiltrated the soil; some of the explosives wastewater reached groundwater. Because of

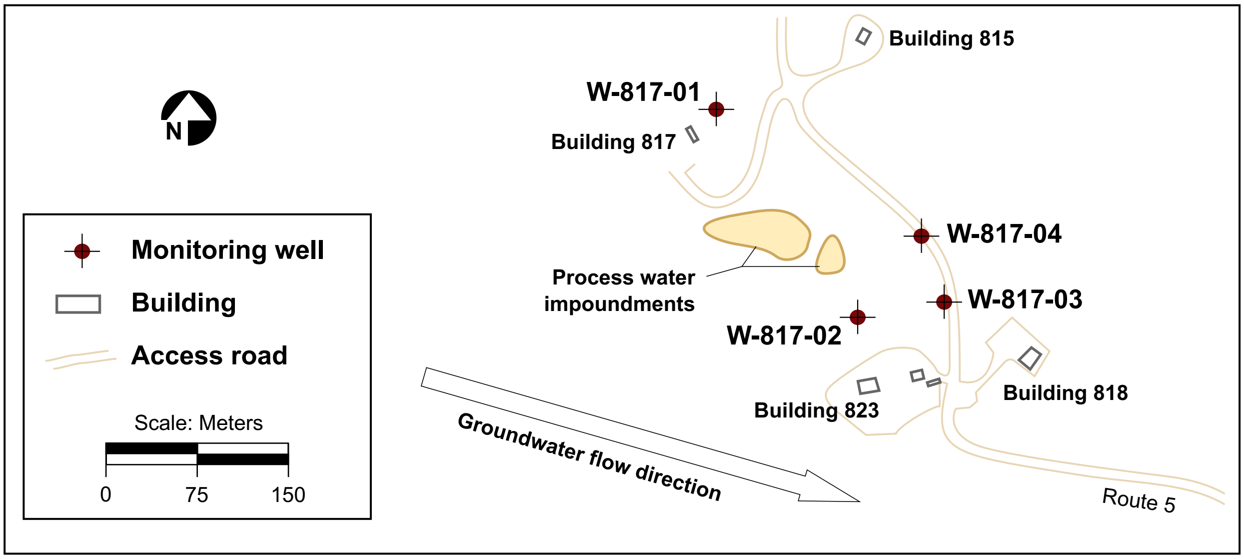


Figure 4-7. Locations of compliance groundwater monitoring wells in the Explosives Process Area, 2004

this past practice, it is necessary under regulations to discriminate between new releases from the surface impoundments and past releases from the unlined ponds. (Background concentrations were statistically calculated for each COC based on historical data from all four monitoring wells. Any sample concentration exceeding background concentration, and by a retest sample, is assumed to come from a new release of that COC.) (See also Chapter 7.) A few concentrations of the energetic compounds PETN, RDX, and 4-amino-2,6-dinitrotoluene that exceeded statistical limits in downgradient monitor wells during the third quarter were determined to be statistical outliers. As statistical outliers, it was not necessary to report them to the CVRWQCB as exceeding statistical limits. LLNL continues to monitor and to track these concentrations. For details, see *LLNL Experimental Test Site 300 Compliance Monitoring Report for Waste Discharge Requirements 96-248, Annual/Fourth Quarter Report 2004* (Brown 2005b).

A split above the waterline in the HDPE liner of the upper surface impoundment was discovered October 13 together with several other weak places or striations. The damage was reported to the CVRWQCB on October 14, observed by the CVRWQCB on October 25, and repaired on November 4, 2004. The surface impoundments are being closed in 2005 because the HDPE liner has exceeded its useful life. An alternate method of wastewater disposal was agreed upon.

Percolation Pits

Percolation pits designed to accept discharges from mechanical equipment are located at Site 300 Buildings 806A, 827A, 827C, 827D, and 827E. In other Site 300 facilities, these types of waste streams are discharged to septic systems. These discharges are permitted by WDR 96-248, which specifies monthly observations and monitoring requirements for overflows of the percolation pits. If an overflow should occur, it is sampled and analyzed to determine concentrations of any metals present. During 2004, all of the percolation pits operated normally with no overflows. Percolation pits at Buildings 827C and 827D contained standing water throughout the fourth quarter (Brown 2005b).

Environmental Impact of Sewage Ponds and Surface Impoundments

All discharges from the Site 300 sewage evaporation pond to the percolation pond, as well as discharges to the surface impoundments from the Explosives Process Area, chemistry buildings, and photographic processes were in compliance with discharge limits. Groundwater monitoring related to these areas indicates that there were no measurable impacts to the groundwater from these LLNL wastewater discharges.

Storm Water Compliance and Surveillance Monitoring

To assess compliance with permit requirements, LLNL monitors storm water at the Livermore site in accordance with WDR 95-174, National Pollutant Discharge Elimination System (NPDES) Permit No. CA0030023, issued in 1995 by the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB 1995). LLNL monitors storm water discharges at Site 300 in accordance with the California NPDES General Permit for Storm Water Discharges Associated with Industrial Activity (WDR 97-03-DWQ), NPDES Permit No. CAS000001, State Water Resources Control Board (SWRCB 1997). For construction projects that disturb 0.4 hectares (1 acre) of land or more LLNL also met the storm water compliance monitoring requirements of the California NPDES General Permit for Storm Water Discharges Associated with Construction Activity (WDR 99-08-DWQ, NPDES Permit No. CAS000002) (SWRCB 1999) and subsequent modifications.

Site 300 storm water monitoring also meets the requirements of the *Post-Closure Plan for the Pit 6 Landfill Operable Unit* (Ferry et al. 1998), which includes specific monitoring and reporting requirements. In addition to the storm water quality constituents required by the closure plan, LLNL monitors other constituents to provide a more complete water quality profile. Appendix A includes the current list of analyses conducted on storm water, including analytical methods and typical reporting limits.

Storm water monitoring at both sites also follows the requirements in the *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (U.S. DOE 1991) and meets the applicable requirements of DOE Order 5400.5, Radiation Protection of the Public and the Environment.

At all monitoring locations at both the Livermore site and Site 300, grab samples are collected from the storm water runoff flowing in the storm drains and stream channels. Grab samples are collected by partially submerging sample bottles directly into the water and allowing them to fill with the sample water. If the water to be sampled is not directly accessible, a stainless-steel bucket or an automatic water sampler is used for sampling. The bucket is triple-rinsed with the water to be sampled, then dipped or submerged into the water and withdrawn in a smooth motion. Sampling is conducted away from the edge of the arroyo to prevent the collection of sediment into the water samples. Sample vials for volatile organics are filled before sample bottles for all other constituents and parameters. In addition to chemical monitoring, LLNL is required by NPDES permit WDR 95-174 to conduct acute and chronic fish toxicity testing on samples from the Arroyo Las Positas (Livermore site) once per wet season. LLNL is not required to test for fish toxicity at Site 300.

For the purpose of evaluating the overall impact of the Livermore site and Site 300 operations on storm water quality, storm water flows are sampled at upstream and downstream locations. Because of flow patterns at the Livermore site, storm water at sampling locations includes runoff from other sources, such as neighboring agricultural land, parking lots, and landscaped areas. In contrast, storm water at Site 300 is sampled at locations that target specific on-site activities with no run-on from off-site sources. These samples provide the information necessary to maintain compliance with the SWRCB.

NPDES permits for storm water require that LLNL sample effluent two times per year. In addition, LLNL is required to visually inspect the storm drainage system during the first hour of one storm event per month in the wet season (defined as October of one year through April [Livermore site] or May [Site 300] of the following year) to observe runoff quality and twice during the dry season to identify any dry weather flows. Influent sampling is also required at the Livermore site. In addition, annual facility inspections are required to ensure that the best management practices (BMPs) to control storm water pollution are implemented and adequate.

Constituent Criteria

There are no numeric criteria that limit concentrations of specific constituents in LLNL's storm water effluent. The U.S. Environmental Protection Agency (EPA) established parameter benchmark values, but stressed that these concentrations are not intended to be interpreted as effluent limits (U.S. EPA 2000). Rather, the values are levels that the EPA has used to determine if storm water discharged from any given facility merits further monitoring. Although these criteria are not directly applicable, they are used as comparison criteria to help LLNL evaluate its storm water management program. To further evaluate the storm water management program, LLNL established or calculated site-specific threshold comparison criteria for a select group of parameters. A value exceeds the threshold if it is greater than the 95% confidence limit computed for the historical mean value for a specific parameter (**Table 4-8**). The threshold comparison criteria are used to identify out-of-the-ordinary data that merit further investigation to determine if concentrations of that parameter are increasing in the storm water runoff. For a better understanding of how LLNL storm water data relate to other target values, LLNL also compares water samples with criteria listed in the *Water Quality Control Plan, San Francisco Bay Basin* (SFBRWQCB 1995), *The Water Quality Control Plan (Basin Plan) for the California Regional Water Quality Control Board, Central Valley Region, Sacramento and San Joaquin River Basins* (CVRWQCB 1998), state and federal maximum contaminant levels (MCLs), and U.S. EPA ambient water quality criteria (AWQC). The greatest importance is placed on the site-specific comparison criteria calculated from historical concentrations in storm runoff.

Storm Water Inspections

Each directorate at LLNL conducts an annual inspection of its facilities to verify implementation of the storm water pollution prevention plans (SWPPPs) and to ensure that measures to reduce pollutant discharges to storm water runoff are adequate. LLNL's associate directors certified in 2004 that their facilities complied with the provisions of LLNL's storm water pollution prevention plans. LLNL submits annual storm water monitoring reports to the SFBRWQCB and to the CVRWQCB with the results of sampling, observations, and inspections (Brown 2004a,b).

For each construction project permitted by WDR 99-08-DWQ, LLNL conducts visual observations of construction sites before, during, and after storms to assess the effectiveness of BMPs. Annual compliance certifications summarize these inspections. Annual compliance certifications for 2004 covered the period of June 2003 through May 2004. When requested by the respective regional water quality control board (RWQCB), LLNL completes annual compliance status reports that cover the same reporting period. During the 2003/2004 reporting period, LLNL had active permits for seven projects located at the Livermore site (see **Table 2-3**). LLNL terminated the permits for four of the projects that were completed during 2004: the Central Cafeteria, East Avenue Security Upgrades, 5th Street, and the International Security Research Facility (formerly known as the Sensitive Compartmented Information Facility).

Table 4-8. Threshold comparison criteria for selected water quality parameters

Parameter	Livermore site	Site 300
Total suspended solids (TSS)	750 mg/L[a]	1,700 mg/L[a]
Chemical oxygen demand (COD)	200 mg/L[a]	200 mg/L[a]
pH	<6.0, >8.5[a]	<6.0, >9.0[b]
Nitrate (as NO_3)	10 mg/L[a]	not monitored
Orthophosphate	2.5 mg/L[a]	not monitored
Beryllium	1.6 µg/L[a]	1.6 µg/L[a]
Chromium(VI)	15 µg/L[a]	not monitored
Copper	13 µg/L[c]	not monitored
Lead	15 µg/L[d]	30 µg/L[a]
Zinc	350 µg/L[a]	not monitored
Mercury	above RL[e]	1 µg/L[a]
Diuron	14 µg/L[a]	not monitored
Oil and grease	9 mg/L[a]	9 mg/L[a]
Tritium	36 Bq/L[a]	3.17 Bq/L[a]
Gross alpha radioactivity	0.34 Bq/L[a]	0.90 Bq/L[a]
Gross beta radioactivity	0.48 Bq/L[a]	1.73 Bq/L[a]

Note: The sources of values above these are examined to determine if any action is necessary.

a Site-specific value calculated from historical data and studies. These values are lower than the MCLs and EPA benchmarks except for zinc, TSS, and COD.

b EPA benchmark

c Ambient water quality criteria (AWQC)

d California and EPA drinking water action level

e RL = reporting limit = 0.0002 mg/L for mercury

Livermore Site

As is commonly the case in urbanized areas, the surface water bodies and runoff pathways at LLNL do not represent the natural conditions. The drainage at the Livermore site was altered by construction activities several times up to 1966 (Thorpe et al. 1990) so that the current northwest flow of Arroyo Seco and the westward flow of Arroyo Las Positas do not represent historical flow paths. About 1.6 km to the west of the Livermore site, Arroyo Seco merges with Arroyo Las Positas, which continues to the west to eventually merge with Arroyo Mocho (see **Figure 4-8**).

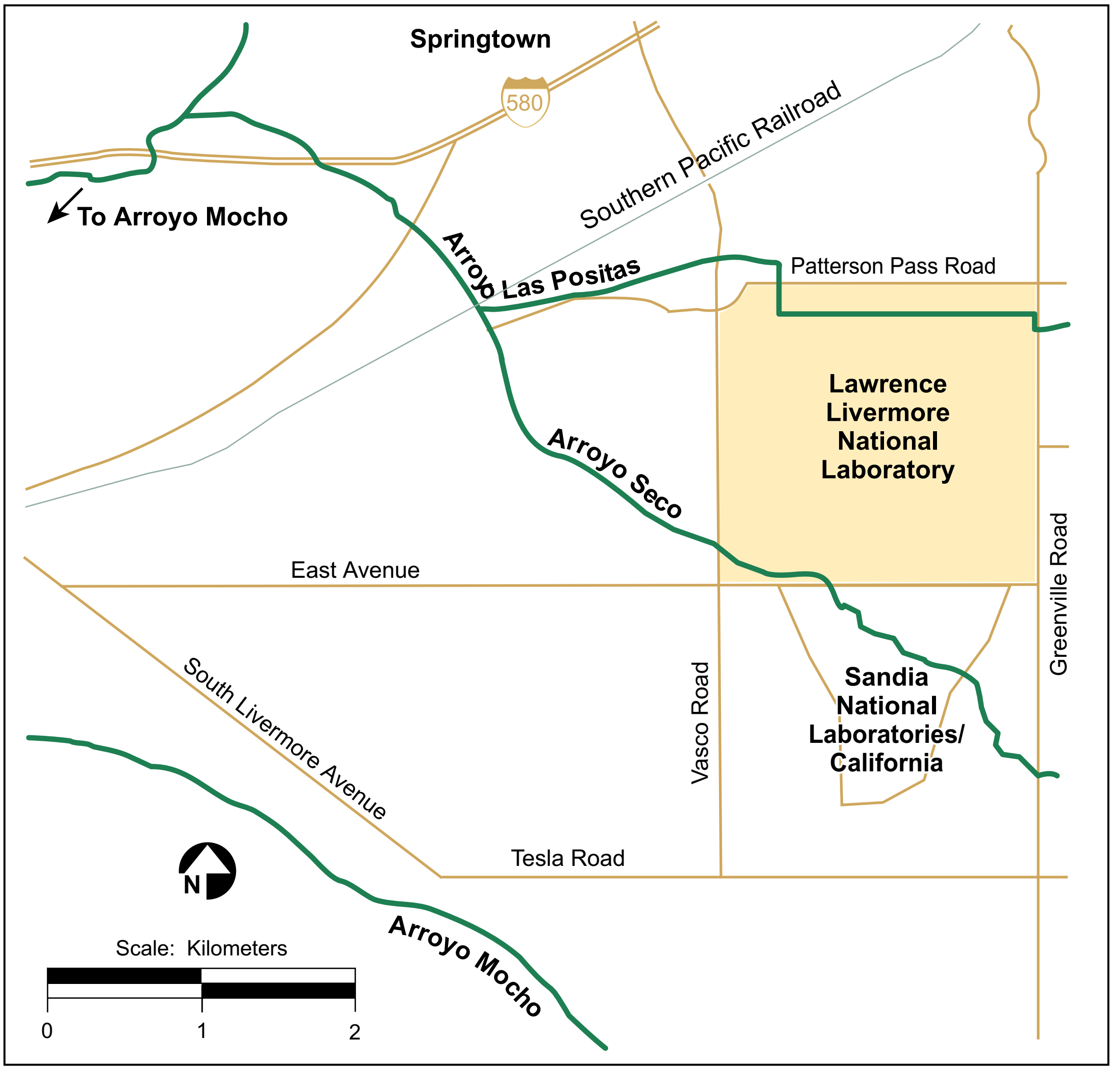


Figure 4-8. Surface waterways in the vicinity of the Livermore site

The Drainage Retention Basin (DRB) was excavated and lined in 1992 to prevent infiltration of storm water that was dispersing groundwater contaminants. It also serves storm water diversion and flood control purposes. The DRB collects about one-fourth of the surface water runoff from the site and a portion of the Arroyo Las Positas drainage (**Figure 4-9**). When full, the DRB discharges north to a culvert that leads to Arroyo Las Positas. The remainder of the site drains either directly or indirectly into the two arroyos by way of storm drains and swales. Arroyo Seco cuts across the southwestern corner of the site. Arroyo Las Positas follows the northeastern and northern boundaries of the site and exits the site near the northwest corner.

