Sewerable Water Monitoring

Henry E. Jones
Michael A. Revelli
Robert A. Williams
Allen R. Grayson
Shari L. Brigdon

Introduction

In 2002, the Livermore site discharged an average of 0.91 million liters (ML) per day of wastewater to the City of Livermore sewer system, an amount that constituted 4.1% of the total flow to the 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 6-1**).

In 2002, Sandia/California generated approximately 9.2% of the total effluent discharged from the Livermore site. LLNL's wastewater contains sanitary sewage and industrial wastewater and is discharged in accordance with permit requirements and the City of Livermore Municipal Code, as discussed below in the "Pretreatment Discharges" and "Categorical Discharges" sections.

The effluent is treated at the Livermore Water Reclamation Plant (LWRP), which is part of the Livermore-Amador Valley Wastewater Management Agency. The treated sanitary wastewater is transported out of the valley through a pipeline and discharged into San Francisco Bay. A small portion (approximately 10%) of this treated wastewater is kept for fire suppression and summer irrigation of the municipal golf course adjacent to the LWRP.

LLNL receives water from two suppliers. LLNL's primary water source is the Hetch-Hetchy Aqueduct. Secondary or emergency water deliveries are taken from the Alameda County Flood Control and Water Conservation District Zone 7. This water is a mixture of groundwater and water from the South Bay Aqueduct of the State Water Project. Water quality parameters for the two sources are obtained from the suppliers and are used to evaluate compliance with the discharge permit conditions that limit changes in water quality between receipt and discharge.

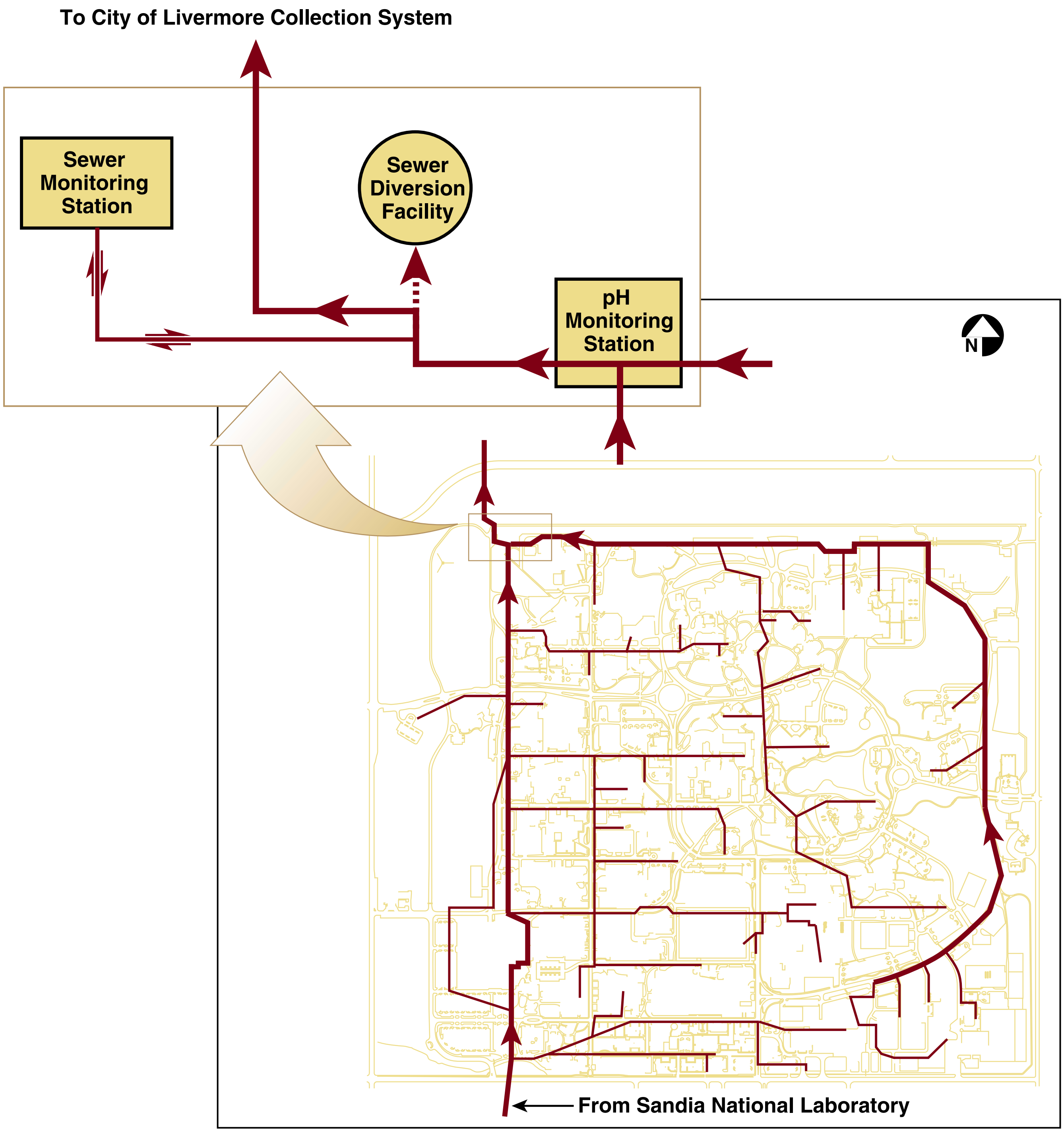


Figure 6-1. LLNL sanitary sewer system, monitoring stations, and diversion facility

Preventive Measures

Administrative and engineering controls at the Livermore site are designed to prevent potentially contaminated wastewater from being discharged directly to the sanitary sewer. Waste generators receive training on proper waste handling. LLNL Environmental Protection Department (EPD) personnel review facility procedures and inspect processes to ensure appropriate discharges. Retention tanks collect wastewater from processes that might release contaminants in quantities sufficient to violate permit conditions or disrupt operations at the LWRP. Wastewater that cannot be discharged into one or more of the surface water collection units at LLNL's Site 300 is transported to LLNL's Livermore site and managed under Livermore site retention tank administrative controls. Groundwater (generated from startup operations associated with new, portable groundwater treatment units, tests of experimental treatment units, and maintenance of existing treatment facilities) is analyzed for pollutants of concern and must meet permit criteria, or LWRP approval must be obtained before it can be discharged to the sanitary sewer. Finally, to verify the success of training and control equipment, wastewater is sampled and analyzed not only at the significant points of generation, as defined by type and quantity of contaminant generated, but also at the point of discharge to the municipal sewer system.

For facilities with installed retention tank systems, collected wastewater is discharged to the sanitary sewer only if analytical laboratory results show that pollutant levels are within allowable limits as defined in the *ES&H Manual*, Document 32.4 (LLNL 2002). LLNL has developed internal guidelines to ensure that sewer effluent for the entire site complies with LLNL's wastewater discharge permit. The process of wastewater generation and discharge frequency from retention tanks varies over time, depending upon the process. During 2002, there were approximately 33 waste retention tank systems in use at the Livermore site.