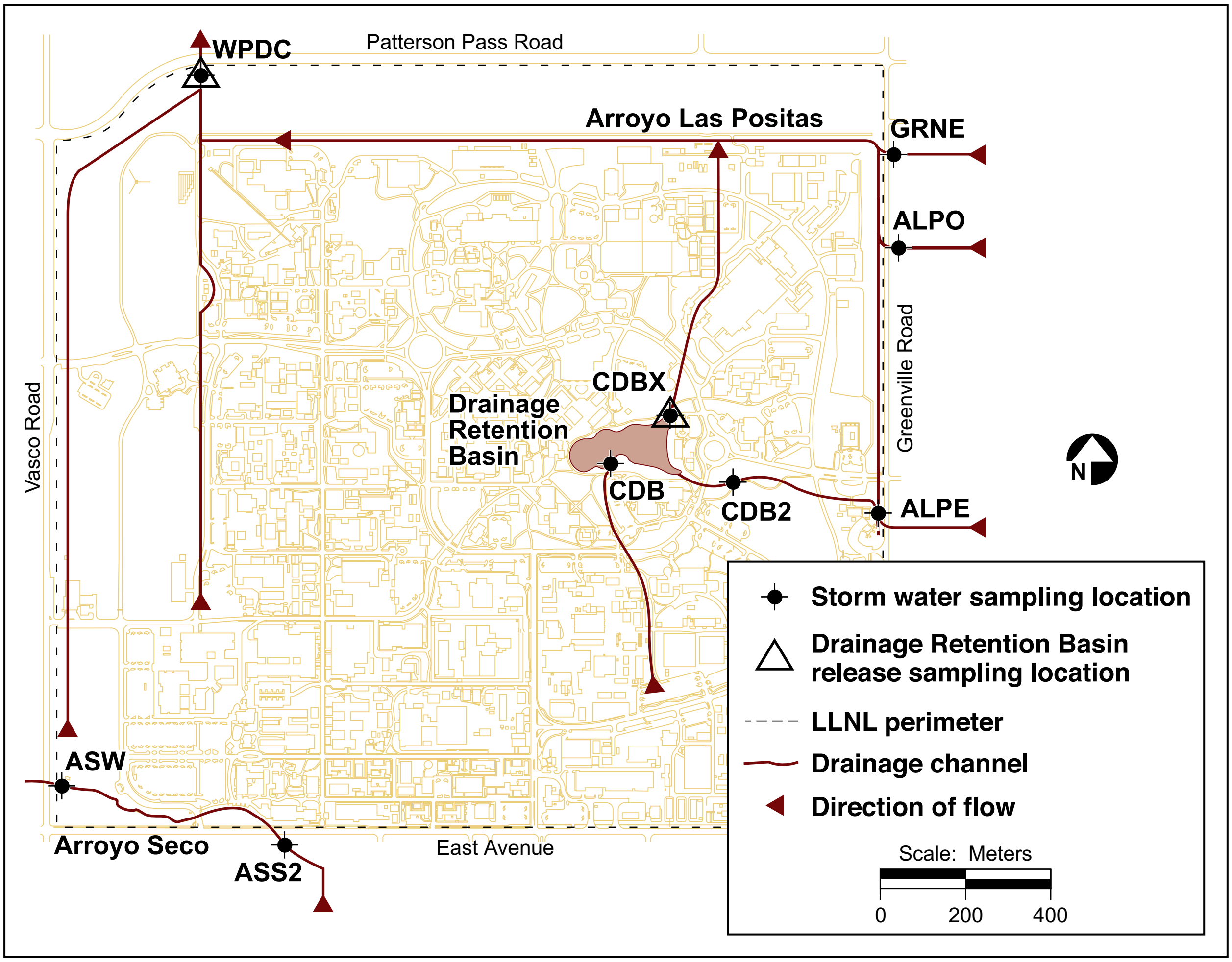


Figure 4-9. Storm water runoff and Drainage Retention Basin sampling locations, Livermore site, 2004

The routine Livermore site storm water runoff monitoring network consists of nine sampling locations (**Figure 4-9**). Six locations characterize storm water either entering (influent: ALPE, ALPO, ASS2, and GRNE) or exiting (effluent: ASW and WPDC) the Livermore site. Sampling locations CDB and CDB2 are internal sites used by LLNL staff, outside the requirements of the storm water permit, to characterize storm water runoff quality entering the DRB; location CDBX characterizes water leaving the DRB. LLNL collected samples at all nine locations on February 2, February 26, and October 26, 2004.

As required by WDR 95-174, grab samples were also collected and analyzed for acute and chronic toxicity using fathead minnows (*Pimephales promelas*) as the test species. In the acute test, 96-hour survival is observed in undiluted storm water collected from location WPDC.

Radiological Monitoring Results

Storm water sampling and analysis were performed for gross alpha, gross beta, plutonium, and tritium. Storm water gross alpha, gross beta, and tritium results are summarized in **Table 4-9**. (Complete analytical results are included in the file "Ch4 Storm Water" provided on the report CD.) Tritium activities at site effluent sampling locations were less than 1% of the MCL. Gross alpha and gross beta radioactivity in the storm water samples collected during 2004 were generally low, with medians around background levels. Gross alpha and gross beta activities exceeded LLNL-specific comparison criteria on February 2, 2004, at influent location ALPO. Activities in samples collected at this location are due to upstream discharges. As radioactive constituents are more likely to be associated with sediments, this result is not an indicator of unusual water quality.

Table 4-9. Statistics on radioactivity in storm water from the Livermore site, 2004[a]

Parameters	Tritium (Bq/L)	Gross Alpha (Bq/L)	Gross Beta (Bq/L)
MCL	740	0.555	1.85
Influent			
Median	0.23	0.060	0.205
Minimum	–0.33	0.022	0.088
Maximum	1.4	0.700	1.2
Effluent			
Median	1.3	0.062	0.135
Minimum	–1.5	0.014	0.099
Maximum	4.1	0.130	0.460

a See Chapter 8 for an explanation of calculated values.

LLNL began analyzing for plutonium in storm water in 1998. Samples from the Arroyo Seco and the Arroyo Las Positas effluent locations (ASW and WPDC) are analyzed. In 2004, there were no plutonium results above the detection limit of 0.0037 Bq/L (0.10 pCi/L).

Nonradiological Monitoring Results

In addition to radioactivity, storm water was analyzed for other water quality parameters. Sample results were compared with the comparison criteria in **Table 4-8**. Of interest are the constituents that exceed comparison criteria at effluent points and whose concentrations are lower in influent than in effluent. If influent concentrations are higher than effluent concentrations, the source is generally assumed to be unrelated to LLNL operations and LLNL conducts no further investigation. (Complete analytical results are included in the file "Ch4 Storm Water" provided on the report CD.) Constituents that exceeded comparison criteria for effluent and/or influent locations are listed in **Table 4-10**. Many of the values above threshold comparison criteria for the Livermore site were found at influent tributaries to Arroyo Las Positas. For instance, all diuron concentrations above threshold limits are at influent locations east of the Livermore site as has occurred in past years and have been explained in Campbell et al. (2004). For most of the data that exceeded LLNL thresholds, the effluent results were either lower than or approximately equal to influent results, indicating that the LLNL activities had no impact. Exceptions to this include copper at ASW on February 2 and zinc at WPDC on February 2 and February 25. Upstream activities near the Livermore site that may explain the influent water quality include a small vineyard and cattle ranching that are potential sources for suspended sediment, nitrogen (including nitrate), and diuron and bromacil (herbicides) with their attendant effect on chemical oxygen demand. Other metals detected are likely associated with elevated suspended sediment loading. LLNL will continue to examine copper and zinc concentrations in storm water runoff to determine if further action is necessary.

LLNL conducted both acute and chronic fish toxicity analyses on storm water samples collected on October 26 from effluent location WPDC in order to catch the first flush of runoff that occurs at the beginning of the wet season. WDR 95-174 states that an acceptable survival rate for the toxicity monitoring is 20% lower than a control sample. The testing laboratory provides water for the control sample, which consists of EPA synthetic moderately-hard water. Thus, a difference of more than 20% between location WPDC and the control sample with the lowest survival rate is considered a failed test. If the test is failed, the permit requires LLNL to conduct toxicity testing during the next significant storm event. After failing two consecutive tests, LLNL must perform a toxicity reduction evaluation to identify the source of the toxicity. During 2004, survival in the acute test at WPDC was 95%, while the control sample survival rate was 100% (**Table 4-11**). Chronic toxicity tests using the fathead minnows exposed to different concentrations of the storm water for seven days also found no significant toxicity. The results show that LLNL's effluent water sample shows no toxicity, either acute or chronic, to the fathead minnows.

Site 300

Surface water at Site 300 consists of seasonal runoff, springs, and natural and man-made ponds. The primary waterway in the Site 300 area is Corral Hollow Creek, an ephemeral stream that borders the site to the south and southeast. No natural continuously flowing streams are present in the Site 300 area. Elk Ravine is the major drainage for most of Site 300; it extends from the northwest portion of the site to the east–central area. Elk Ravine drains the center of the site into Corral Hollow Creek, which drains eastward toward the San Joaquin River Basin. Some smaller canyons in the northeast portion of the site drain to the north and east toward Tracy.

Table 4-10. Water quality parameters in storm water runoff above LLNL-specific threshold comparison criteria, Livermore site in 2004

Parameter	Date	Location	Influent, Effluent, or Internal[a]	Result (mg/L)	LLNL threshold criteria (mg/L)
Nonradioactive (mg/L)					
Total suspended solids	2/2	ALPO	Influent	1900	750
Chemical oxygen demand	2/2	ALPO	Influent	230	200
Beryllium	2/2	ALPO	Influent	0.0018	0.0016
Copper	2/2	ASW	Effluent	0.017	0.013
	2/2	ALPE	Influent	0.023	0.013
	2/2	ALPO	Influent	0.069	0.013
	2/2	CDB	Internal	0.018	0.013
	2/2	ACB2	Internal	0.020	0.013
	2/2	WPDC	Effluent	0.030	0.013
	2/25	ALPE	Influent	0.022	0.013
	2/25	ALPO	Influent	0.021	0.013
	2/25	CDB	Internal	0.013	0.013
	2/25	CDB2	Internal	0.014	0.013
	2/25	WPDC	Effluent	0.013	0.013
Diuron	10/26	ALPE	Influent	0.043	0.016
	10/26	CDBX	Internal	0.052	0.016
Lead	2/2	ALPO	Influent	0.025	0.015
	2/2	WPDC	Effluent	0.016	0.015
Mercury	2/25	CDB	Internal	0.00021	0.0002
Nitrate (as NO_3)	10/26	ALPE	Influent	11.5	10
	10/26	GRNE	Influent	18.4	10
Zinc	2/2	WPDC	Effluent	0.63	0.35
	2/25	WPDC	Effluent	0.35	0.35
Radioactive (Bq/L)					
Gross alpha	2/2	ALPO	Influent	0.703 ± 0.26	0.34
Gross beta	2/2	ALPO	Influent	1.17 ± 0.26	0.48

a Internal sites are located on site and discharge into the arroyos. Samples from internal sites provide additional data on storm water constituents at the Livermore site. However, because the analyses from these sampling locations are not permit driven, the data were not reported in the annual monitoring report (Brown 2004a).

There are at least 23 springs at Site 300. Nineteen are perennial, and four are intermittent. Most of the springs have very low flow rates and are recognized only by small marshy areas, pools of water, or vegetation. Several artificial surface water bodies at

Table 4-11. Chronic toxicity test results for fish (fathead minnow) assay from location WPDC, Livermore site, October 26, 2004

Storm water percent solution	Average percent survival
Lab Control	100
12.5	100
25	100
50	100
75	90[(a)]
100	95

a Two of the four replicates tested at this concentration were affected by a contaminant pathogen unrelated to the storm water sample, as identified by the analytical laboratory. Correcting for these results, average survival would be 95%.

Site 300 are in fact wastewater treatment units discussed above. Three wetlands created by now-discontinued flows from cooling towers located at Buildings 827, 851, and 865 were maintained in 2004 by discharges of potable water.

In 2004, storm water runoff was characterized at six sampling locations that could be affected by specific Site 300 activities. In addition, off-site location CARW is used to characterize Corral Hollow Creek upstream and, therefore, is unaffected by Site 300 industrial storm water discharges. Prior to the beginning of the rainy season 2004–2005, the off-site location CARW was moved to the east to location CARW2, and on-site location NLIN was moved up stream, to the northwest, in Elk Ravine for easier access for sampling technologists to location NLIN2. (Off-site location CARW and on-site location NLIN have been discontinued as of the rainy season 2004–2005.) Off-site location GEOCRK is used to characterize Corral Hollow Creek downstream of Site 300. These locations are shown in **Figure 4-10**.

The Site 300 storm water permit specifies sampling a minimum of two storms per rainy season. Typically, a single storm does not produce runoff at all Site 300 locations because Site 300 receives relatively little rainfall and is largely undeveloped with few paved areas. Therefore, at many locations, a series of large storms is required to saturate the ground before runoff can occur. At some of the sampling locations in some years, there is not enough rain to generate runoff over an entire rainy season. On February 2, storm water samples were collected and analyzed from location N883. A major storm on February 25 generated runoff everywhere, and storm water samples were collected from the remaining three locations that flowed then. The next major storm sampled was on October 19.

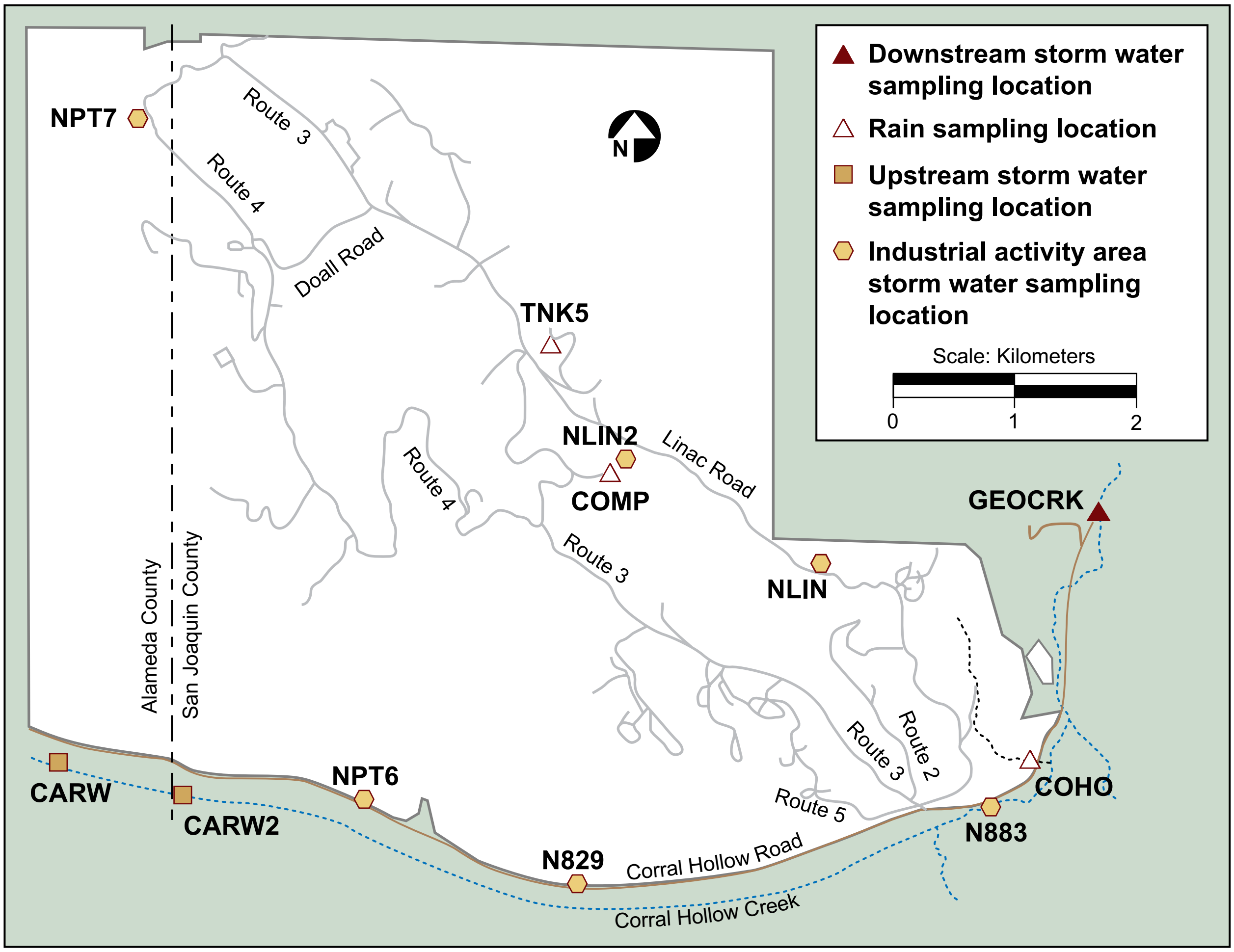


Figure 4-10. Storm water and rainwater sampling locations at Site 300, 2004

Radiological Monitoring Results

Storm water sampling and analysis was performed for gross alpha and gross beta radioactivities, uranium isotopes, and tritium, and results were compared with the comparison criteria in **Table 4-8**. (Complete analytical results are included in the file "Ch4 Storm Water" provided on the report CD.) Concentrations of gross alpha or beta radioactivities exceeding Site 300's threshold concentrations are reported in **Table 4-12**. Tritium activities at all sampled locations were less than 1% of the MCL and less than Site 300's threshold concentration. Gross alpha and gross beta radioactivity in the storm water samples collected from effluent location NLIN on February 25 and those collected from upstream location CARW2 on October 19 exceeded LLNL's site-specific criteria. Both of those samples were associated with higher than normal TSS concentrations. Previous environmental sampling has shown that suspended sediments from this area contain significant quantities of naturally occurring uranium and its daughter decay products that

Table 4-12. Water quality parameters in storm water runoff above LLNL-specific threshold comparison criteria, Site 300, 2004

Parameter	Date	Location	Upstream or Effluent,	Result	Threshold criteria
Nonradioactive (mg/L)					
Total suspended solids	2/25	NLIN	Effluent	4400	1700
Beryllium[a]	10/19	CARW2	Upstream	0.0026	0.0016
Lead[a]	10/19	CARW2	Upstream	0.037	0.030
Radioactive (Bq/L)					
Gross alpha[b]	2/25 10/19	NLIN CARW2	Effluent Upstream	1.5 1.2	0.90 0.90
Gross beta[b]	2/25 10/19	NLIN CARW2	Effluent Upstream	2.6 2.1	1.73 1.73

a Total metals including particulates

b Total radiation including particulates

account for the elevated gross alpha and beta radioactivity. No concentration of gross alpha or gross beta radioactivity measured in downstream location GEOCRK exceeded the site-specific threshold concentrations.

Nonradiological Monitoring Results

Site 300 storm water samples were analyzed for nonradiological water quality parameters, and sample results were compared with the comparison criteria in **Table 4-8**. Of most interest would be the constituents that exceed comparison criteria at GEOCRK, the downstream location, and whose concentrations are lower in influent than at location GEOCRK. During 2004 no constituent concentrations exceeded comparison criteria at GEOCRK. Constituents that exceeded comparison criteria for effluent and upstream locations are listed in **Table 4-12**. Concentrations of TSS in a storm water sample collected from location NLIN on February 25 reached 4400 mg/L, greater than the Site 300 threshold value of 1700 mg/L. High TSS concentrations are not unusual in large storms generating runoff in Elk Ravine. Concentrations of beryllium (2.6 µg/L) and lead (37 µg/L) in storm water samples collected from upstream location CARW2 on October 19 exceeded their site-specific criteria for those metals. Although the TSS associated with the October 19 sample (1100 mg/L) was less than the site-specific criteria, it is likely that the metals concentrations are associated with particulates carried in the storm water runoff. (Complete analytical results are included in the file "Ch4 Storm Water" provided on the report CD.)

Because of a Comprehensive Environmental Response Compensation Liability Act (CERCLA) remedial investigation finding of past releases of dioxins and polychlorinated biphenyls (PCBs) related to activities in the vicinity of Building 850, analysis for these compounds was conducted on runoff samples collected on February 25 from location NLIN and on October 19 from location NLIN2, the storm water sampling location downstream from Building 850. It was also conducted for downstream off-site location GEOCRK. The intent of the sampling was to determine whether these constituents are being released down Elk Ravine and, eventually, off site in storm water runoff. (Complete analytical results are included in the file "Ch4 Storm Water" provided on the report CD.) No PCBs were detected in those samples. All dioxins detected were below the equivalent federal MCL of 30 pg/L.

The federal MCL for dioxin is for the congener 2,3,7,8-TCDD, the most toxic dioxin. The other dioxin congeners reported have varying degrees of toxicity. EPA has assigned toxicity equivalency factors (TEFs) to specific dioxin congeners. 2,3,7,8-TCDD is assigned a TEF of 1; the other dioxin congeners have TEFs less than 1. The toxicity equivalency (TEQ) is determined by multiplying the concentration of a dioxin congener by its TEF. **Table 4-13** shows the concentrations of dioxin compounds that were detected at locations NLIN2 and GEOCRK in those samples along with their TEQs. These values are well below the concentrations of similar dioxins measured in 2002 (see *LLNL Site 300 Annual Storm Water Monitoring Report for Waste Discharge Requirements 97-03-DWQ Annual Report 2002–2003* [Sanchez 2003]). LLNL will continue to monitor storm water concentrations to determine if any trends are developing.

Table 4-13. Total toxicity equivalents of dioxin congeners in storm water runoff (pg/L) at Site 300, October 19, 2004

Dioxin cogener	NLIN2 concentration	TEQ[a]	GEOCRK concentration	TEQ[a]
1,2,3,4,6,7,8-HpCDD	13	0.13	54	0.54
Total-HpCDD	25	0.00	93	0.00
Total-OCDD	120	0.12	390	0.39

a Toxicity Equivalents compared to 2,3,7,8-TCDD

Environmental Impact of Storm Water

Storm water runoff from the Livermore site did not have any apparent environmental impacts in 2004. Tritium activities in storm water runoff effluent were less than 1% of the drinking water MCL. Gross alpha and gross beta activities in effluent samples were both less than 25% of their respective MCLs. The fish toxicity tests showed no discernible toxicity in Livermore site storm water runoff. Site 300 storm water runoff monitoring continues to show that contaminants may be transported as part of suspended sediments, but not at concentrations harmful to humans or the environment.

GROUNDWATER

Groundwater monitoring affirms LLNL's commitment to protect the environment. LLNL conducts surveillance monitoring of groundwater in the Livermore Valley and at Site 300 in the Altamont Hills through networks of wells and springs that include private wells off site and DOE CERCLA wells on site.

The groundwaters of the two monitored areas are not connected; they are separated by a major drainage divide and numerous faults. The Livermore site in the Livermore Valley drains to the San Francisco Bay via Alameda Creek. Most of Site 300 drains to the San Joaquin River Basin via Corral Hollow Creek, with a small undeveloped portion in the north draining to the north and east onto grazing land.

To maintain a comprehensive, cost-effective monitoring program, LLNL determines the number and locations of surveillance wells, the analytes to be monitored, the frequency of sampling, and the analytical methods to be used. A wide range of analytes is monitored to assess the impact, if any, of current LLNL operations on local groundwater resources. Because surveillance monitoring is geared to detecting substances at very low concentrations in groundwater, contamination can be detected before it significantly impacts groundwater resources. Wells at the Livermore site, in the Livermore Valley, and at Site 300 in the Altamont Hills are included in LLNL's surveillance monitoring plan.

Historically, the surveillance and compliance monitoring programs have detected higher than natural background concentrations of various metals, nitrate, perchlorate, and depleted uranium (uranium-238) in groundwater at Site 300. Subsequent CERCLA studies have linked several of these contaminants, including uranium-238, to past operations, while the sources of other contaminants, such as nitrate and perchlorate, are the objects of continuing study.

Beginning in January 2003, LLNL implemented a new CERCLA comprehensive compliance monitoring plan at Site 300 (Ferry et al. 2002) that adequately covers the DOE requirements for on-site groundwater surveillance; LLNL monitoring related to CERCLA activities is described in Chapter 7. Additional monitoring programs at Site 300 comply with numerous federal and state controls such as state-issued permits associated with closed landfills containing solid wastes and with continuing discharges of liquid waste to surface impoundments, sewage ponds, and percolation pits, the latter discussed previously in this chapter. Compliance monitoring is specified in WDRs issued by the CVRWQCB and in landfill closure and post-closure monitoring plans. (See **Table 2-2** for a summary of LLNL permits.)

The WDRs and post-closure plans specify wells and effluents to be monitored, COCs and parameters to be measured, frequency of measurement, inspections to be conducted, and the frequency and form of required reports. These monitoring programs include quarterly and semiannual monitoring of groundwater, monitoring of various influent waste streams, and visual inspections. LLNL performs the maintenance necessary to ensure the physical integrity of closed facilities, such as those that have undergone CERCLA or RCRA closure, and their monitoring networks. As described in a previous section, LLNL conducts additional operational monitoring of wastewater effluents discharged to surface impoundments and sewage evaporation and percolation ponds to comply with WDRs. Quarterly and annual written reports of analytical results, inspection findings, and maintenance activities are required for each compliance monitoring network.

Typically, because they are both accurate and sensitive, analytical methods approved by EPA are used to measure dissolved constituents in water. Appendix A lists the analytical methods and reporting limits that are used to detect organic and inorganic constituents in groundwater (including specific radioisotopes analyzed by alpha spectroscopy and other sensitive methods). The listed methods are not all used for samples from each groundwater monitoring location. Rather, for cost effectiveness, only those contaminants that have been detected historically or that might result from continuing LLNL operations are monitored at each groundwater sampling location. However, present-day administrative, engineering, and maintenance controls at both LLNL sites are specifically tailored to prevent releases of potential contaminants to the environment.

During 2004, representative samples of groundwater were obtained from monitoring wells in accordance with the LLNL Livermore Site and Site 300 Environmental Restoration Project Standard Operating Procedures (SOPs) (Goodrich and Depue 2003). These protocols cover sampling techniques and specific information concerning the chemicals that are routinely analyzed for in groundwater. Different sampling techniques were applied to different wells depending on whether they were fitted with submersible pumps, or had to be bailed. All of the chemical and radioactivity analyses of groundwater samples were performed by California-certified analytical laboratories. For comparison purposes only, some of the results are compared with drinking water limits (MCLs); however, the MCLs do not apply as regulatory limits to any of these groundwaters.

Livermore Site and Environs

Livermore Valley

LLNL has monitored tritium in water hydrologically downgradient of the Livermore site since 1988. Tritiated water (HTO) is potentially the most mobile groundwater contaminant from LLNL. Rain and storm water runoff in the Livermore Valley, which recharge local aquifers, contain small amounts of HTO from natural sources, past worldwide atmospheric nuclear weapons tests, and atmospheric emissions from LLNL. (See Chapters 3 and 6 for further discussion of air emissions, and other parts of this chapter for further discussion of rain and storm water runoff.)

Groundwater is recharged at the Livermore site, primarily from arroyos by rainfall. Groundwater flow beneath the Livermore site is generally southwestward. An overview of groundwater flow is provided in Chapter 1 and is discussed in detail in the *CERCLA Remedial Investigation Report for the LLNL Livermore Site* (Thorpe et al. 1990) and in the *LLNL Ground Water Project 2004 Annual Report* (Karachewski et al. 2005).

Groundwater samples were obtained during 2004 from 23 of 25 water wells in the Livermore Valley (see **Figure 4-11**) and measured for tritium activity. Two wells were either dry or could not be sampled during 2004.

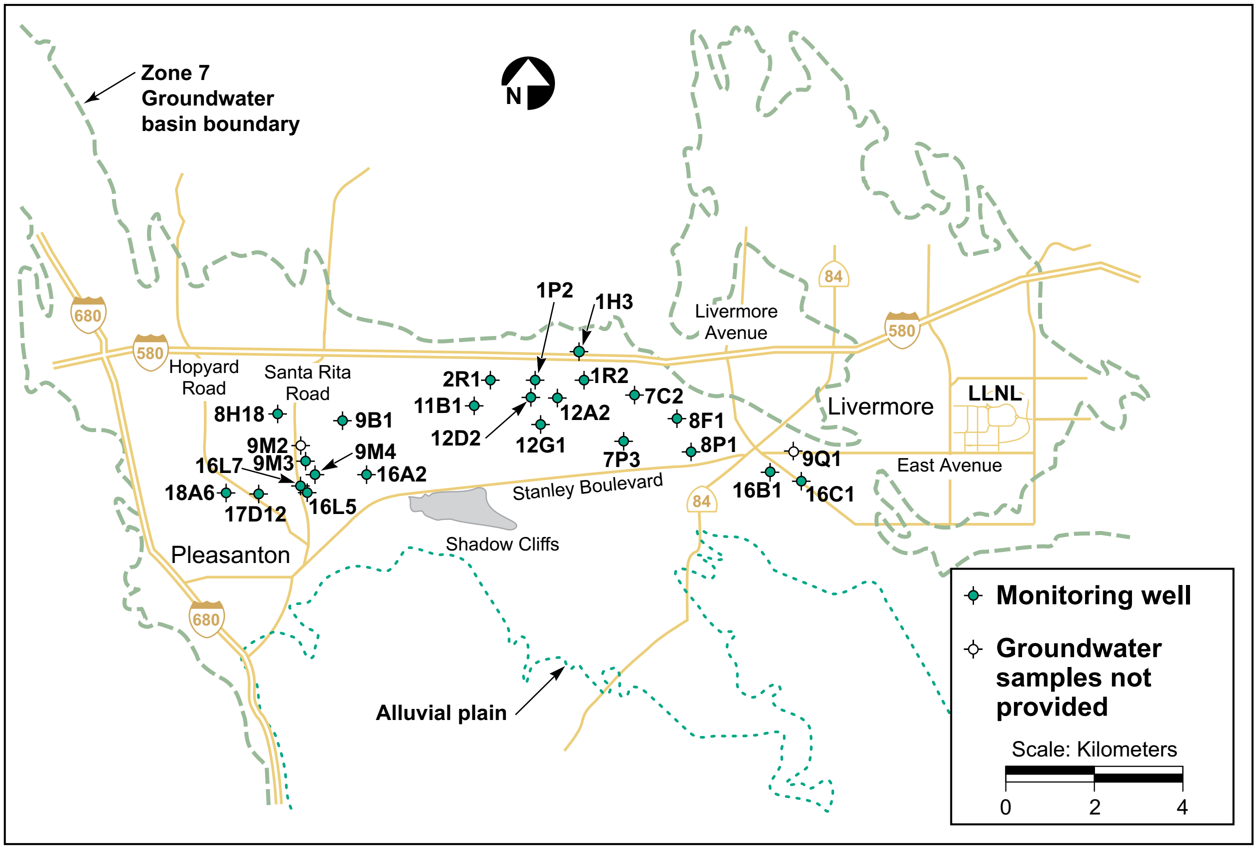


Figure 4-11. Locations of off-site tritium monitoring wells in the Livermore Valley, 2004

Tritium measurements of Livermore Valley groundwaters are contained in the file "Ch4 LV Groundwater" provided on the report CD. They continue to show very low and decreasing activities compared with the 740 Bq/L (20,000 pCi/L) MCL established for drinking water in California. The maximum tritium activity measured off site was in the groundwater at well 12D2, located about 11 km west of LLNL (see **Figure 4-11**). The measured activity there was 5.4 Bq/L (150 pCi/L) in 2004, less than 1% of the MCL.