Processes that discharge to the sanitary sewer are subject to the general pretreatment self-monitoring program specified in the Wastewater Discharge Permit issued by the LWRP and, as such, are managed by LLNL using requirements as applied at the point of discharge into the LLNL sewer.

If pollutant levels exceed concentrations that would result in a violation of of LLNL's LWRP permit, the wastewater is either treated to reduce pollutants to levels that preclude a permit violation, or it is shipped to an off-site treatment or disposal facility. Liquids containing radioactivity are handled on site and may be treated using processes that reduce the activity to levels well below those required by DOE Order 5400.5, or they are shipped to an off-site treatment or disposal facility.

For the year as a whole, the monitoring data reflect the success of LLNL's discharge control program in preventing any adverse impact on the operations of the LWRP and are consistent with past values.

Monitoring

Monitoring at the Sewer Monitoring Station

LLNL's sanitary sewer discharge permit 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 upset the LWRP treatment process or otherwise impact the public welfare. The effluent is continuously analyzed for pH, regulated metals, and radioactivity. If concentrations above warning levels are detected, an alarm is registered at the LLNL Fire Dispatcher's Station, which is attended 24 hours a day, and the site effluent is diverted to the Sewer Diversion Facility (SDF). 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.

Monitoring at the Upstream pH Monitoring Station

In addition to the continuous monitoring at the SMS, LLNL monitors pH at the upstream pH Monitoring Station (pHMS) (see **Figure 6-1** for a system diagram). The pHMS continuously monitors pH 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. Earlier detection allows LLNL to divert all of the unpermitted site effluent detected by the pHMS.

Diversion System

LLNL operates and maintains a diversion system that activates automatically when either the SMS continuous monitoring system or the pHMS sounds an alarm. 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 required 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. All the diverted sewage in 2002 was returned to the sanitary sewer.

Pretreatment Discharges

The general pretreatment regulations establish both general and specific standards for the discharge of prohibited substances that apply to all industrial users (40 Code of Federal Regulations [CFR] 403.5). These regulations apply even if LLNL is subject to other federal, state, or local pretreatment standards. The pretreatment standards contain prohibitions intended to protect the LWRP and its operations from interference with its treatment processes or pass-through that would cause the LWRP to violate its own effluent limitations. The LWRP, under the authorization of the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB), requires self-monitored pretreatment programs at both the Livermore site and Site 300. The sampling and monitoring of nondomestic, industrial sources covered by pretreatment standards defined in 40 CFR 403 are required in the 2002-2003 Wastewater Discharge Permit No. 1250 issued for the discharge of wastewater from LLNL into the City of Livermore sewer system.

Permit 1250 lists all the self-monitoring parameters that are applied at the SMS before wastewater enters the municipal collection system at LLNL's effluent outfall (see **Figure 6-1**). Parameters with numerical limits are listed in **Table 6-1**. The additional discharge limits shown in **Table 6-1** are discussed in the "Categorical Discharges" and "Discharges of Treated Groundwater" sections. Other required parameters such as flow rate, biological oxygen demand, total dissolved solids,

Table 6-1. Permit discharge limits for nonradioactive parameters in LLNL wastewaters

Parameter	Permit discharge limits			
	Permit 1250			Permit 1510G
	SMS[(a)]	Metal finishing[(b)]	Electric component[(b)]	Treated groundwater
Metals (mg/L)				
Arsenic	0.06	—[(c)]	0.83	0.06
Cadmium	0.14	0.07	—[(c)]	0.14
Chromium (total)	0.62	1.71	—[(c)]	0.62
Copper	1.0	2.07	—[(c)]	1.00
Lead	0.20	0.43	—[(c)]	0.20
Mercury	0.01	—[(c)]	—[(c)]	0.01
Nickel	0.61	2.38	—[(c)]	0.61
Silver	0.20	0.24	—[(c)]	0.20
Zinc	3.00	1.48	—[(c)]	3.00
Organics (mg/L)				
TTO[(d)]	1.00	2.13	1.37	1.00
Other (mg/L)				
Cyanide[(e)]	0.04	0.65	—[(c)]	0.04[(f)]
pH (pH units)	5–10	—[(c)]	—[(c)]	5–10

a These standards apply at the Sewer Monitoring Station (SMS) (the point of discharge to the municipal sewer).

b Values shown for these categorical standards were specified by Environmental Protection Agency (EPA). By regulation, the EPA or City of Livermore limit is used, whichever is lower. The internal limits in **Table 6-1** are applied by LLNL where no other standard is specified.

c There is no specific categorical limit for this parameter; therefore, the **Table 6-1** internal discharge limits apply.

d Total toxic organics (TTO) is defined by the Livermore Municipal Code as the sum total of all detectable organic compounds that are on EPA's current priority pollutant list and that are present in concentrations of 0.01 mg/L or greater. Analysis using EPA Methods 624 and 625 satisfies this requirement. A listing of the specific compounds included may be found in the Data Supplement, Chapter 6.

e Limits apply to cyanide discharges other than cyanide salts. Cyanide salts are classified by the State of California as "extremely hazardous waste" and cannot be discharged to the sewer.

f Although Permit 1510G lists a discharge limit for cyanide, sample collection is not required by the self-monitoring program.

total suspended solids, and tributyltin are also monitored at the SMS but have no specific numerical limits.

LLNL received only one Letter of Warning from the LWRP for a permit infraction in 2002. The only effluent discharge limit for wastewater that was exceeded was the discharge limit for lead.

Categorical Discharges

The U.S. Environmental Protection Agency (EPA) publishes categorical standards as regulations separate from the general pretreatment regulations and developed 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. The number of processes at LLNL using these pollutants is subject to change as programmatic requirements dictate. During 2002, 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). The discharge limits for these standards are shown in **Table 6-1**. Under the terms in Permit 1250, only those processes that discharge to the sanitary sewer require sampling, inspection, and reporting. Three of the 15 identified processes meet these criteria. In 2002, LLNL analyzed samples for all regulated parameters from these three processes and demonstrated compliance with all Federal Categorical Discharge limits.

One of the three categorical processes that discharge directly into the sanitary sewer system is an abrasive jet machine (or water-jet) that is regulated under the Metal-Finishing Point Source Category; the filtered water from this process is discharged to the sanitary sewer.

The other two discharging categorical processes are both regulated under the Federal Electrical and Electronic Component Point Source Category. One is a series of processes clustered within a single building that houses research-scale microfabrication laboratories used for developing prototype semiconductor devices. These laboratories discharge into a building wastewater retention system, and because they are housed within the same building with no diluting flow, they share a single point of compliance. The other categorical process is a small gallium arsenide cutting operation; this process discharges directly to the sanitary sewer.

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. The wastewater from these processes was contained for removal and off-site shipment by LLNL's RHWM Division.

Discharges of Treated Groundwater

LLNL's groundwater discharge permit (1510G 2001/2002) allows treated groundwater from site-wide cleanup activities under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) to be discharged to the City of Livermore sanitary sewer in compliance with **Table 6-1** effluent limitations taken from the Livermore Municipal Code. During calendar year 2002, however, no LLNL groundwater, treated under CERCLA activities, was discharged to the sanitary sewer.

Radioactive Pollutants in Sewage

Monitoring Results

LLNL determines the total radioactivity released from tritium, gross alpha emitters, and gross beta emitters based on the measured radioactivity in the monthly effluent samples (see **Table 6-2**). The 2002 combined releases of alpha and beta sources was 0.155 GBq (0.0042 Ci). The combined total is based on the alpha and beta results shown in **Table 6-2**. The tritium total was 0.74 GBq (0.02 Ci), and the annual mean concentration of tritium in LLNL sanitary sewer effluent based on monthly samples was 0.0025 Bq/mL (0.068 pCi/mL). Summary results for tritium measured in the sanitary sewer effluent from LLNL and LWRP are presented in **Table 6-3**.

Table 6-2. Estimated total radioactivity in LLNL sanitary sewer effluent, 2002

Radioactive emitter	Estimate based on effluent activity (GBq)[a]	Limit of sensitivity (GBq)
Tritium	0.74	0.84
Gross alpha sources	0.005	0.049
Gross beta sources	0.15	0.067

a 37 GBq = 3.7×10^{10} Bq = 1 Ci

Summary statistics for tritium measured in the sanitary sewer effluent from LLNL and LWRP are presented in **Table 6-3**.

The monthly tritium concentrations are based on the flow-weighted average of the monthly sample results for a given month. The total monthly activity is based on the multiplication of each monthly concentration by the total flow volume over which the sample was collected. The total annual activity is the sum of the monthly activities. (All total annual results presented in this chapter for radioactive emitters are calculated by using the analysis results regardless of whether they were above or below the detection limit.)

The historical trend in the monthly concentration of tritium is shown in **Figure 6-2** (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), which are discussed in the "Environmental Impact" section. Note that in 2002 the LOS values are approimately 4 times lower than previous years due to an improved analytical technique. The trend indicates a well-controlled tritium discharge, orders of magnitude below the DOE tritium limit.

The concentrations of plutonium-239 and cesium-137 measured in the sanitary sewer effluent from LLNL and LWRP are presented in **Table 6-4**. The plutonium and cesium numbers are the direct results of analyses of monthly composite samples of LLNL and LWRP effluent, and quarterly composites of LWRP sludge. At the bottom of the table, the total annual activity released is given by radioisotope.

Figure 6-3 shows the average monthly plutonium and cesium concentrations in sewage since 1993. For 2002, the annual mean concentration of cesium-137 was 8.5×10^{-7} Bq/mL (2.3×10^{-5} pCi/mL); the annual mean concentration of plutonium-239 was 1.3×10^{-7} Bq/mL (3.5×10^{-6} pCi/mL).

Environmental Impact

During 2002, no inadvertent discharges exceeded any discharge limits for release of radioactive materials to the sanitary sewer system.

Table 6-3. Summary statistics of tritium in sanitary sewer effluents, LLNL and LWRP, 2002

Monitoring results			
	LLNL		LWRP
	Daily	Monthly	Monthly
Maximum (Bq/mL)	0.069 ± 0.008[a]	0.010[b]	0.0017[c]
Median (Bq/mL)	0.0009	0.002	0.0004
IQR[d] (Bq/mL)	0.004	0.001	0.001
LLNL annual total (GBq)	0.74		
Discharge limits for LLNL effluent			
	Discharge limit	**Monitoring results as percentage of limit**	
		Maximum	**Median**
LWRP permit daily (Bq/mL)	12	0.58%	0.008%
DOE 5400.5 monthly (DCG)[e] (Bq/mL)	370	0.003%[f]	0.0005%[f]
10 CFR 20 annual total (GBq)	185	0.4%	

a This daily result is for a December sample. See the Data Supplement, Chapter 6, for all daily results.

b This is the monthly value is for December. All monthly values above limit of sensitivity (LOS) are plotted in **Figure 6-2.**

c This is a monthly result for a December sample. The result was not above the detection limit for the analysis. None of the LWRP monthly monitoring results were greater than the detection limits for the analyses; a detection limit is the smallest concentration of radioactive material that can be detected with a large degree of confidence. (See Chapter 14.) See the Data Supplement, Chapter 6, for all monthly results.

d IQR = Interquartile range

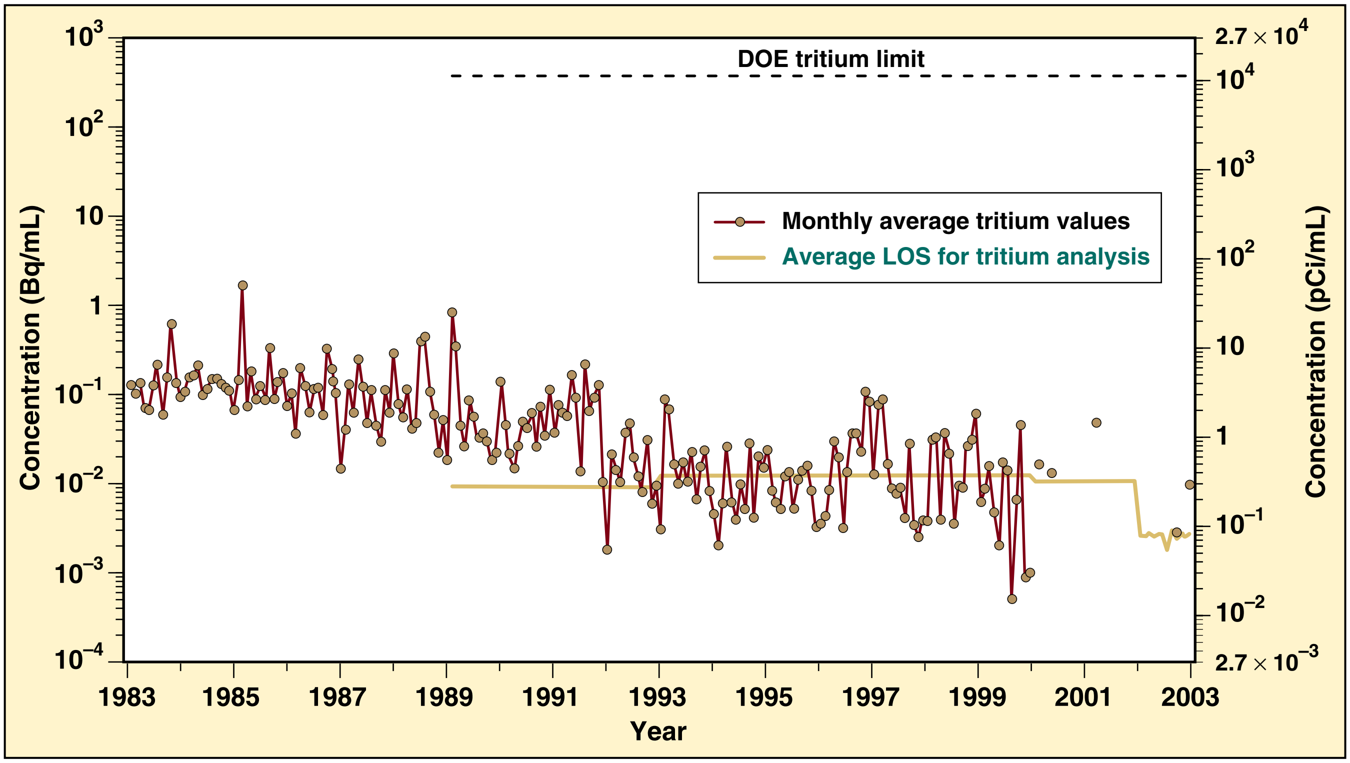
e DCG = Derived Concentration Guide

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

In 1999, the Work Smart Standards (WSS) developed for LLNL became effective. Included in the WSS are the standards selected for sanitary sewer discharges. For radioactive material releases, complementary (rather than overlapping) sections from 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. **Table 6-3** and **Table 6-4** include the DCGs for the specific radioisotopes with potential to be in the sanitary sewer effluent at LLNL.