Livermore Site Perimeter

LLNL designed a surveillance monitoring program to complement the Livermore Site GWP (discussed in Chapter 7). The intent of the surveillance monitoring network is to monitor for potential groundwater contamination from continuing LLNL operations. The perimeter portion of this surveillance groundwater monitoring network makes use of three upgradient (background) monitoring wells (wells W-008, W-221, and W-017) near the eastern boundary of the site and seven (downgradient) monitoring wells located near the western boundary (wells 14B1, W-121, W-151, W-1012, W-571, W-556, and W-373) (see **Figure 4-12**). These seven wells, located in the regions of groundwater Treatment Facilities (TF) A, B, and C (see **Figure 7-2**) are located at or beyond the

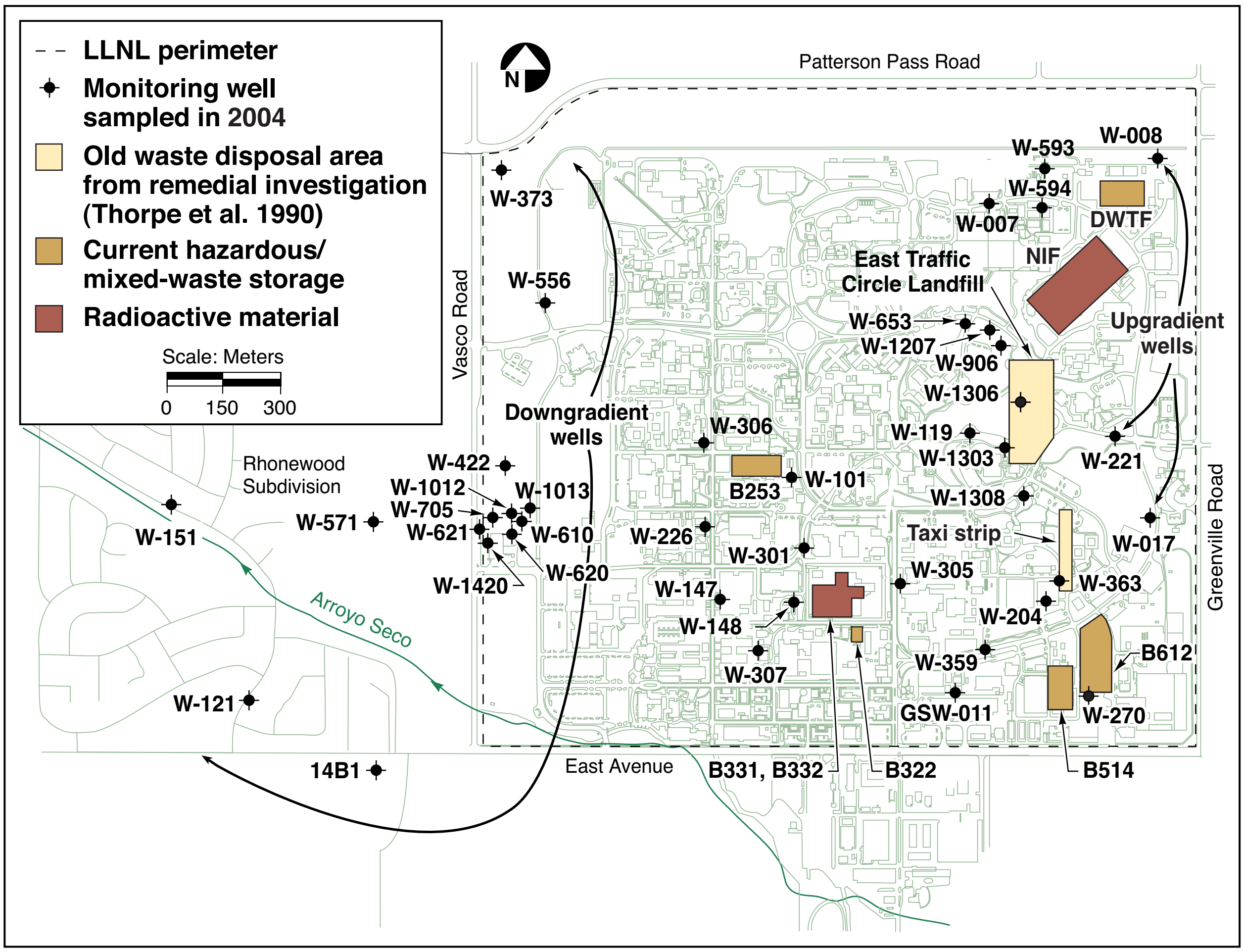


Figure 4-12. Locations of routine surveillance groundwater monitoring wells at the Livermore site, 2004

hydrologically downgradient boundary of the Livermore site. The western perimeter wells are screened (depth range from which groundwater is drawn) in the uppermost aquifers near the areas where groundwater is being remediated. As discussed in Chapter 7, the alluvial sediments have been divided into nine hydrostratigraphic units (HSUs) dipping gently westward, which are shown in **Figure 7-1**. Screened intervals for these monitoring wells range from the shallow HSU 1B, in which some of the western monitoring wells are screened, to the deeper HSU 5, in which background well W-017 and some wells around Buildings 514 and 612 are screened.

Two of the background wells, W-008 and W-221, are screened partially in HSU 3A; well W-017 is considered a background well for the deeper HSU 5. These background wells were sampled and analyzed in 2004 for pesticide and herbicide compounds that are used on site and off site, for nitrate, for hexavalent chromium (chromium(VI)), and for certain radioactive constituents including plutonium.

To detect contaminants as soon as possible, the seven western downgradient wells (except for well 14B1) are screened in shallower HSUs 1B and 2, the uppermost water-bearing HSUs at the western perimeter. (Because it was originally a production well, well 14B1 is screened over a depth range that includes HSUs 2, 3A, and 3B.) These wells were sampled and analyzed at least once during this reporting period for pesticides, herbicides, radioactive constituents, nitrate, and chromium(VI).

Analytical results for the Livermore site background wells and perimeter wells are contained in the file "Ch4 LV Groundwater" provided on the report CD. No pesticide or herbicide organic compounds were detected above analytical reporting limits in the groundwater during 2004. The inorganic compounds detected include dissolved trace metals and minerals, which occur naturally in the groundwater at variable concentrations. The concentrations detected in the groundwater samples from the background wells represent background values for 2004, although there have been variations in the concentrations since regular surveillance monitoring began in 1996.

Since 1996 concentrations of nitrate detected in groundwater samples from downgradient well W-1012 have been greater than the MCL of 45 mg/L. The nitrate concentrations detected in samples from this well during 2004 were reported at 61 and 45 mg/L; somewhat less than the values of 62 and 68 mg/L observed in 2003. Because of the hydrologic influence of TFB that pumps and treats groundwater from HSUs 1B and 2, groundwater with high nitrate concentrations is restrained from moving off site to the west. The highest concentrations measured in the downgradient off-site wells (screened in these HSUs) were below the MCL: 39 mg/L in monitoring well W-151 and 36 mg/L in monitoring well W-571. During 2004, concentrations of nitrate in on-site shallow background wells W-008 and W-221 ranged from 23 mg/L to 28 mg/L. Detected concentrations of nitrate in western perimeter wells, with the exception of well W-1012, ranged from 13 mg/L (in well W-373) to 39 mg/L (in well W-151).

Nitrate concentrations were also analyzed in groundwater samples collected from seven additional monitoring wells located nearby well W-1012 (**Figure 4-12**), similarly screened in HSUs 1B and 2. Again, other than well W-1012, no groundwater sample had a nitrate concentration greater than the MCL. Fluctuations in nitrate concentrations have occurred since regular surveillance monitoring began in 1996, but nitrate concentrations have not increased overall in groundwater from the western perimeter monitoring wells since 1996. The nitrate may originate as an agricultural residue (Thorpe et al. 1990).

Livermore Site

Groundwater sampling locations within the Livermore site include areas where releases to the ground may have occurred in the recent past, where previously detected COCs have low concentrations that do not require CERCLA remedial action, and where baseline information needs to be gathered for the area near a new facility or operation. Wells selected for monitoring are screened in the uppermost aquifers, and are situated downgradient from and as near as possible to the potential release locations. Well locations are shown in **Figure 4-12**. All analytical results are included in the file "Ch4 LV Groundwater" provided on the report CD.

The Taxi Strip and the East Traffic Circle Landfill areas within the Livermore site are two historic potential sources of groundwater contamination. Samples from monitoring wells screened in HSUs 2 (W-204) and 3A (W-363) downgradient from the Taxi Strip Area were analyzed in 2004 for copper, lead, zinc, americium-241, plutonium-238, plutonium–239, radium-226, radium-228, and tritium. Samples from monitoring wells screened at least partially in HSU 2 (W-119, W-906, W-1303, W-1306, and W-1308) within and downgradient from the East Traffic Circle Landfill were analyzed for the same elements as in the Taxi Strip Area. Plutonium-238 and plutonium-239+240 were reported above minimum detectable activities in one sample, collected in March 2004, from well W-1303. Retests of this well in September 2004 and February 2005 failed to confirm this detection. No other concentrations of plutonium or americium radioisotopes were detected above the radiological laboratory's minimum detectable activities. Concentrations of tritium and radium isotopes remain well below drinking water MCLs.

Of the trace metals (copper, lead, and zinc), only zinc was detected in any of these monitoring wells during 2004. The maximum zinc concentration reported (40 µg/L in well W-204) is more than two orders of magnitude below the secondary MCL for zinc in drinking water (5 mg/L).

Although the National Ignition Facility (NIF) has not yet begun full operations, LLNL obtains a baseline of groundwater quality prior to start of operations. During 2004, tritium analyses were conducted on groundwater samples collected from wells W-653 and W-1207 (screened in HSUs 3A and 2, respectively) downgradient of NIF. Another new facility where groundwater baseline information is being acquired is the Decontamination and Waste Treatment Facility (DWTF) in the northeastern portion of LLNL. Samples were obtained downgradient from this facility from wells W-007, W-593 (screened in HSU 3A), and W-594 during 2004 and were also analyzed for tritium.

Monitoring results from the wells near NIF and DWTF show no detectable concentrations of tritium present, above the limit of sensitivity of the analytical method, in the groundwater samples collected during 2004. Monitoring will continue near these facilities to determine baseline conditions.

The old hazardous waste/mixed waste storage facilities around Area 514 and Building 612 are also a potential source of contamination. They are monitored by wells W-270 and W-359 (screened in HSU 5), and well GSW-011 (screened in HSU 3A). Groundwater from these wells was sampled and analyzed for general minerals, gross alpha, gross beta, americium-241, plutonium-238, plutonium-239, radium-226, and tritium in 2004. No significant contamination was detected in the groundwater samples collected from wells W-270, W-359, or GSW-011 downgradient from this area in 2004.

Groundwater samples were obtained downgradient from areas where releases of metals to the ground have occurred. Samples were obtained from monitoring well W-307 (screened in HSU 1B), downgradient from a fume hood vent on the roof of Building 322, a metal plating shop. Soil samples obtained from the area show elevated concentrations (in comparison with Livermore site's background levels) of total chromium, copper, lead, nickel, zinc, and occasionally other metals. LLNL removed contaminated soils near Building 322 in 1999 and replaced them with clean fill. The area was then paved over, making it less likely that metals will migrate from the site.

Groundwater samples were obtained downgradient from a location where sediments containing metals (including cadmium, copper, lead, mercury, and zinc) had accumulated in a storm water catch basin near Building 253 (Jackson 1997). In 2004, the samples obtained from monitoring wells W-226 and W-306 (screened in HSUs 1B and 2, respectively) contained dissolved chromium at elevated concentrations. Concentrations of chromium(VI) were measured as 23 µg/L at well W-226 and 38 µg/L at well W-306. The accumulated sediment in the catch basin is a potential source of several metals (Jackson 1997). No concentration of either dissolved chromium or chromium(VI) was greater than the MCL of 50 µg/L for total chromium in drinking water.

Additional surveillance groundwater sampling locations, established in 1999, surround the area of the Plutonium Facility (Building 332) and the Tritium Facility (Building 331) (see **Figure 4-12**). Possible contaminants include plutonium and tritium from these respective facilities. Plutonium is much more likely to bind to the soils than migrate into the groundwater. Tritium, as HTO, could migrate into groundwater if spilled in sufficient quantities. Upgradient of these facilities, well W-305 is screened in HSU 2; downgradient wells W-101, W-147, and W-148 are screened in HSU 1B; and well W-301 is screened in HSU 2. Groundwater samples collected from these wells during 2004 showed no detectable concentration, above the limit of sensitivity for the analytical method, of either plutonium-238 or plutonium-239.

In August 2000, relatively elevated tritium activity was measured in the groundwater sampled at well W-148 (115 ± 5.0 Bq/L [3100 ± 135 pCi/L]) that was concluded to be most likely related to local infiltration of storm water containing elevated tritium activity. Tritium activities in groundwater of this area have been cyclic since that time. LLNL continues to collect groundwater samples from these wells periodically for surveillance purposes, primarily to demonstrate that tritium and plutonium contents remain below environmental levels of concern.

Site 300 and Environs

For surveillance and compliance groundwater monitoring at Site 300, LLNL uses DOE CERCLA wells and springs on site and private wells and springs off site. Representative groundwater samples are obtained at least once per year at every monitoring location; they are routinely measured for various elements (primarily metals), a wide range of organic compounds, general radioactivity (gross alpha and gross beta), uranium activity, and tritium activity.

Figure 4-13 shows the locations of numerous wells and three springs at or near Site 300 that are used for groundwater surveillance monitoring. The locations of compliance monitoring wells are shown in **Figures 4-14**, **4-15**, **4-16**, and **4-17**. Groundwater from the shallowest water-bearing zone is the target of most of the monitoring because it would be the first to show contamination from LLNL surface or sub-surface operations at Site 300.

Twelve groundwater monitoring locations are off site. Two are springs, identified as MUL2 and VIE1, which are located near the northern boundary of Site 300. Off-site surveillance well VIE2 is located 6 km west of Site 300 in the upper reaches of the Livermore Valley watershed. Eight off-site surveillance locations are wells located near the southern boundary of Site 300 in or adjacent to the Corral Hollow Creek floodplain.

On-site wells, installed primarily for CERCLA site-characterization studies, continue to be used to monitor closed landfills, a former open-air high explosives (HE) burn pit, two connected surface water impoundments, and two connected sewer ponds (**Figure 4-13**). The closed landfills—identified as Pit 1, Pit 2, Pit 7 Complex, Pit 8, and Pit 9—are located in the northern portion of Site 300 in the Elk Ravine drainage area, while Pit 6, the former burn pit, the two process water impoundments, and the sewage ponds are located in the southern portion of Site 300 in the Corral Hollow Creek drainage area. Two on-site water supply wells, identified as wells 18 and 20, are also used for surveillance monitoring purposes. Well 20 provides potable water to the site. Well 18 is maintained as a standby potable supply well.

Brief descriptions of the Site 300 groundwater monitoring networks that are reported in this chapter are given below. Networks of wells within the Elk Ravine drainage area are described first, followed by the well networks in the Corral Hollow Creek drainage area. Subsets of CERCLA wells, installed mainly for site characterization, have been selected for compliance and surveillance monitoring use based on their locations and our general understanding of local geologic and hydrogeologic conditions at Site 300. (Chapter 7 includes a summary of Site 300 stratigraphy and hydrogeology. All analytical data from 2004 are included in the file "Ch4 S300 Groundwater" provided on the report CD.)