The median monthly concentration of tritium in LLNL sanitary sewer effluent was 0.0005% of the DOE DCG, and the maximum monthly average concentration of tritium was 0.003% of the DCG (see **Table 6-3**).



Note: Only values above the LOS are plotted for 2000–2002.

Figure 6-2. Historical trend in tritium concentration in LLNL sanitary sewer effluent

The annual total discharge of cesium-137 was 0.0023% of the DOE DCG; and the annual average plutonium-239 concentration was 0.00034% of the DOE DCG. These results are shown at the bottom of Table 6-4.

From 10 CFR 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 20 limit on total tritium activity dischargeable during a single year (185 GBq) overrides the DOE Order 5400.5 concentration-based limit for tritium for facilities such as LLNL that generate wastewater in large volumes. In 2002, the total LLNL tritium release was 0.4% of the 10 CFR 20 limit. Total LLNL releases (see Table 6-2), in the form of alpha and beta emitters (excluding tritium), were 0.083% of the corresponding 10 CFR 20 limit.

In addition to the DOE average concentration discharge limit for tritium and the 10 CFR 20 annual total discharge limit for tritium, the LWRP established in 1999 an effluent concentration discharge limit for LLNL 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 maximum daily concentration for

Table 6-4. Cesium and plutonium in sanitary sewer effluents, LLNL and LWRP, 2002

Month	Cesium-137 (µBq/mL)				Plutonium-239 (nBq/mL)			
	LLNL		LWRP		LLNL		LWRP	
	Radio–activity	MDC	Radio-activity	MDC	Radio-activity	MDC	Radio-activity	MDC
Jan	0.253 ± 3.92	3.46	0.655 ± 3.47	3.1	173 ± 26.4	5.99	0.607 ± 2.72	5.4
Feb	5.07 ± 4.29	4.03	0.488 ± 3.81	3.39	126 ± 21.9	2.98	–1.1 ± 2.67	6.99
Mar	–1.57 ± 4.14	3.57	0.000603 ± 3.44	3.05	82.1 ± 19.9	7.77	–1.11 ± 1.28	5.48
Apr	1.95 ± 3.74	3.39	2.86 ± 3.74	3.45	74 ± 19.4	4.07	–0.881 ± 3.24	8.44
May	0.138 ± 3.81	3.37	2.31 ± 4.11	2.54	156 ± 26.1	6.51	0.223 ± 2.58	5.33
Jun	0.463 ± 4.11	3.67	0.169 ± 3.2	2.84	40.7 ± 15.4	8.07	1.67 ± 3.17	5
Jul	2.83 ± 4.03	2.15	1.3 ± 4.03	3.64	365 ± 43.7	8.7	1.08 ± 3.23	5.88
Aug	2.64 ± 6.99	3.01	3.05 ± 3.52	3.28	114 ± 20.7	2.96	1.68 ± 2.88	4.55
Sep	–0.574 ± 4.14	3.62	–2.57 ± 3.43	2.84	88.1 ± 19.2	3.33	1.2 ± 2.26	3.89
Oct	1.59 ± 3.81	3.46	2.16 ± 3.34	3.07	181 ± 30.4	3.96	2.57 ± 4	5.74
Nov	–0.433 ± 3.6	3.16	0.895 ± 3.16	2.85	42.2 ± 15.8	7.22	5.22 ± 4.59	4.88
Dec	–2.11 ± 3.62	3.05	–1.14 ± 3.44	2.96	67.7 ± 15.8	6.88	0.685 ± 2.61	5.85
Median	0.36		0.78		101		0.88	
IQR[a]	2.76		2.11		68.6		1.73	
	pCi/mL[b]							
Median	9.7×10^{-6}		2.1×10^{-5}		2.7×10^{-6}		2.4×10^{-8}	
IQR[a]	7.5×10^{-5}		5.7×10^{-5}		1.9×10^{-6}		4.7×10^{-8}	
	Annual LLNL total discharges by radioisotope							
	Cesium-137				Plutonium-239			
Bq/y	2.8×10^{6}				4.2×10^{5}			
Ci/y	1.0×10^{-7}				1.5×10^{-8}			
	Fraction of limit[c]							
DOE 5400.5 DCG[d]	2.3×10^{-5}				3.4×10^{-6}			

Table 6-4. Cesium and plutonium in sanitary sewer effluents, LLNL, and LWRP, 2002 (continued)

Month	Cesium-137 (mBq/dry g)		Plutonium-239 (mBq/dry g)	
	LWRP Sludge[e]			
	Radioactivity	MDC	Radioactivity	MDC
Mar	–0.286 ± 1.18	1.02	0.227 ± 0.0297	0.00529
Jun	0.659 ± 0.759	1.02	0.11 ± 0.0173	0.00562
Sep	0 ± 0	0.955	0.215 ± 0.0231	0.00426
Dec	0.466 ± 1.08	0.662	1.85 ± 0.125	0.00781
Median	0.23		0.22	
IQR[a]	0.59		0.44	
	pCi/mL[b]			
Median	6.3×10^{-3}		6.0×10^{-3}	
IQR[a]	1.6×10^{-2}		1.2×10^{-2}	

Note: Results in this table are reported as radioactivity (the measured concentration and a $\pm 2\sigma$ counting uncertainty) along with the detection limit or minimum detectable concentration (MDC). A measure concentration exhibiting a 2σ counting uncertainty greater than or equal to 100% is considered to be a nondetection. See Chapter 14.

a IQR= Interquartile range

b 1 Ci = 3.7×10^{10} Bq

c 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.

d DCG = Derived Concentration Guide

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

tritium in 2002 was 0.58% of the permit discharge limit. **Table 6-3** shows this result and the daily effluent discharge limit for tritium. The 2002 values are lower than the 2001 values.

LLNL also compares annual discharges with historical values to evaluate the effectiveness of ongoing discharge control programs. **Table 6-5** summarizes the radioactivity in liquid effluent released over the past 10 years. During 2002, a total of 0.74 GBq (0.03 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 over the past 10 years.