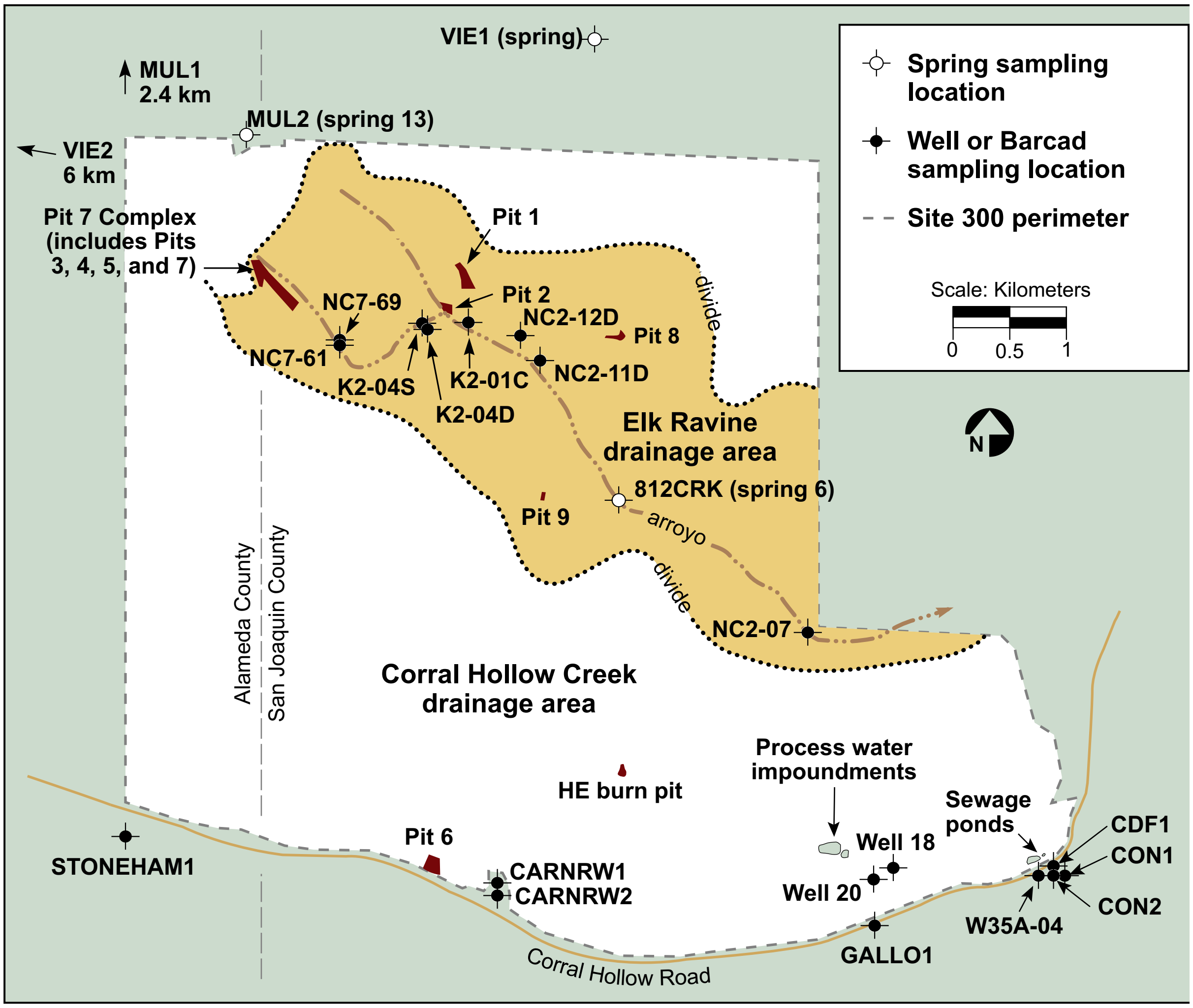


Figure 4-13. Locations of surveillance groundwater wells and springs at Site 300, 2004

Elk Ravine Drainage Area

The Elk Ravine drainage area, a branch of the Corral Hollow Creek drainage system, includes most of northern Site 300 (see **Figure 4-13**). Storm water runoff in the Elk Ravine drainage area collects in arroyos and quickly infiltrates into the ground. Groundwater from wells in the Elk Ravine drainage area is monitored for COCs because of the system of surface and underground flows that connects the entire Elk Ravine drainage area. The area contains eight closed landfills known as Pits 1 through 5 and 7 through 9 and firing tables where explosives tests are conducted. None of the closed landfills has a liner, which is consistent with disposal practices in the past when the landfills were constructed. The following descriptions of monitoring networks within Elk Ravine begin

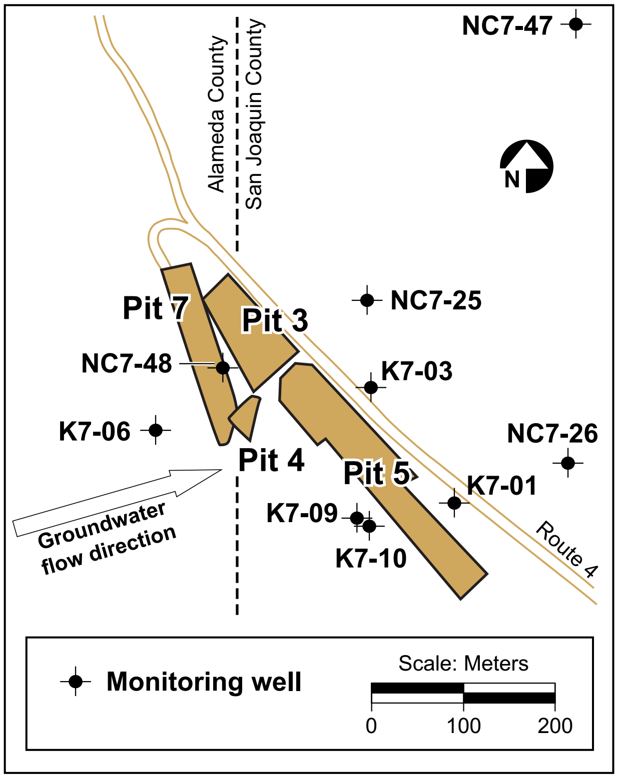


Figure 4-14. Locations of Pit 7 compliance groundwater monitoring wells, 2004

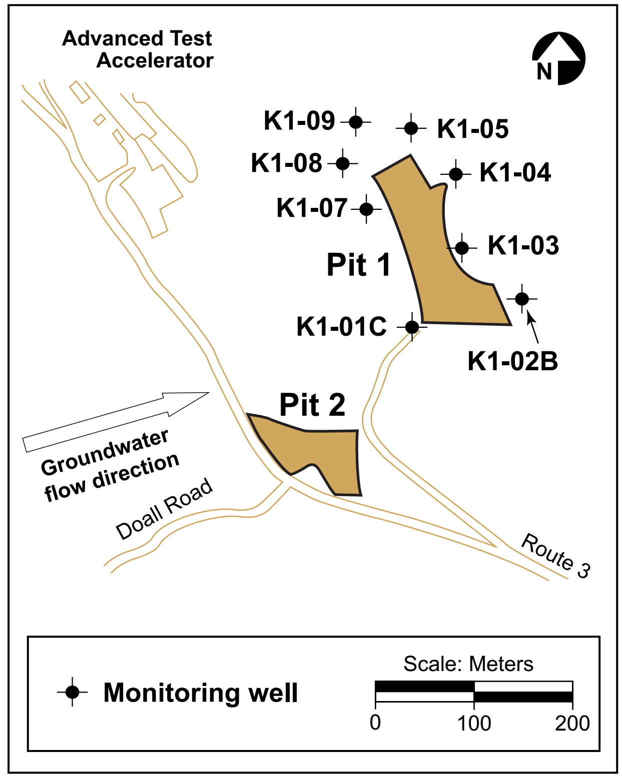


Figure 4-15. Locations of Pit 1 compliance groundwater monitoring wells, 2004

with the headwaters area and proceed downstream. (See Chapter 7 for a review of groundwater contamination in this drainage area as determined from numerous CERCLA remedial investigations.)

Pit 7 Complex

Monitoring requirements for the Pit 7 landfill, which was closed under the Resource Conservation and Recovery Act (RCRA) in 1993, are specified in WDR 93-100 administered by the CVRWQCB (1993 and 1998) and in *LLNL Site 300 RCRA Closure and Post-Closure Plans—Landfill Pits 1 and 7* (Rogers/Pacific Corporation 1990). The main objective of this monitoring is the early detection of any new release of COCs from Pit 7 to groundwater.

The Pit 7 Complex area is located at an elevation of about 400 m in the most elevated portion of the Elk Ravine drainage area. The complex consists of four adjacent landfills identified as Pits 3, 4, 5, and 7 (see **Figure 4-14**). From 1963 to 1988, the landfills received waste gravels and debris from hydrodynamic tests of explosive devices conducted on firing tables at Site 300. The gravels contained concrete, cable, plastic, wood, tritium, uranium-238, beryllium, lead, and other metals in trace amounts. In

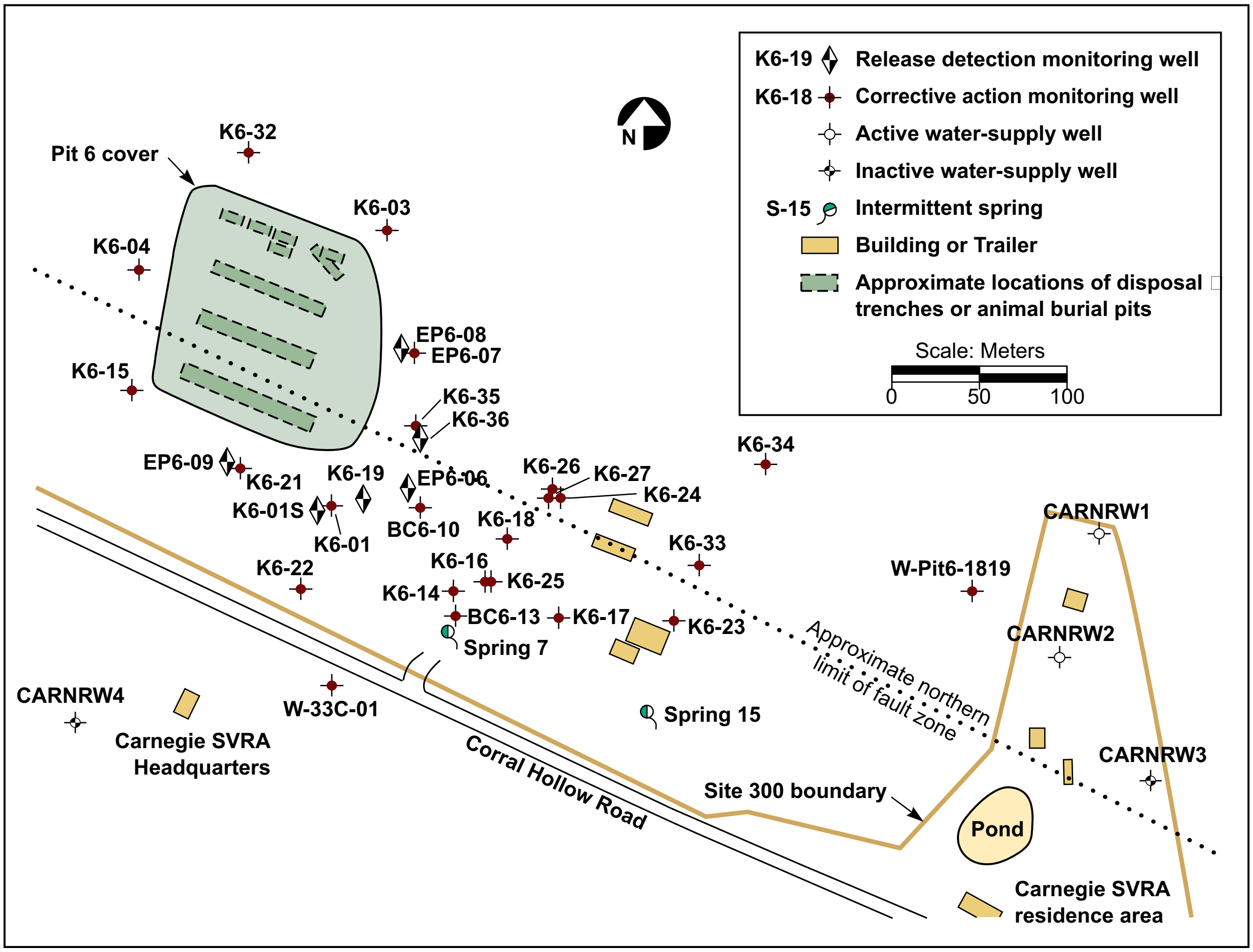


Figure 4-16. Locations of Pit 6 compliance groundwater monitoring wells and springs, 2004

1988, 9440 m^3 of gravel were removed from six firing tables at Site 300 and placed in Pit 7 (Lamarre and Taffet 1989). These were the last solid wastes to be placed in any landfill at Site 300.

As planned for compliance purposes, LLNL obtained groundwater samples quarterly during 2004 from the Pit 7 monitoring well network. Samples were analyzed for inorganic COCs (mostly metallic elements), general radioactivity (gross alpha and beta), activity of certain radioisotopes (tritium, radium, uranium, and thorium), explosive compounds (HMX and RDX), and volatile organic compounds (VOCs). Field measurements of groundwater depth, temperature, pH, and specific conductance were obtained at each well at the time of sample collection.

No new release of COCs to groundwater from Pit 7 is evident in the chemical data obtained during 2004. The COCs detected in groundwater include several metals, depleted uranium, tritium, and several VOCs. These are associated with releases that

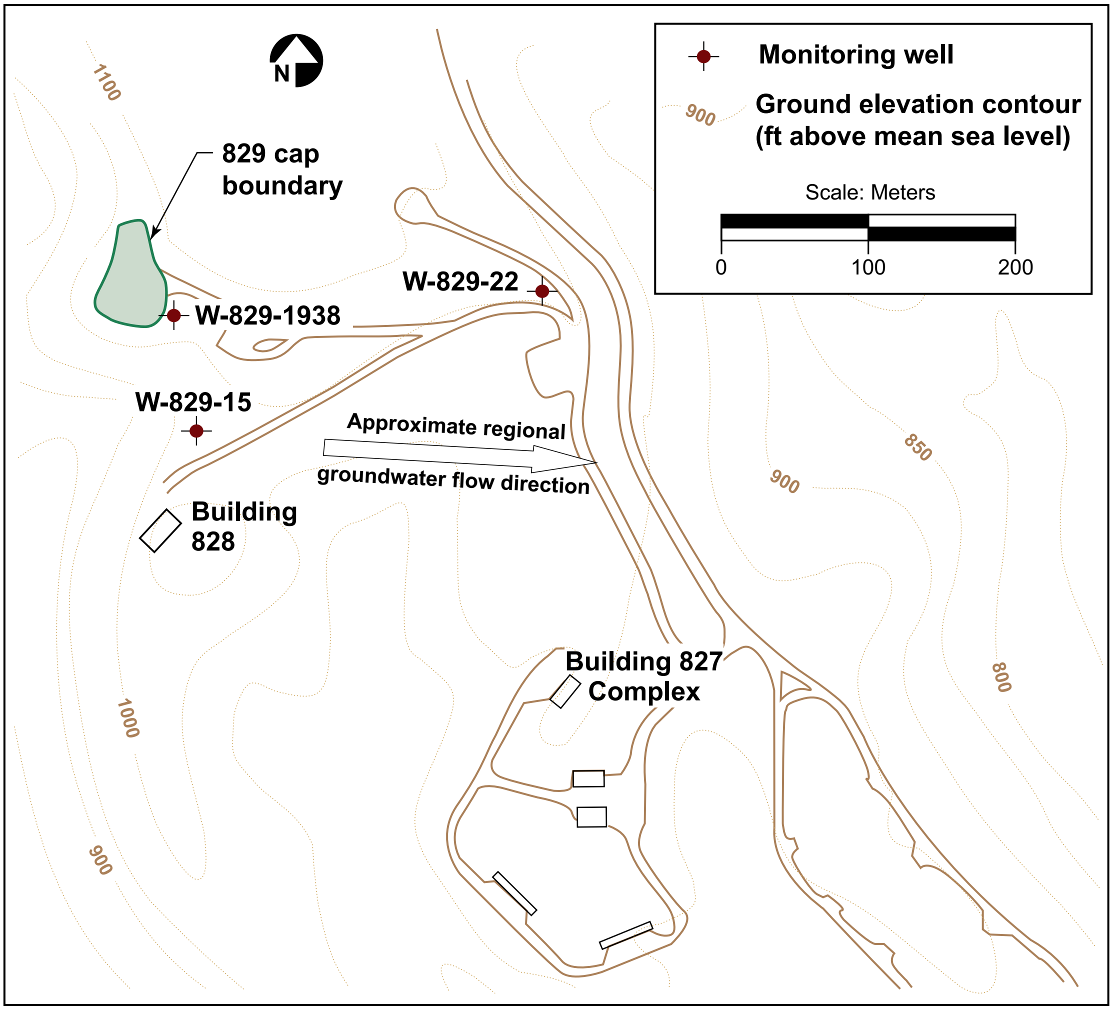


Figure 4-17. Locations of Building 829 closed burn pit compliance groundwater monitoring wells

occurred prior to 2004. The primary sources of COCs detected by the network of Pit 7 monitoring wells are the closed landfills known as Pits 3 and 5, which are adjacent to Pit 7 (**Figure 4-14**). Natural sources in the rocks and sediments surrounding Pit 7 also have contributed arsenic, barium, uranium, and, possibly nitrate to the groundwater. In the past, especially during the El Niño winters of 1982/1983 and 1997/1998, excessive seasonal rainfall caused groundwater levels to rise into Pit 3 and Pit 5 from beneath, leading to the release of COCs, mainly tritium in the form of HTO. Because of reduced rainfall since 1998, groundwater elevations have fallen generally at Site 300, thus reducing the potential for releases to occur by this mechanism. CERCLA modeling studies indicate that tritium and other COCs released in the past will not reach off-site aquifers at concentrations above MCLs. See Chapter 7 for a review of CERCLA activities regarding groundwater contamination in the upper reaches of the Elk Ravine drainage area. For a detailed account of Pit 7 compliance monitoring during 2004, including tables and graphs of groundwater COC analytical data, see *LLNL Experimental Test Site 300 Compliance Monitoring Program for RCRA-Closed Landfill Pits 1 and 7, Annual Report for 2004* (Campbell and MacQueen 2005).

Elk Ravine

Groundwater samples were obtained on five various dates in 2004 from the widespread Elk Ravine surveillance monitoring network (see **Figure 4-13**). Samples were analyzed for inorganic constituents (mostly metallic elements), VOCs, general radioactivity (gross alpha and beta), tritium and uranium activity, and explosive compounds (HMX and RDX).

No new release of COCs from LLNL operations in Elk Ravine to groundwater is indicated by the chemical and radioactivity data obtained during 2004. The major source of contaminated groundwater beneath Elk Ravine is from historical operations in the Building 850 firing table area (Webster-Scholten 1994; Taffet et al. 1996). Constituent measurements for the Elk Ravine drainage area surveillance monitoring network are listed in Appendix A.

Concentrations of arsenic range up to 46 µg/L (well NC2-07) in Elk Ravine monitoring wells. Earlier CERCLA characterization studies determined that the arsenic is from natural sources, particularly from the dissolution of the mineral arsenopyrite, which is a component of the underlying volcanogenic sediments and sedimentary rocks (Raber and Carpenter 1983). It should be noted that there are no wells in this area that are used for potable domestic, livestock, or industrial water supply. However, a perennial spring in Elk Ravine (location 812CRK on **Figure 4-13**), which is used by the indigenous wildlife there, contains concentrations of naturally occurring arsenic (29 µg/L arsenic in 2004).

Tritium activity was relatively elevated above background in many of the shallow groundwater surveillance samples obtained during 2004 from Elk Ravine. Tritium, as HTO, has been released in the past in the vicinity of Building 850. The largest HTO plume, which extends eastward more than a kilometer from a source beneath the Building 850 firing table area to the vicinity of Pits 1 and 2, is confined to shallow depths in the Neroly lower blue sandstone unit and overlying alluvium.

The majority of the Elk Ravine surveillance network tritium measurements made during 2004 support earlier CERCLA studies that show that the tritium in the plume is diminishing over time because of natural decay and dispersion (Ziagos and Reber-Cox 1998). For example, tritium activity in groundwater at well NC7-61 has decreased from 6500 Bq/L (1.8×10^5 pCi/L) in 1996 to 1500 Bq/L (4.1×10^4 pCi/L) in 2004. CERCLA modeling studies indicate that the tritium will decay to background levels before it can reach a site boundary. Note that the tritium plume has not yet reached the surveillance monitoring perennial spring location 812CRK, which is approximately one mile upstream from where the Site 300 boundary crosses Elk Ravine.

Except in the immediate vicinity of Pit 7, groundwater surveillance measurements of gross alpha, gross beta, and uranium radioactivity in Elk Ravine are all low and are indistinguishable from background levels. (Note that gross beta measurements do not detect the low-energy beta emission from tritium decay.) Additional detections of nonradioactive elements including arsenic, barium, chromium, selenium, vanadium, and zinc are all within the natural ranges of concentrations typical of groundwater elsewhere in the Altamont Hills.

Pit 1

Monitoring requirements for the Pit 1 landfill, which was closed under RCRA in 1993, are also specified in WDR 93-100 administered by the CVRWQCB (1993 and 1998) and in Rogers/Pacific Corporation (1990). The main objective of this monitoring is the early detection of any release of COCs from Pit 1 to groundwater.

Pit 1 lies in the Elk Ravine drainage area about 330 m above sea level. The Pit 1 landfill and the positions of the eight groundwater wells used to monitor it are shown in **Figure 4-15**. The eight wells are K1-01C, K1-02B, K1-03, K1-04, K1-05, K1-07, K1-08, and K1-09.

As planned for compliance purposes, LLNL obtained groundwater samples quarterly during 2004 from the Pit 1 monitoring well network. Samples were analyzed for inorganic COCs (mostly metallic elements), general radioactivity (gross alpha and beta), activity of certain radioisotopes (tritium, radium, uranium, and thorium), explosive compounds (HMX and RDX), and VOCs (EPA method 601). Every other quarter, analyses were conducted for an additional seven elements. Additional annual analyses were conducted on fourth-quarter samples for extractable organics (EPA method 625), pesticides and PCBs (EPA method 608), and herbicides (EPA method 615). Field measurements of groundwater depth, temperature, pH, and specific conductance were obtained at each well at the time of quarterly sample collection.

No release of COCs to groundwater from Pit 1 is evident in the monitoring data collected during 2004. A detailed account of Pit 1 compliance monitoring during 2004, including tables and graphs of groundwater COC analytical data, is in *LLNL Experimental Test Site 300 Compliance Monitoring Program for RCRA-Closed Landfill Pits 1 and 7, Annual Report for 2004* (Campbell and MacQueen 2005).

During 2004, average tritium activities measured above background level (about 4 Bq/L [100 pCi/L]) in the groundwater at Pit 1 monitoring wells K1-01C (21 Bq/L [570 pCi/L]), K1-02B (150 Bq/L [4000 pCi/L]), K1-03 (27 Bq/L [730 pCi/L]), and K1-08 (7.0 Bq/L [190 pCi/L]). The tritium activity in the groundwater sampled at these wells represents a distal lobe of the Building 850 tritium plume. Measurements of radium, thorium, and uranium made during 2004 in groundwater samples from Pit 1 compliance monitoring wells showed low activities indistinguishable from background levels.

The VOC 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) decreased from a maximum concentration of 140 µg/L measured in 1999 to 41 µg/L in 2004 in groundwater at Pit 1 monitoring wells K1-05 (13 µg/L), K1-08 (23 µg/L), and K1-09 (41 µg/L). The drinking water MCL for this VOC is 1200 µg/L. Previous CERCLA investigations have linked the Freon 113 detected in Pit 1 monitoring wells to past spills of Freon in the Advanced Test Accelerator area, about 200 m northwest of the affected wells (Webster-Scholten 1994; Taffet et al. 1996).

Corral Hollow Creek Drainage Area

Pit 6

Compliance monitoring requirements for the closed Pit 6 landfill in the Corral Hollow Creek drainage area are specified in the *Post-Closure Plan for the Pit 6 Landfill Operable Unit Lawrence Livermore National Laboratory Site 300* (Ferry et al. 1998) and in the *Compliance Monitoring Plan/Contingency Plan for Interim Remedies at Lawrence Livermore National Laboratory Site 300* (Ferry et al. 2002). The closed Pit 6 landfill covers an area of about 1 hectare (2.5 acres), at an elevation of approximately 215 m above sea level. From 1964 to 1973, approximately 1500 m^3 of solid wastes were buried there in nine separate trenches. The trenches were not lined, consistent with historical disposal practices. Three larger trenches contain 1300 m^3 of solid waste that includes empty drums, glove boxes, lumber, ducting, and capacitors. Six smaller trenches contain 230 m^3 of biomedical waste, including animal carcasses and animal waste. During 1997, a multilayered cap was constructed over all the trenches, and a storm water drainage control system was installed around the cap. The cap and the drainage control system are engineered to keep rainwater from contacting the buried waste (Ferry et al. 1998).

The Pit 6 disposal trenches were constructed in Quaternary terrace deposits (Qt) north of the Corral Hollow Creek flood plain. Surface runoff from the pit area flows southward to Corral Hollow Creek. The Carnegie-Corral Hollow Fault zone extends beneath the southern third of Pit 6. The northern limit of the fault zone is shown in **Figure 4-16**. Beneath the northern two-thirds of Pit 6, groundwater flows south-southeast, following the inclination of the underlying sedimentary rocks. Groundwater seepage velocities are less than 10 m/y. Depths to the water table range from 10 to 20 m. Beneath the southern third of Pit 6, a trough containing terrace gravel within the fault zone provides a channel for groundwater to flow southeast, parallel to the Site 300 boundary fence (Webster-Scholten 1994).

Two Pit 6 groundwater monitoring programs, which operate under CERCLA, ensure compliance with all regulations. They are (1) the Detection Monitoring Program (DMP), designed to detect any new release of COCs to groundwater from wastes buried in the Pit 6 landfill, and (2) the Corrective Action Monitoring Program (CAMP), which monitors the movement and fate of historical releases. **Figure 4-16** shows the locations of Pit 6 and the wells used to monitor the groundwater there.

To comply with monitoring requirements, LLNL obtained groundwater samples monthly, quarterly, semiannually, and annually during 2004 from specified Pit 6 monitoring wells. DMP samples were obtained quarterly and were analyzed for beryllium and mercury, general radioactivity (gross alpha and beta), tritium and uranium activity, specified VOCs, nitrate and perchlorate. CAMP samples were measured for VOCs, tritium activity, nitrate and perchlorate. Field measurements of groundwater depth, temperature, pH, and specific conductance were obtained at each well at the time of sample collection.

No new release of COCs from Pit 6 is indicated by the chemical analyses of groundwater samples obtained from Pit 6 monitoring wells during 2004. COCs that were released prior to constructing an impermeable cap over the closed landfill in 1997 continued to be detected in the groundwater at low concentrations during 2004. These COCs include tritium, perchlorate, trichloroethylene (TCE), perchloroethylene (PCE), and cis-1,2-dichloroethene (cis-1,2-DCE). All contaminant plumes associated with Pit 6 are confined to shallow depths. None has been detected beyond the Site 300 boundary. For a detailed account of Pit 6 compliance monitoring during 2004, including tables of groundwater analytical data and map figures showing the distribution of COC plumes, see *LLNL Experimental Test Site 300 Compliance Monitoring Program for the CERCLA-Closed Pit 6 Landfill, Annual Report for 2004* (Campbell and Blake 2005).

Building 829 Closed HE Burn Facility

Compliance monitoring requirements for the closed burn pits in the Corral Hollow Creek drainage area are specified in the *Final Closure Plan for the High-Explosives Open Burn Treatment Facility at Lawrence Livermore National Laboratory Experimental Test Site 300* (Mathews and Taffet 1997), and in the *Revisions to the Post-Closure Permit Application for the Building 829 HE Open Burn Facility – Volume 1* (LLNL 2001) as modified by the *Hazardous Waste Facility Post-Closure Permit for the Building 829 HE Open Burn Facility* (DTSC 2003).

The former HE Open Burn Treatment Facility, part of the Building 829 Complex, is located on a ridge within the southeast portion of Site 300 at an elevation of about 320 m. The facility included three shallow, unlined pits constructed in unconsolidated sediments that cap the ridge (Tps formation). The facility was used to thermally treat explosives process waste generated by operations at Site 300 and similar waste from explosives research operations at the Livermore site. The facility was covered with an impervious cap in 1998 following RCRA guidance.

Surface water drains southward from the facility toward Corral Hollow Creek. The nearest site boundary lies about 1.6 km to the south at Corral Hollow Road. Stratified rocks of the Neroly (Tn) formation underlie the facility and dip southeasterly. Two water-bearing zones exist at different depths beneath the facility. The shallower zone, at a depth of about 30 m, is perched within the Neroly upper siltstone/claystone aquitard ($Tnsc_2$). The deeper zone, at a depth of about 120 m, represents a regional aquifer within the Neroly upper sandstone member ($Tnbs_2$).

Based on groundwater samples recovered from boreholes, previous CERCLA remedial investigations determined that the perched groundwater near the burn facility was contaminated with VOCs, primarily TCE, but that the deeper regional aquifer was free of any contamination stemming from operation of the facility (Webster-Scholten 1994). Subsequent assays of soil samples obtained from shallow boreholes prior to closure revealed that low concentrations of HE compounds, VOCs, and metals exist beneath the burn pits (Mathews and Taffet 1997). Conservative transport modeling indicates that the shallow contamination will not adversely impact the regional aquifer primarily because its downward movement is blocked by more than 100 m of unsaturated Neroly Formation sediments that include interbeds of claystone and siltstone.

Beginning in 1999, LLNL implemented the intensive groundwater monitoring program for this area described in the post-closure plan (Mathews and Taffet 1997) to track the fate of contaminants in the soil and the perched water-bearing zone, and to monitor the deep regional aquifer for the appearance of any potential contaminants from the closed burn facility.

This monitoring program remained in effect through the first quarter of 2003, at which time LLNL began implementation of the provisions specified in the *Hazardous Waste Facility Post-Closure Permit for the B829 Facility* (DTSC 2003). Following the guidance outlined in the DTSC *Technical Completeness* (DTSC 2002) assessment, LLNL installed one additional groundwater monitoring well at the point of compliance within three meters of the edge of the capped High Explosive Open Burn Treatment Facility. This well (W-829-1938) was screened in the regional aquifer, the uppermost aquifer beneath the Building 829 facility. Since the first quarter of 2004, well W-829-1938 has been sampled as part of the permit-specified groundwater monitoring network (**Figure 4-17**). Also shown in **Figure 4-17** are two previously existing wells (W-829-15 and W-829-22) that were used throughout 2004 for quarterly collection of groundwater samples from the regional aquifer.

As planned for compliance purposes, LLNL obtained groundwater samples quarterly during 2004 from the Building 829 monitoring well network. Groundwater samples from the wells screened in the deep regional aquifer were analyzed quarterly for inorganic COCs (mostly metals), general minerals, turbidity, explosive compounds (HMX, RDX, and TNT), VOCs (EPA method 624), extractable organics (EPA method 625), pesticides (EPA method 608), herbicides (EPA method 615), general radioactivity (gross alpha and beta), radium activity, total organic carbon (TOC), total organic halides (TOX), and coliform bacteria.

No new release of COCs to groundwater from the closed HE burn facility is indicated by the monitoring data obtained during 2004. For a detailed account of compliance monitoring of the closed HE burn pit during 2004, including tables and graphs of groundwater COC analytical data, see *LLNL Experimental Test Site 300—Compliance Monitoring Program for the Closed Building 829 Facility— Annual Report 2004* (Revelli 2005b).

During 2004, no organic or explosive COCs were detected above their respective reporting limits in groundwater samples from any of the three monitoring wells. The inorganic constituents that were detected in samples from the two established wells (W-829-15 and W-829-22) show concentrations that do not differ significantly from background concentrations for the deep aquifer beneath the HE Process Area (Webster-Scholten 1994). Although zinc and mercury were detected in routine quarterly samples from well W-829-22, these results were subsequently invalidated.

With one exception, the concentrations of inorganic COCs detected in the new well (W-829-1938) were consistent with background concentrations reported for the other wells that were also sampled for this network. Only nickel, detected in two of the quarterly samples from well W-829-1938 (at 14 µg/L and 5.1 µg/L), had not previously been detected in groundwater samples from this monitoring network. Nickel, however, is typically found in Site 300 groundwater at background concentrations of 21 µg/L (Webster-Scholten 1994). Continued quarterly sampling at well W-829-1938 through 2005 will provide additional data to better establish background concentrations and statistically determined limits of concentrations in accordance with state regulations.

Water Supply Well

Water supply well 20, located in the southeastern part of Site 300 (**Figure 4-13**), is a deep, high-production well. The well is screened in the Neroly lower sandstone aquifer ($Tnbs_1$) and can produce up to 1500 L/min of potable water. As planned for surveillance purposes, LLNL obtained groundwater samples quarterly during 2004 from well 20. Groundwater samples were analyzed for inorganic COCs (mostly metals), VOCs, general radioactivity (gross alpha and gross beta), and tritium activity.

Quarterly measurements of groundwater from well 20 do not differ significantly from previous years. As in past years, the primary potable water supply well at Site 300 showed no evidence of contamination. Gross alpha, gross beta, and tritium activities were very low and are indistinguishable from background level activities.

Off-site Surveillance Wells and Springs

As planned for surveillance purposes, LLNL obtained groundwater samples from two off-site springs and ten off-site wells during 2004. With the exception of one well, all off-site monitoring locations are near Site 300. The exception, well VIE2, is located at a private residence 6 km west of the site. It represents a typical potable water supply well in the Altamont Hills. One stock watering well, MUL1, and two stock watering springs, MUL2 and VIE1, are adjacent to Site 300 on the north. Eight wells, CARNRW1, CARNRW2, CDF1, CON1, CON2, GALLO1, STONEHAM1, and W35A-04, are adjacent to the site on the south (**Figure 4-13**). Well W35A-04 is a DOE CERCLA well that was installed off site for monitoring purposes only. The remaining seven wells south of Site 300 are privately owned and were constructed to supply water either for human consumption, stock watering, or fire suppression. They are monitored to determine the concentrations of dissolved constituents in the groundwater beneath the Corral Hollow Creek flood plain.

Groundwater samples were obtained quarterly during 2004 at six of the off-site surveillance well locations south of Site 300. As planned, CARNRW1 and CON2 samples were analyzed for VOCs; samples from well CARNRW1 were also sampled for perchlorate and tritium. Samples from CARNRW2, CDF1, CON1, and GALLO1 were analyzed quarterly for inorganic COCs (mostly metals), general radioactivity (gross alpha and beta), tritium activity, explosive compounds (HMX and RDX), and VOCs (EPA method 502.2). Additional annual analyses were conducted on third-quarter samples for uranium activity and extractable organic compounds (EPA method 625).