Figure 6-3 summarizes the plutonium-239 monitoring data over the past 10 years. The historical levels observed since 1993 average approximately 1 µBq/mL (3×10^{-5} pCi/mL). These historical levels generally are three-millionths (0.000003) of the DOE DCG for plutonium-239. The greatest part of the plutonium discharged in LLNL effluent is ultimately concentrated in LWRP sludge. The median plutonium concentration observed in 2002 sludge (**Table 6-4**), 0.22 mBq/dry g, is approximately 420 times lower than the EPA

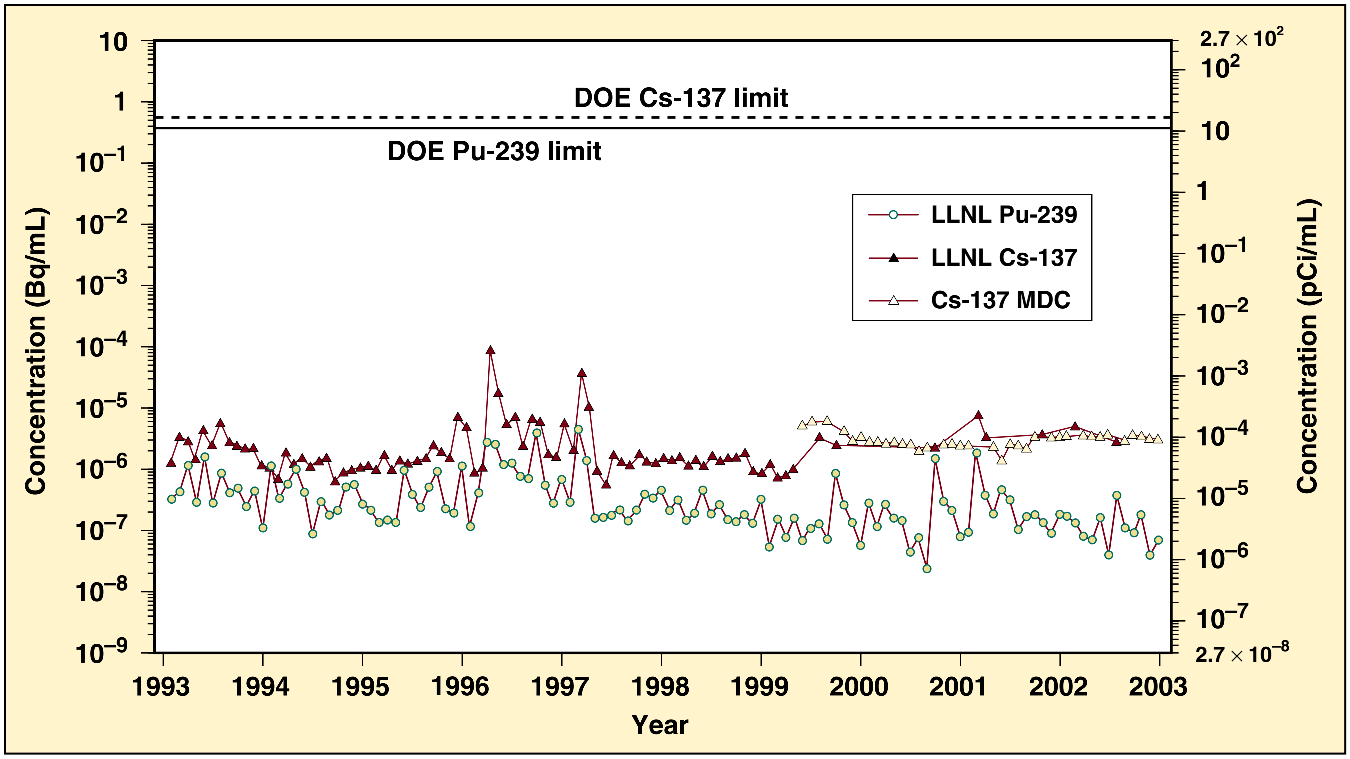


Figure 6-3. Historical trends in average monthly plutonium and cesium concentrations in LLNL sanitary sewer effluent

preliminary remediation goal for residential soil (93 mBq/dry g) and is nearly 1700 times lower than the remediation goal for industrial or commercial soil (370 mBq/dry g).

As first discussed in the *Environmental Report 1991* (Gallegos et al. 1992), plutonium and cesium concentrations were slightly elevated during 1991 and 1992 over the lowest values seen historically. As was established in 1991, the overall upward trend was related to sewer cleaning with new, more-effective equipment. The concentrations in 1996 and the first quarter of 1997 were also slightly higher than the lowest values seen historically, although slightly lower than those of 1990 through 1992. In fact, the cyclic nature of the data in **Figure 6-3** suggests a potential frequency relationship in LLNL sewer lines for radionuclide buildup and subsequent liberation by line cleaning. The higher plutonium and cesium concentrations are all well below applicable DOE DCGs. In general, the plutonium and cesium concentrations for 2002 are comparable to the lowest values seen historically, and are well below the applicable DOE DCGs. (Note that because minimum detectable concentration [MDC] values for cesium analysis increased in May 1999, most analytical results are below their respective MDCs; see **Table 6-4**.)

Nonradioactive Pollutants in Sewage

Monitoring Results

Table 6-6 presents monthly average concentrations for all regulated metals in LLNL's sanitary sewer effluent for 2002. The averages were

Table 6-5. Radioactive liquid effluent releases from the Livermore site, 1993–2002

Year	Liquid effluent (GBq)	
	Tritium	Plutonium-239
1993	13	2.6×10^{-4}
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	7.7×10^{-5}
1999	7.1	6.8×10^{-5}
2000	5.0	9.6×10^{-5}
2001	4.9	1.1×10^{-4}
2002	0.74	4.2×10^{-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.

obtained by a flow-proportional weighting of the analytical results for the weekly composite samples collected each month. Each result was weighted by the total flow volume for the period during which the sample was collected. The results for 2002 are generally typical of the values seen from 1994 to 2001, and median concentrations for the nine regulated metals remained at or near their respective values reported last year.

Figure 6-4 presents historical trends for the monthly 24-hour composite sample results from 1994 through 2002 for eight of the nine regulated metals; cadmium is not presented because this metal is typically not detected. All of the monthly 24-hour composite samples were in compliance with the permit discharge limits for the SMS (**Table 6-1**). As noted in both 2000 and 2001, arsenic continues to show an occasional elevated concentration, although it never exceeds 20% of the effluent pollutant limit (EPL). Both silver and lead each exhibit a single elevated monthly concentration during calendar year 2002; but neither exceed 50% of their respective EPLs. The other metals have no discernible trends in their concentrations.

The concentrations measured in the routine analysis of LLNL's 2002 sewage samples, collected once a week (seven-day composite sample) and once a month (24-hour composite sample), are presented in **Figure 6-5** 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 (PQL) of 0.005 mg/L in any of the weekly or monthly samples. The EPL is equal to the maximum pollutant concentration allowed per 24-hour composite sample, as specified by the LLNL wastewater discharge permit. When a weekly sample concentration is at or above 50% of its EPL, all daily (24-hour composite) samples collected in the SMS corresponding to the weekly sample period must be analyzed to determine if any of their concentrations are above the EPL. The two elevated monthly concentrations discussed above, silver at 50% of its EPL in April and lead at 30% of its EPL in August, are shown in **Figure 6-5**. In addition, a total of five weekly concentrations values (**Figure 6-5**) are at or above 50% of their respective EPLs.

The elevated arsenic values, reported at 67% of the EPL for the weeks of June 5–12 and June 12–17, can be attributed to an analytical artifact resulting from matrix interference. As shown in Data Supplement Table 6-5, the actual arsenic concentrations for these two weeks were reported as <0.04 mg/L, a factor of twenty greater than the typical PQL for arsenic of 0.002 mg/L. The three remaining weekly sample concentration values (one chromium and two lead) at or above the specified action level, shown in **Figure 6-5**, are discussed further in the "Environmental Impact" section.

Table 6-6. Monthly average results for regulated metals in LLNL sanitary sewer effluent (mg/L), 2002

Month	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Jan	<0.010	0.0029	<0.0050	0.015	0.14	0.00045	0.0057	0.016	0.39
Feb	0.017	0.0042	<0.0050	0.019	0.13	0.00041	0.0063	0.014	0.29
Mar	0.011	0.0022	<0.0050	0.011	0.12	0.00025	0.0051	0.012	0.27
Apr	0.011	0.0027	<0.0050	0.012	0.15	0.00033	<0.0050	0.013	0.30
May	0.012	0.0030	<0.0050	0.016	0.15	0.00027	0.0051	0.024	0.28
Jun	<0.010	0.021	<0.0050	0.020	0.22	<0.00028	0.0058	0.026	0.39
Jul	<0.010	0.0076	<0.0050	0.040	0.24	0.00026	0.0084	0.026	0.41
Aug	0.014	0.0082	<0.0050	0.11	0.24	0.00034	0.0085	0.045	0.42
Sep	0.013	0.0058	<0.0050	0.021	0.20	0.00042	0.0083	0.020	0.38
Oct	0.022	0.0040	<0.0050	0.021	0.19	0.00060	0.0095	0.033	0.38
Nov	0.019	0.0034	<0.0050	0.017	0.18	0.00036	0.0079	0.062	0.42
Dec	0.011	0.0035	<0.0050	0.015	0.11	0.00034	0.0077	0.015	0.34
Median	0.012	0.0038	<0.0050	0.018	0.17	0.00034	0.0070	0.022	0.38
IQR[(a)]	0.0039	0.0033	—[(b)]	0.0058	0.063	0.00013	0.0027	0.013	0.10
EPL[(c)]	0.20	0.06	0.14	0.62	1.0	0.01	0.61	0.20	3.00
Median fraction of EPL	0.06	0.06	<0.04	0.03	0.17	0.03	0.01	0.11	0.13

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 for cadmium. See Chapter 14.

c Effluent pollutant limit (LLNL Wastewater Discharge Permit 2001–2002 and 2002–2003)

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 6-7**. (All analytical results are provided in the Data Supplement, Table 6-7.) Although monthly (24-hour) composite samples were analyzed for hydroxide alkalinity (as $CaCO_3$), beryllium, and cadmium, these analytes were not detected in any sample acquired during 2002, and so are not presented in **Table 6-7**. Similarly, analytes not detected in any of the 2002 monthly grab samples are not shown in **Table 6-7**. These monthly monitoring results for physical and chemical characteristics of the LLNL sanitary sewer effluent are typical of those seen in previous years. See the "Environmental Impact" section for further discussion.

Environmental Impact

Table 6-6 presents monthly average concentrations and summary statistics for all regulated metals monitored in LLNL's sanitary sewer effluent. At the bottom of the table, the 2002 median concentration for each metal is shown and compared with the discharge limit. In 2002, the monthly average median concentration values remained essentially unchanged from the corresponding 2001 values for all nine regulated metals. These results are

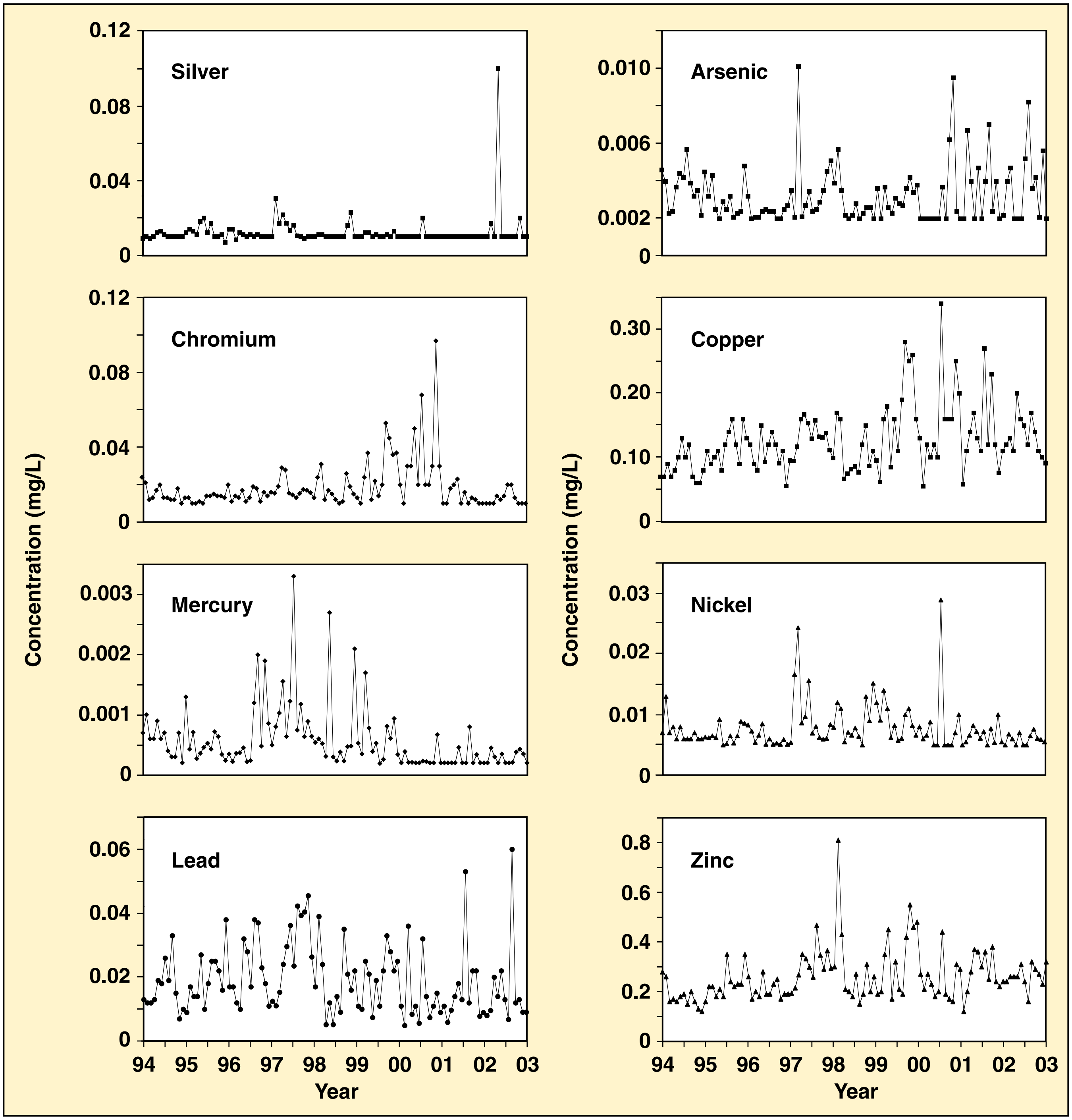


Figure 6-4. Monthly 24-hour composite sample concentrations for eight of the nine regulated metals in LLNL sanitary sewer effluent showing trends from 1994 through 2002