Groundwater samples were obtained once (annually) during 2004 from the remaining off-site surveillance monitoring locations—MUL1, MUL2, and VIE1 (north of Site 300); VIE2 (west of Site 300); and STONEHAM1 and W-35A-04 (south of

Site 300). Samples were analyzed for inorganic COCs (mostly metals), general radioactivity (gross alpha and beta), tritium and uranium activity, explosive compounds (HMX and RDX), VOCs, and extractable organic compounds (EPA method 625).

Generally, no COC attributable to LLNL operations at Site 300 was detected in the off-site groundwater samples. Arsenic and barium were widely detected at the off-site locations, but their concentrations were below MCLs and their occurrence is consistent with natural sources in the rocks. Scattered detections of metals are probably related to metals used in pumps and supply piping. As in past years, TCE was detected at concentrations of less than 1 µg/L in the groundwater samples obtained from well GALLO1. Previous CERCLA remedial investigations concluded that the TCE in the GALLO1 well water was likely caused by a localized surface spill on the property, possibly solvents used to service the private well (Webster-Scholten 1994). (Surveillance monitoring of a similarly sited well, GALLO2, was terminated in 1991 because of contamination from chemicals leaking from the pumping apparatus.) Radioactivity measurements of off-site groundwater are generally indistinguishable from background activities. Groundwater samples collected from CARNRW1 and CARNRW2 during October had elevated tritium activities; however, continued monitoring did not replicate these results. It appears likely that these results are related to laboratory error (Campbell and Blake 2005).

Environmental Impact on Groundwater

Groundwater monitoring at the Livermore site and Site 300 and their environs indicates that LLNL operations have minimal impact on groundwater beyond the site boundaries. During 2004, neither radioactivity nor concentrations of elements or compounds detected in groundwater were confirmed to be above potable water MCLs.

Other Monitoring Programs

Rainwater

Rainwater is sampled and analyzed for tritium activity in support of DOE Order 5400.5, Radiation Protection of the Public and the Environment. LLNL collects rainwater samples according to written standardized procedures which are summarized in the *Environmental Monitoring Plan* (Woods 2005). Rainwater is collected in stainless-steel buckets at fixed locations. The buckets are in open areas and are mounted about 1 m above the ground to prevent collection of splashback water. Rainwater samples are decanted into 250 mL amber glass bottles with Teflon-lined lids. The tritium activity of each sample is measured at a contracted laboratory by a scintillation counting method equivalent to EPA Method 906 that has a low reporting limit of about 3.7 Bq/L (100 pCi/L). All analytical results are included in the file "Ch4 Other Waters" provided on the report CD.

Livermore Site and Environs

Historically, the tritium activity measured in rainwater in the Livermore Valley was caused by atmospheric emissions of HTO from stacks at LLNL's Tritium Facility (Building 331), and prior to 1995, from the former Tritium Research Laboratory at Sandia/California. During 2004, tritium activity in air-moisture and, thence, in rainwater at the Livermore site and in the Livermore Valley, resulted primarily from atmospheric emissions of HTO from stacks at Building 331. Atmospheric emission of HTO from Building 331 in 2004 was approximately 0.61 TBq (16.5 Ci), down from 4.1 TBq (110 Ci) in 2003. Other sources include the Waste Management Area (WMA) at Building 612 and the newly operating DWTF (see Chapter 3).

Rain sampling locations are shown in **Figure 4-18**. The fixed locations are used to determine the areal extent of detectable tritium activity in rainwater. A new rain-tritium sampling location, DWTF, was established in mid-year 2003. During 2004, LLNL collected sets of rainwater samples following three rain events in the Livermore Valley and two rain events at Site 300. All of the rainwater sampling dates correspond to storm water runoff sampling.

Although the Livermore site rainwater has exhibited elevated tritium activities in the past (Gallegos et al. 1994), during 2004, no on-site measurement of tritium activity was above the MCL of 740 Bq/L (20,000 pCi/L) established by the EPA for drinking water. As in past years, the on-site rainwater sampling location B343 showed the highest tritium activity for the year, 19 Bq/L (510 pCi/L), for the rain event that was sampled on February 27. The maximum tritium activity measured in an off-site rainwater sample during 2004 was 3.2 Bq/L (86 pCi/L) in the rainwater sample obtained on February 26 from location AMON (**Figure 4-18**). The maximum off-site activity equals 0.4% of the MCL for tritium activity in drinking water.

Site 300 and Environs

Three on-site locations (COHO, COMP, and TNK5) were positioned to collect rainfall for tritium activity measurements at Site 300 during 2004 (**Figure 4-10**). During 2004, only two rain events were sampled. As in past years, none of the rainwater samples from monitoring locations at Site 300 during 2004 had tritium activities above the analytical laboratory reporting limit of 3.7 Bq/L.

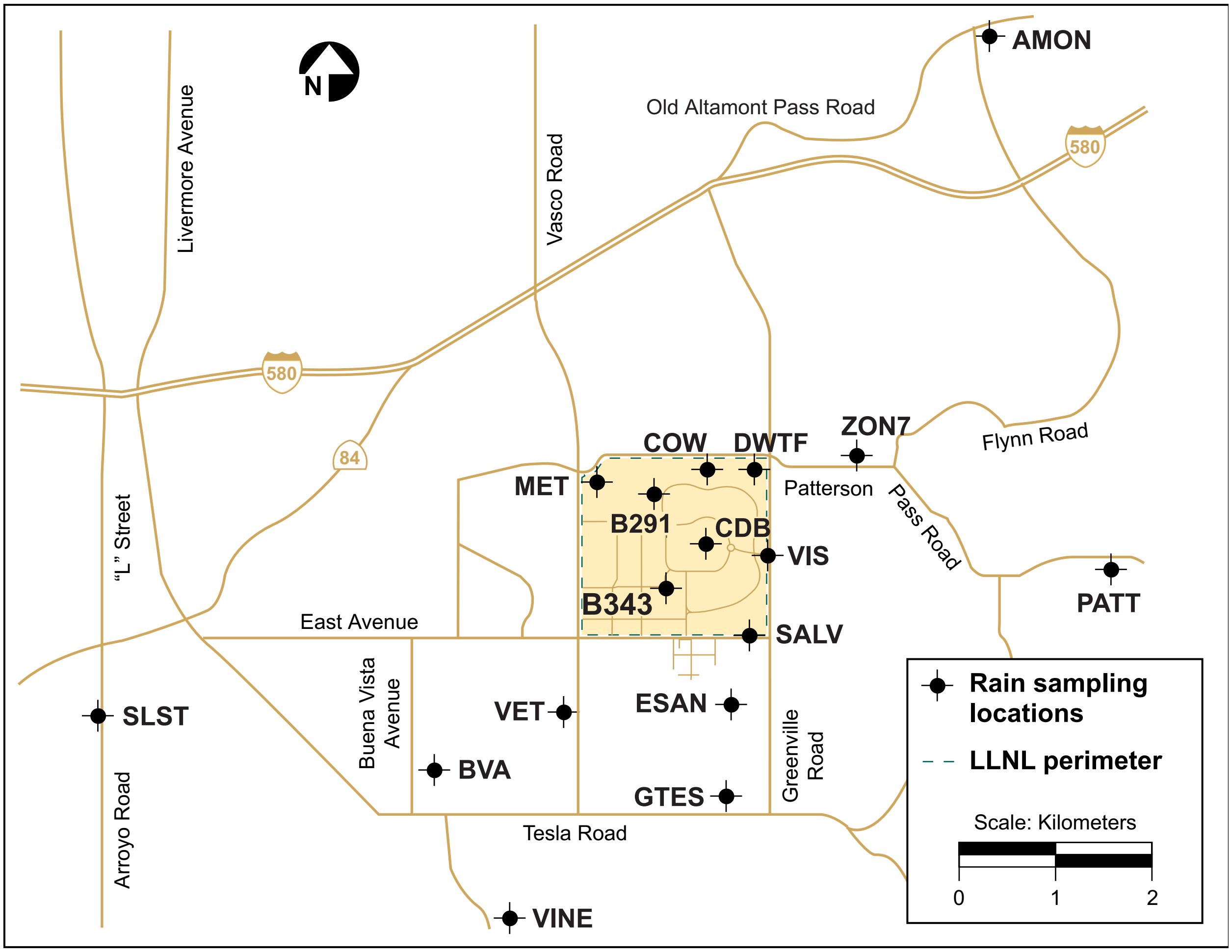


Figure 4-18. Rain sampling locations, Livermore site and Livermore Valley, 2004

Livermore Valley Surface Waters

LLNL conducts additional surface water surveillance monitoring in support of DOE Order 5400.5, Radiation Protection of the Public and the Environment. Surface and drinking water near the Livermore site and in the Livermore Valley are sampled at the locations shown in **Figure 4-19**. Off-site sampling locations DEL, ZON7, DUCK, ALAG, SHAD, and CAL are surface water bodies; of these, DEL, ZON7, and CAL are drinking water sources. BELL, GAS, PALM, ORCH, and TAP are drinking water outlets. Location POOL is the on-site swimming pool. The on-site pool was closed during the second quarter of 2004, so sampling at location POOL was discontinued. Also, monitoring at the residence known as the PALM location was discontinued after

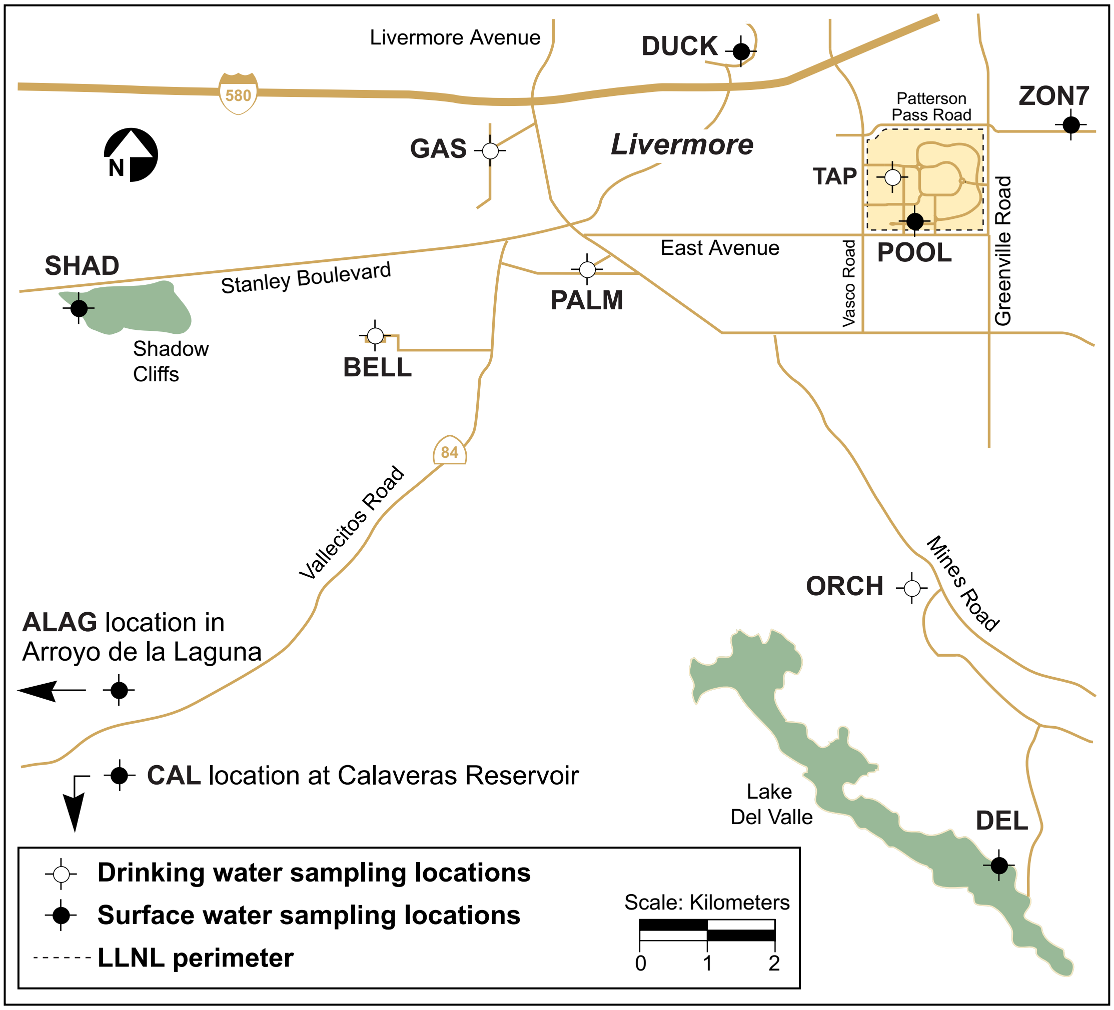


Figure 4-19. Livermore Valley surface and drinking water sampling locations, 2004

the first quarter of 2004 due to lack of access to LLNL staff. Radioactivity data from drinking water sources are used to calculate drinking water statistics (see **Table 4-14**).

Samples are analyzed according to written standardized procedures summarized in the *Environmental Monitoring Plan* (Woods 2005). LLNL sampled these locations semiannually, in March and July 2004, for gross alpha, gross beta, and tritium. The on-site swimming pool location (POOL) was sampled in March for gross alpha and gross beta, and in March and April for tritium. All analytical results are included in the file "Ch4 Other Waters" provided on the report CD.

The median activity for tritium in surface and drinking waters was estimated from calculated values to be below the analytical laboratory's minimum detectable activities, or minimum quantifiable activities. The maximum tritium activity detected (3.05 ± 1.96 Bq/L [82 ± 53 pCi/L]) was less than 1% of the MCL of 740 Bq/L (20,000 pCi/L) in residential well water from an off-site residence location known as ORCH, located south of LLNL along Mines Road (**Figure 4-19**). Median activities for gross alpha and gross beta radiation in surface and drinking water samples were both less than 5% of their respective MCLs. Maximum activities detected for gross alpha and gross beta, respectively, were 0.068 Bq/L (1.8 pCi/L) and 0.317 Bq/L (8.6 pCi/L); both were less than 20% of their respective MCLs (see **Table 4-14**). Historically, concentrations of gross alpha and gross beta radiation have fluctuated around the laboratory minimum detectable activities. At these very low levels, the counting error associated with the measurements is nearly equal to, or in many cases greater than, the calculated values so that no trends are apparent in the data.

Table 4-14. Radioactivity in surface and drinking waters in the Livermore Valley, 2004

Locations	Tritium (Bq/L)	Gross alpha (Bq/L)	Gross beta (Bq/L)
All locations			
Median	–0.110	0.017	0.098
Minimum	–1.90	–0.020	0.019
Maximum	3.05	0.068	0.317
Interquartile range	1.075	0.014	0.061
Drinking water locations			
Median	0.242	0.008	0.077
Minimum	–1.48	–0.02	0.02
Maximum	3.05	0.040	0.317
Interquartile range	1.15	0.02	0.099
Drinking water MCL	740	0.555	1.85

Note: A negative number means the sample radioactivity was less than the background radioactivity.

Historical median tritium values in surface and drinking waters in the Livermore Valley since 1988 are shown in **Figure 4-20**. Since 1988, when measurements began, water in the LLNL swimming pool has had the highest tritium activities because it is close to tritium sources within LLNL. After the first quarter of 2004 and the draining of the swimming pool, the Drainage Retention Basin became the closest routinely monitored source to the Tritium Facility at Building 331.