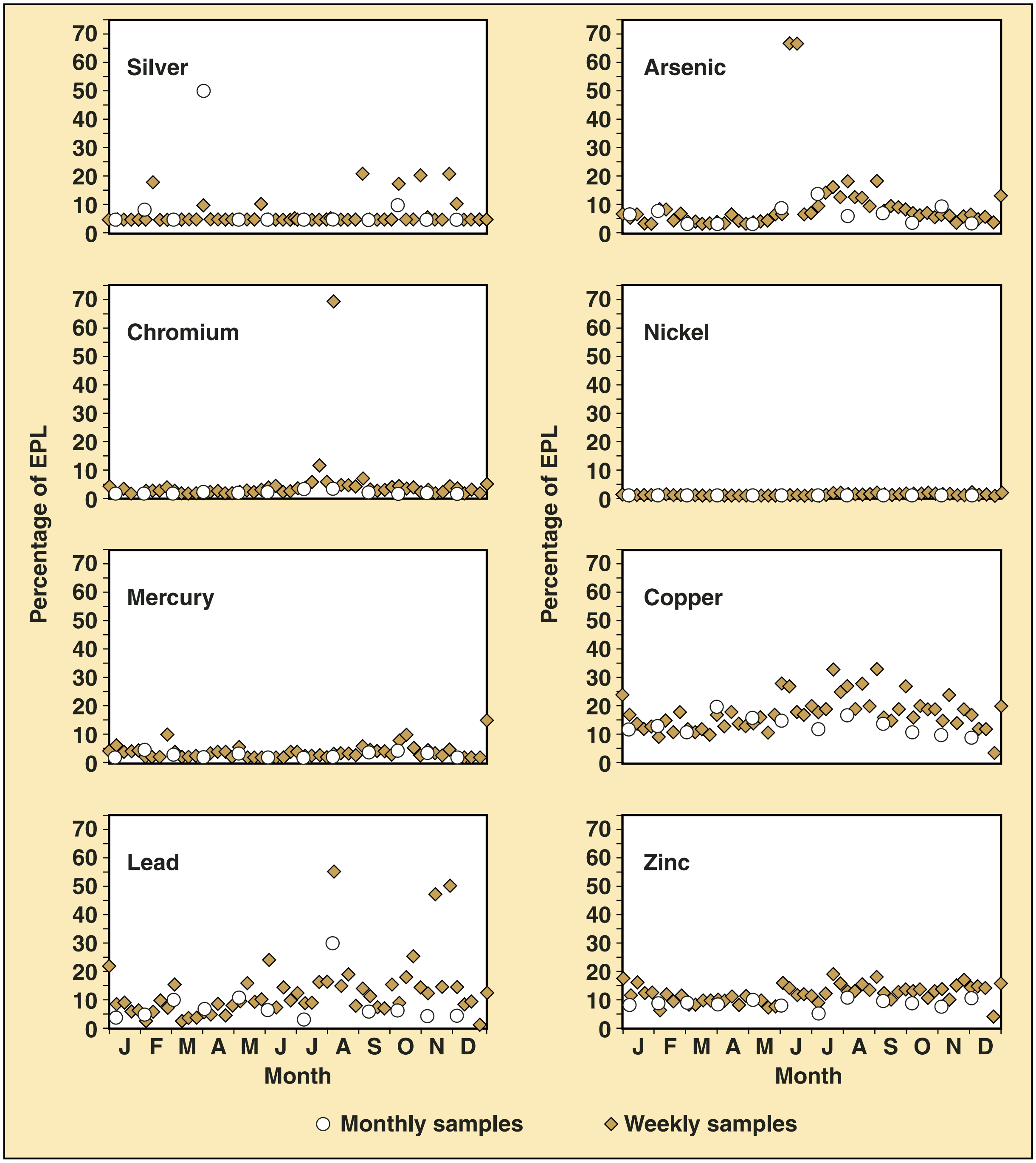


Figure 6-5. Results as percentages of effluent pollutant limits (EPLs) for eight of the nine regulated metals in LLNL sewage, 2002

Table 6-7. Monthly monitoring results for physical and chemical characteristics of the LLNL sanitary sewer effluent, 2002[(a)]

Parameter	Detection frequency[(b)]	Minimum	Maximum	Median	IQR[(c)]
24-hour composite sample parameter (mg/L)					
Alkalinity (mg/L)					
Bicarbonate alkalinity (as $CaCO_3$)	12 of 12	175	300	250	24.0
Carbonate alkalinity (as $CaCO_3$)	2 of 12	<5	55.0	<5	—[(d)]
Total alkalinity (as $CaCO_3$)	12 of 12	230	300	250	22.5
Anions (mg/L)					
Bromide	10 of 12	<0.1	1.1	0.25	—[(d)]
Chloride	12 of 12	41	114	61	28
Fluoride	10 of 12	<0.05	2.3	0.11	0.16
Nitrate (as N)	1 of 12	<0.1	<1	<0.44	—[(d)]
Nitrate (as NO_3)	1 of 12	<0.4	<4.4	<4.4	—[(d)]
Nitrate plus Nitrite (as N)	2 of 12	<0.1	<1	<1	—[(d)]
Nitrite (as N)	8 of 12	<0.02	0.33	0.19	—[(d)]
Nitrite (as NO_2)	8 of 12	<0.065	1.1	0.63	—[(d)]
Orthophosphate	12 of 12	15	23	20	4.3
Sulfate	12 of 12	12	19	15	2.3
Nutrients (mg/L)					
Ammonia nitrogen (as N)	12 of 12	43	56	47	5.0
Total Kjeldahl nitrogen	12 of 12	49	95	60	11
Total phosphorus (as P)	12 of 12	6.8	14	9.8	2.6
Oxygen demand (mg/L)					
Biochemical oxygen demand	12 of 12	163	473	315	107
Chemical oxygen demand	12 of 12	257	776	565	121
Solids (mg/L)					
Settleable solids	12 of 12	14.0	50.0	28.5	11.3
Total dissolved solids (TDS)	12 of 12	236	540	273	78.5
Total suspended solids (TSS)	12 of 12	190	660	330	138
Volatile solids	12 of 12	210	477	350	142
Total metals (mg/L)					
Aluminum	12 of 12	0.30	0.80	0.49	0.16
Calcium	12 of 12	15	27	18	2.3
Iron	12 of 12	1.0	2.5	1.6	0.30
Magnesium	12 of 12	2.5	3.0	2.8	0.15
Potassium	12 of 12	19	26	22	2.0
Selenium	2 of 12	<0.002	<0.02	<0.002	—[(d)]
Sodium	12 of 12	35	87	47	15
Total organic carbon (TOC)	12 of 12	39	56	53	6.3
Tributyltin[(e)]	1 of 2	<6	10	—[(f)]	—[(d)]

Table 6-7. Monthly monitoring results for physical and chemical characteristics of the LLNL sanitary sewer effluent, 2002[(a)] (continued)

Parameter	Detection frequency[(b)]	Minimum	Maximum	Median	IQR[(c)]
Grab sample parameter					
Semivolatile organic compounds (μg/L)					
Benzoic acid	10 of 12	<10	110	21	39
Benzyl alcohol	10 of 12	<2	1900	12	49
Bis(2-ethylhexyl)phthalate[(g)]	10 of 12	<5	32	8.1	4.7
Butylbenzylphthalate[(g)]	2 of 12	<2	9.4	<2	—[(d)]
Dibutylphthalate[(g)]	3 of 12	<2	16	<2	—[(d)]
Diethylphthalate[(g)]	12 of 12	6.2	35	21	15
Phenanthrene[(g)]	1 of 12	<2	2.3	<2	—[(d)]
Phenol[(g)]	7 of 12	<2	29	2.8	—[(d)]
m- and p-Cresol	11 of 12	<2	450	19	26
Total cyanide[(h)]	1 of 3	<0.02	0.024	—[(f)]	—[(d)]
Total oil and grease (mg/L)[(i)]	8 of 8	12	37	28	17
Volatile organic compounds (μg/L)					
1,1,2-Trichloroethane[(g)]	1 of 12	<0.5	0.58	<0.5	—[(d)]
1,4-Dichlorobenzene[(g)]	1 of 12	<0.5	0.67	<0.5	—[(d)]
2-Butanone	1 of 12	<20	52	<20	—[(d)]
Acetone	12 of 12	140	560	310	190
Bromoform[(g)]	1 of 12	<0.5	0.87	<0.5	—[(d)]
Chloroform[(g]	12 of 12	5.7	17	11	3.9
Freon 113	1 of 12	<0.5	0.61	<0.5	—[(d)]
Methylene chloride[(g)]	3 of 12	<1	3.5	<1	—[(d)]
Styrene	1 of 12	<0.5	0.59	<0.5	—[(d)]
Toluene[(g)]	2 of 12	<0.5	0.67	<0.5	—[(d)]

a The monthly sample results plotted in **Figure 6-5** and nondetected values reported in the Data Supplement, Chapter 6, are not reported 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%, there is no range, or there are fewer than four results for a sample parameter, the interquartile range is omitted.

e Sampling for this parameter is required on a semiannual rather than a monthly basis.

f When there are fewer than four results for a sample parameter, the median is not calculated.

g Priority toxic pollutant parameter used in assessing compliance with the total toxic organic (TTO) permit limit of 1 mg/L (1000 μg/L) issued by the Livermore Water Reclamation Plant.

h Sampling for this parameter is required on a semiannual (January and July) rather than a monthly basis. An additional sample was taken in October during the annual co-sampling event with the LWRP.

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

consistent with the weekly composite median values shown in Data Supplement Table 6-5. Medians of the monthly average concentrations were less than 10% of the discharge limits for all but copper, lead, and zinc, which were at 17%, 11%, and 13%, respectively.

Although median values of monthly average metal concentrations have remained well below discharge limits (see **Table 6-6**), and only one monthly (24-hour) composite sample showed any regulated metal above one-third of the respective EPL (silver was detected in the April monthly composite at 0.10 mg/L; 50% of its EPL), three weekly metal sample concentrations were identified for additional analyses based on 7-day composite results at or near the action limit (see **Figure 6-5**). (As discussed above, the two elevated weekly arsenic values can be attributed to an analytical artifact.) Action limit investigations examined a weekly sample in August (for chromium and lead at 69% and 55% of their respective EPLs) and a weekly sample in November (for lead at 50% of its EPL). The daily samples that correspond to the appropriate 7-day composite sampling periods were submitted to an off-site contract analytical laboratory for analysis.

Lead concentrations in daily samples from the week of August 1–7 show two samples (August 3 at 0.226 mg/L and August 6 at 0.208 mg/L, representing effluent collected during the prior 24-hour periods) exceeding the 0.2 mg/L permitted discharge limit for lead. In October 2002, the LWRP issued a Warning Notice as a result of these exceedances of the EPL for lead. No corrective action was suggested or required, because LLNL had demonstrated a return to compliance and sufficient measures had been taken to investigate this inadvertent discharge. The results of similar analyses showed no chromium concentrations in the August 1–7 daily samples, or lead concentrations in the November 21–27 daily samples above their respective EPLs. Although each of these incidents was reported to the LWRP, none represented a threat to the integrity of the LWRP operations.

Table 6-7 presents summary results and statistics for monthly monitoring of physical and chemical characteristics of LLNL's sanitary sewer effluent. The results are generally similar to typical values seen in previous years for the two regulated parameters (cyanide and total toxic organics [TTO]) and all other nonregulated parameters. Cyanide was detected only in the January 2002 semiannual sample (at 0.024 mg/L, which is below the 0.04 mg/L permit limit). This constituent was below analytical detection limits (0.02 mg/L) in both the second semiannual (July 2002) sampling and the annual (October 2002) joint LLNL/LWRP co-sampling events. The monthly TTO values ranged from less than 0.010 mg/L to 0.10 mg/L (median was 0.039 mg/L), well below the TTO permit limit of 1.0 mg/L. In addition to the organic compounds regulated under the TTO standard, seven nonregulated organics were also detected in LLNL's sanitary sewer effluent: four volatile organic compounds (2-butanone, acetone, Freon 113, and styrene) and three semivolatile organic compounds (benzoic acid, benzyl alcohol, and 3-& 4-methylphenol).

In 2002, the SMS continuous monitoring system detected a total of six inadvertent discharges outside the permitted pH range of 5 to 10. Four of these events, one with a pH below 5 and three with a pH above 10, were completely captured by the SDF. The other two events, both with a pH below 5, occurred off-hours when the upstream pHMS was off-line. As a result, two front-end volumes (small quantity) of low pH sanitary effluent were released to the LWRP system before a diversion to the SDF could be made. The LWRP was immediately notified of both low pH discharges; however, neither incident represented a threat to the integrity of the operations of the LWRP nor were these events considered enforceable exceedances of permit conditions. The lowest pH recorded for effluent contained in the first release, February 9, 2002, was 4.6; the second release, October 13, 2002, contained effluent with a pH as low as 4.96.

Monitoring results for 2002 reflect a very effective year for LLNL's sewerable water discharge control program and indicate no adverse impact to the LWRP or the environment from LLNL sanitary sewer discharges. Overall, LLNL achieved greater than 99% compliance with the provisions of its wastewater discharge permit.