Drainage Retention Basin Release

The DRB was constructed and lined in 1992 after remedial action studies indicated that infiltration of storm water from the existing basin increased dispersal of groundwater contaminants. Located in the center of the Livermore site, the DRB can hold approximately 45.6 ML (37 acre-feet) of water. Previous *Environmental Reports* detail the

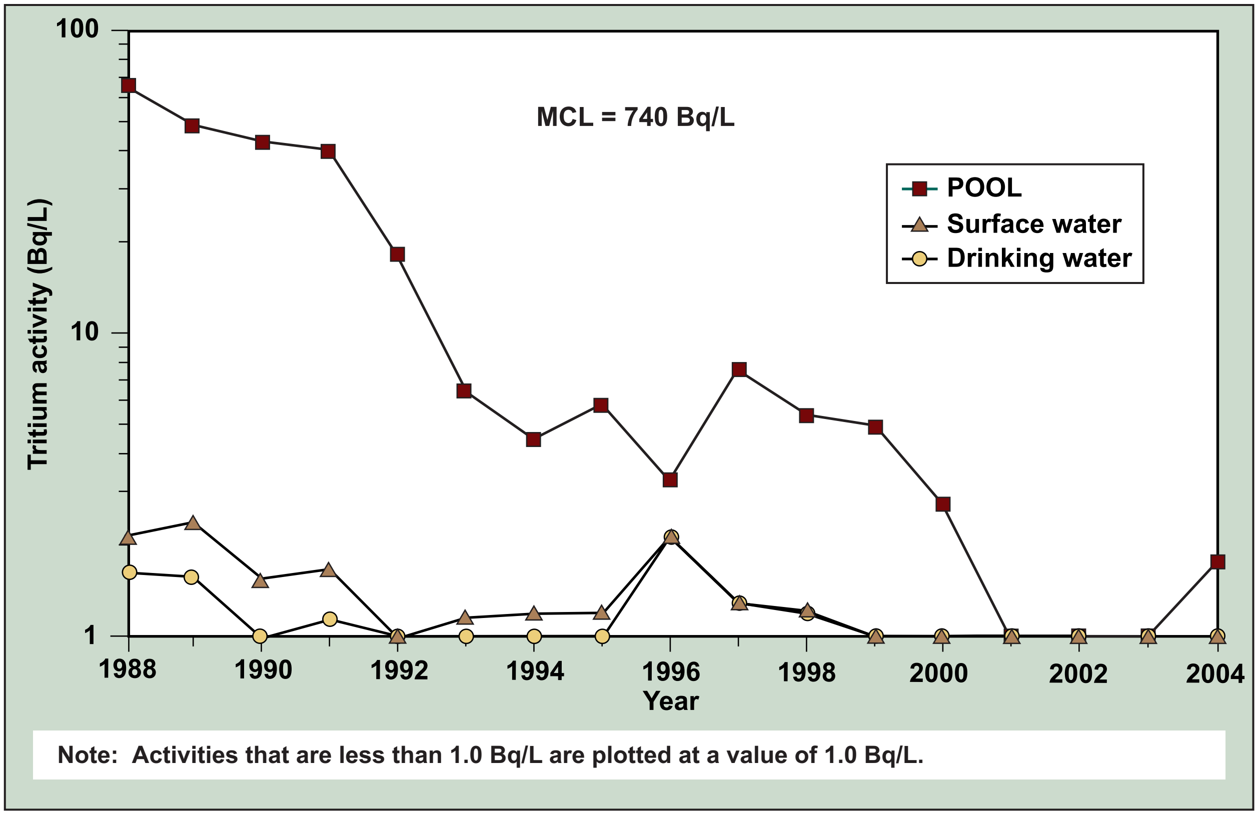


Figure 4-20. Annual median tritium activity in Livermore Valley surface and drinking water, 1988 to 2004

history of the construction and management of the DRB (see Harrach et al. 1995, 1996, 1997). Beginning in 1997, LLNL discharges to the DRB included routine treated groundwater from TFD and TFE, and from related portable treatment units. These discharges contribute a year-round source of water entering and exiting the DRB. Discharge rate is approximately 100 gpm. Storm water runoff still dominates wet weather flows through the DRB, but discharges from the treatment facilities now constitute a substantial portion of the total water passing through the DRB.

The SFBRWQCB regulates discharges from the DRB. The document *Drainage Retention Basin Monitoring Plan Change* (Jackson 2002) lists constituents of interest, sample frequencies, and discharge limits based on the Livermore site CERCLA Record of Decision (ROD) (U.S. DOE 1993), as modified by the *Explanation of Significant Differences for Metals Discharge Limits at the Lawrence Livermore National Laboratory Livermore Site* (Berg et al. 1997). The ROD established discharge limits for all remedial activities at the Livermore site to meet applicable, relevant, and appropriate requirements derived from laws and regulations identified in the ROD, including federal Clean Water Act, federal and state Safe Drinking Water Acts, and the California Porter-Cologne Water Quality Control Act. See Appendix B for the limits used.

The DRB sampling program implements requirements established by the SFBRWQCB. The program consists of monitoring wet and dry weather releases for compliance with discharge limits and performing routine reporting. For purposes of determining discharge monitoring requirements and frequency, the wet season is defined as October 1 through May 31, the period when rain-related discharges usually occur (Galles 1997). Discharge limits are applied to the wet and dry seasons as defined in the *Explanation of Significant Differences for Metals Discharge Limits at the Lawrence Livermore National Laboratory Livermore Site* (Berg et al. 1997) (wet season December 1 through March 31, dry season April 1 through November 30).

To characterize wet-season discharges, LLNL samples DRB discharges at location CDBX and the Livermore site outfall at location WPDC during the first release of the rainy season, and from a minimum of one additional release (chosen in conjunction with storm water runoff sampling). During the dry season, samples are collected from each discrete discharge event or monthly while discharge is continuous. Discharge sampling locations CDBX and WPDC are shown in **Figure 4-9**. LLNL collects samples at CDBX to determine compliance with discharge limits. Sampling at WPDC is done to identify any change in water quality as the DRB discharges travel through the LLNL storm water drainage system and leave the site.

Written standardized sample collection procedures are summarized in the *Environmental Monitoring Plan* (Woods 2005). State-certified laboratories analyze the collected samples for chemical and physical parameters. All analytical results are included in the file "Ch4 Other Waters" provided on the report CD.

Water releases typically occurred continuously to maintain relatively low nutrient levels in the DRB and because treatment facility discharge to the DRB exceeded the evaporation rate. Samples collected at CDBX and WPDC exceeded only the pH discharge limits. The higher pH readings seen in the DRB discharge samples during the summer and fall correspond to the peak of the summer and fall algae blooms within the DRB. During 2004, total dissolved solids and specific conductance continued to reflect the levels found in groundwater discharged to the DRB. While some metals were detected, none were above discharge limits. All organics, pesticides, and PCBs were below analytical discharge limits. Gross alpha, gross beta, and tritium levels were well below discharge limits.

LLNL collects and analyzes samples for acute fish toxicity using fathead minnow (*Pimphales promelas*) and for chronic toxicity using three species (fathead minnow, water flea daphnid [*Ceriodaphnia dubia*], and green algae [*Selanastrum capricomutum*]). LLNL collects acute toxicity samples at the first wet-season release and from each discrete dry season release from location CDBX. Samples for chronic fish toxicity were collected at location CDBX at the first wet-season release. Aquatic bioassay for toxicity showed no toxicity effects in DRB discharge water.

Site 300 Drinking Water System

LLNL samples large-volume discharges from the Site 300 drinking water distribution system that reach surface water drainage courses in accordance with the requirements of WDR 5-00-175, NPDES General Permit No. CAG995001. The monitoring and reporting program that LLNL developed for these discharges was approved by the CVRWQCB.

Discharges that are subject to sampling under WDR 5-00-175 and their monitoring requirements are:

- Drinking water storage tanks—discharges that have the potential to reach surface waters are monitored.
- System flushes—one flush per pressure zone per year is monitored for flushes that have the potential to reach surface waters.
- Dead-end flushes—all flushes that have the potential to reach surface waters, and for any discharge that continues for more than four months are monitored.

Discharges must comply with the effluent limits for residual chlorine and pH established by the permit, that is, residual chlorine must not be greater than 0.02 mg/L, and the pH must be between 6.5 and 8.5. Discharges are also visually monitored to ensure that no erosion results and no other pollutants are washed into surface waters. To meet the chlorine limit, drinking water system discharges with the potential to reach surface waters are dechlorinated.

Sample collection procedures are discussed in the *Lawrence Livermore National Laboratory Site 300 Water Suppliers' Pollution Prevention and Monitoring and Reporting Program* (Mathews 2000). Grab samples are collected in accordance with written standardized procedures summarized in the *Environmental Monitoring Plan* (Woods 2005). Residual chlorine and pH are immediately analyzed in the field, using a spectrophotometer and calibrated pH meter, respectively.

Samples are collected at the point of discharge and at the point where the discharge flows into a surface water. If the discharge reaches Corral Hollow Creek, samples are collected at the upstream sampling location, CARW, and the downstream sampling location, GEOCRK.

Small volumes of water (less than 2000 gallons) were discharged in the first and fourth quarters of 2004, as a result of routine pressure tests conducted by the Site 300 fire department. Because of the nature of fire department activities, these small-volume discharges were not monitored. The annual pressure zone testing, required by the CVRWQCB, was completed during the third quarter, when LLNL conducted flushing of the drinking water system for water quality purposes. These system flush releases were monitored and met the effluent limits. All 2004 releases from the Site 300 drinking water system quickly percolated into the drainage ditches or streambed, and did not reach Corral Hollow Creek, the receiving water (Raber 2004). Monitoring results are detailed in the quarterly self monitoring reports to the CVRWQCB.

Site 300 Cooling Towers

The CVRWQCB rescinded WDR 94-131, NPDES Permit No. CA0081396, on August 4, 2000, which previously governed discharges from the two primary cooling towers at Site 300. The CVRWQCB determined that these cooling towers discharge to the ground rather than to surface water drainage courses. Therefore, the CVRWQCB is issuing a new permit to incorporate these cooling tower discharges, and other low-threat discharges, going to ground. Pending the issuance of the new permit, LLNL continues to monitor the cooling tower wastewater discharges following the WDR 94-131 monitoring requirements at the direction of CVRWQCB staff.

Two primary cooling towers, located at Buildings 801 and 836A, regularly discharge to the ground. Blowdown flow from the cooling towers located at these two buildings is monitored biweekly. Total dissolved solids (TDS) and pH are monitored quarterly at both of these locations. The 13 secondary cooling towers routinely discharge to percolation pits under a waiver of Waste Discharge Requirements from the CVRWQCB. Cooling tower locations are shown in **Figure 4-21**

Written standardized sample collection procedures are summarized in the *Environmental Monitoring Plan* (Woods 2005). To determine the effects of the cooling tower blowdown on Corral Hollow Creek, LLNL quarterly monitors pH, both upstream (background) and downstream of the cooling tower discharges, whenever the creek is flowing. CARW is the upstream sampling location, and GEOCRK is the downstream sampling location (**Figure 4-21**).

The GEOCRK sampling location is also fed by discharges of treated groundwater from Site 300. Therefore, even when the upstream location is dry, there may be flow at GEOCRK. Field pH measurements, taken by LLNL using calibrated meters, are used to monitor Corral Hollow Creek. LLNL also performs the required visual observations that are recorded on field tracking forms along with the field pH measurements.

If the blowdown flow from any of the 13 secondary cooling towers is diverted to a surface water drainage course, the discharge is sampled for pH and TDS immediately. If the discharge continues, that location is monitored for the same constituents and on the same schedule as the primary cooling towers.

Monitoring results in 2004 indicate that all discharges from the Buildings 801 and 836A cooling towers were below the maximum TDS (2400 mg/L) and pH (10) values that were previously imposed for discharges to surface water drainage courses under WDR 94-131. The blowdown flows from these towers were typical of volumes reported in recent years, except for one unusually high flow recorded on May 6 at the Building 836A tower. On this one day, the flow from that tower was reported as 58,148 L/day,

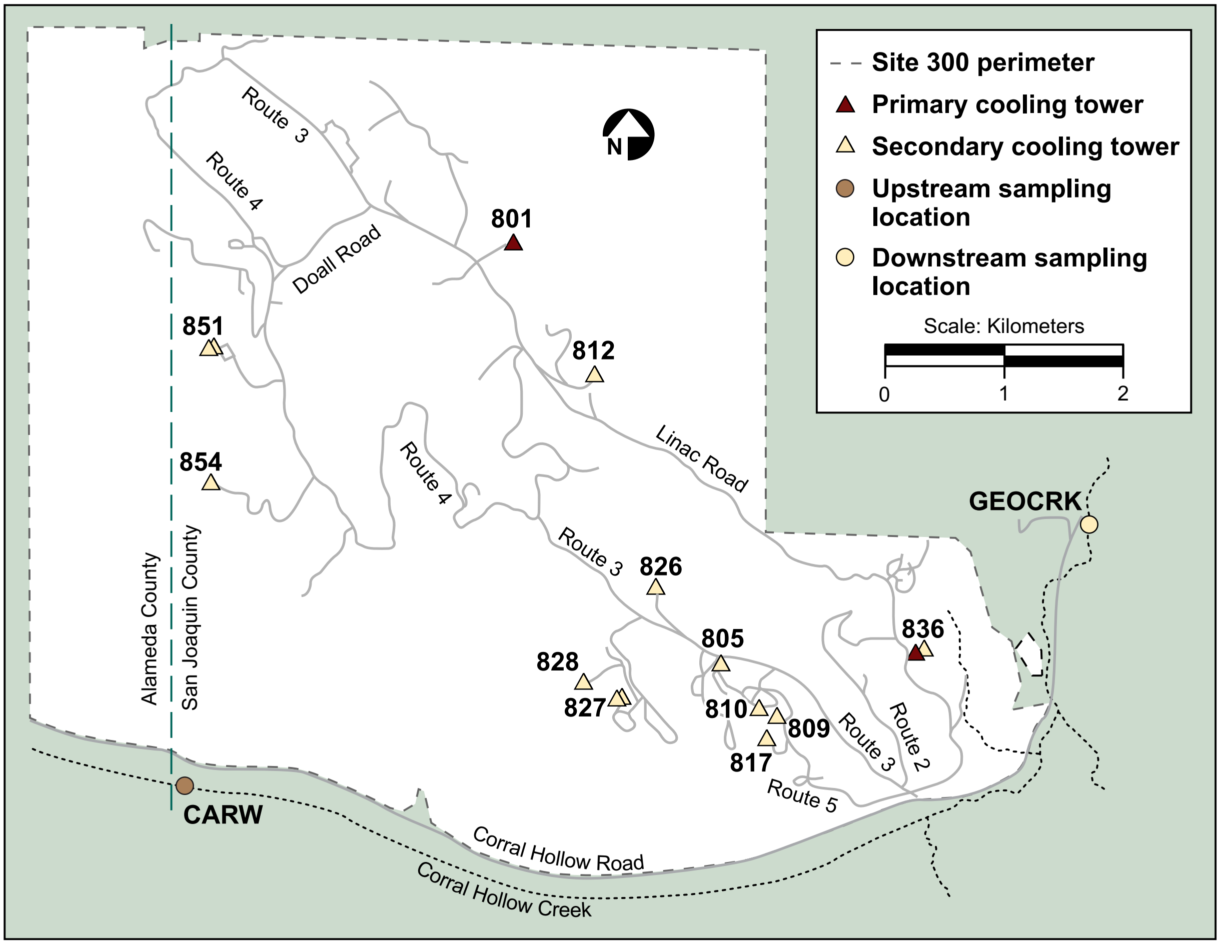


Figure 4-21. Cooling tower locations and receiving water monitoring locations, Site 300, 2004

approximately a factor of six above the next highest value. Flow readings for the preceding (April 19) and following (May 17) observation periods were 2256 L/day and 6783 L/day, respectively, indicating that this high flow was a transient event. Nevertheless, no flow was observed at either the CARW or GEOCRK locations during the period in question. **Table 4-15** summarizes the data from the quarterly TDS and pH monitoring, as well as the biweekly measurements of blowdown flow.

The biweekly observations at CARW and GEOCRK reported dry or no flow conditions for both sampling locations throughout most of 2004. Only on October 18 was there adequate flow to measure pH. The resulting field pH measurements were 7.88 and 7.96 for CARW and GEOCRK locations, respectively, indicating essentially no change between the upstream and downstream locations. Visual observations of Corral Hollow Creek were performed each quarter, and no visible oil, grease, scum, foam, or floating suspended materials were noted in the creek during 2004.

Table 4-15. Summary data from monitoring of primary cooling towers, Site 300, 2004

Test	Tower no.	Minimum	Maximum	Median	Interquartile range	Number of samples
Total dissolved solids (TDS) (mg/L)	801	955	1,680	1,120	—(a)	4
	836A	880	1,280	1,063	—(a)	4
Blowdown (L/day)	801	0	58,148	7,435	4,826	25(b)
	836A	0	5,443	2,406	2,592	26
pH (pH units)	801	8.9	9.1	9.0	—(a)	4
	836A	8.7	9.0	8.8	—(a)	4

a Not enough data points to determine

b One biweekly blowdown reading could not be collected because the area around Tower 801 was closed due to a lightning alert.

No drinking water or cooling tower water releases from Site 300 reached Corral Hollow Creek. There is no evidence of any adverse environmental impact on surrounding waters resulting from these LLNL activities during 2004.