Environmental Monitoring Plan

Operations and Regulatory Affairs Division

Environmental Protection Department

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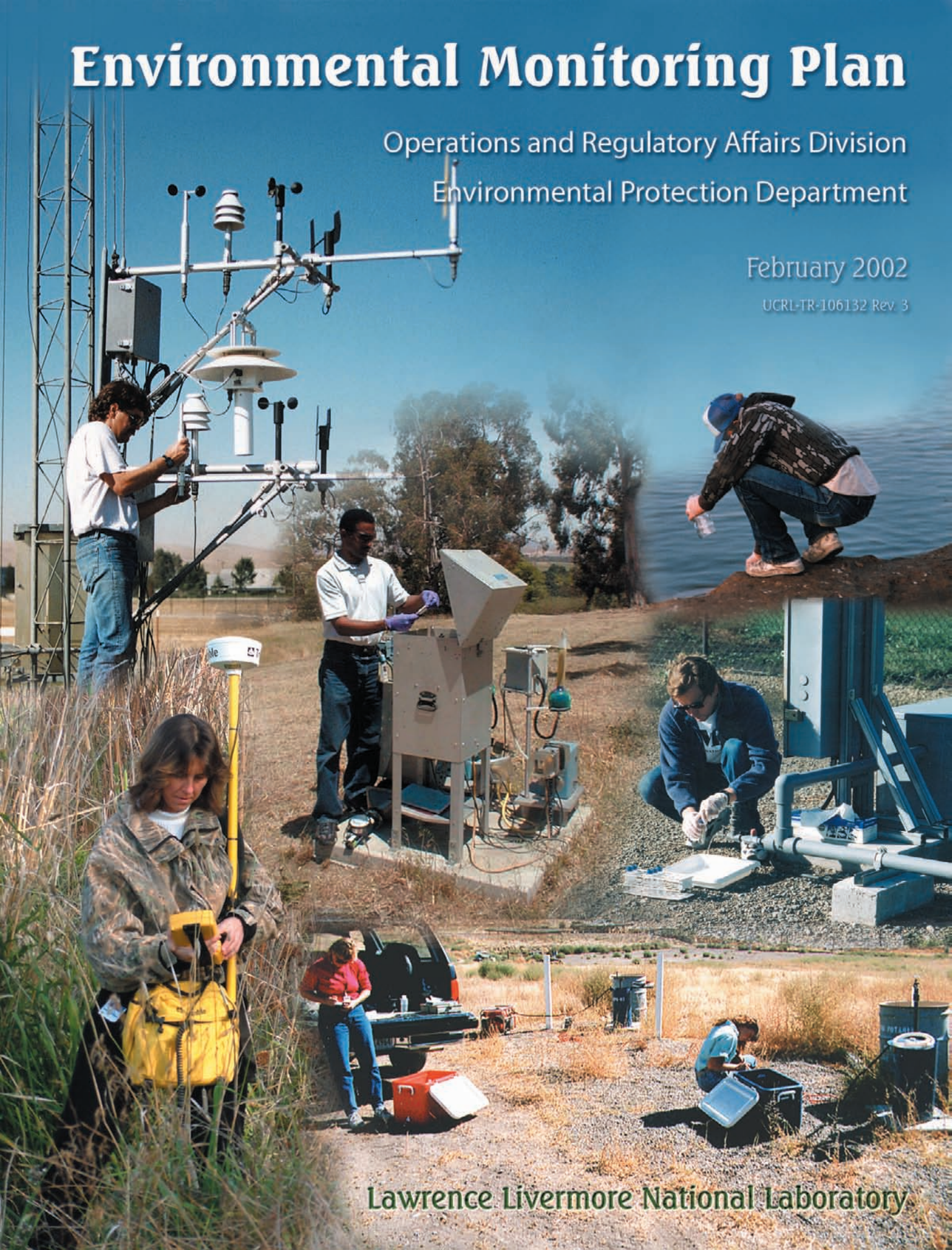

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1 Introduction

Willam G. Hoppes

1.1 Purpose of the E*nvironmental Monitoring Plan*

Environmental monitoring personnel from Lawrence Livermore National Laboratory (LLNL) prepared this *Environmental Monitoring Plan* (EMP) to meet the requirements in the U.S. Department of Energy (DOE) *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (DOE 1991) and applicable portions of DOE Orders 5400.1 and 5400.5 (see WSS B93 and B94 in Appendix B). *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* is followed as a best management practice; under Work Smart Standards, LLNL complies with portions of DOE Orders 5400.1 and 5400.5 as shown in Appendix B. This document is a revision of the May 1999 EMP (Tate et al. 1999) and is current as of March 1, 2002.

1.2 Mission of the Laboratory

LLNL is one of the nation's premier applied-science national security laboratories. Its primary mission is to ensure that the nation's nuclear weapons remain safe, secure, and reliable, and to prevent the spread and use of nuclear weapons worldwide. LLNL's programs in advanced technologies, energy, environment, biosciences, and basic science apply LLNL's unique capabilities and enhance the competencies needed for this national security mission. LLNL's mission also involves working with industrial and academic partners to increase national competitiveness and improve science education. LLNL's mission is dynamic and has changed over the years to meet new national needs.

In keeping with the Laboratory's mission, the environment, safety, and health (ES&H) have top priority. LLNL's policy is to perform work in a manner that protects the health and safety of employees and the public, preserves the quality of the environment, and prevents property damage. The environment, safety, and health are to be priority considerations in the planning and execution of all work activities at the Laboratory (LLNL 2001). Furthermore, it is the policy of LLNL to comply with applicable ES&H laws, regulations, and requirements. Under Contract 48, Appendix F, the Laboratory commits to minimizing its waste streams and to avoiding adverse impacts to the environment from its operations (UC/DOE 2001).

1.3 Organizational Responsibilities

All LLNL staff have responsibilities that include environmental protection and environmental compliance. The level of responsibility is dependent upon the position held by the individual. Document 2.1 of the *Environment, Safety, and Health Manual* (LLNL 2001), lists these responsibilities for all levels of staff; however, the Laboratory has designated the Environmental Protection Department (EPD) as the lead organization with responsibility for helping the Laboratory to ensure that operations do not adversely affect the environment or public health.

1.3.1 Environmental Protection Department

To carry out its responsibilities for environmental support at the Laboratory, EPD performs environmental monitoring, regulatory compliance activities, environmental restoration, and hazardous waste management. EPD's specific mission is to:

- Assist LLNL programs to develop environmentally sound practices in their day-to-day tasks. EPD provides assistance through support activities such as:
  - Conducting environmental evaluations and addressing requirements under federal, state, and local laws and regulations
  - Identifying and developing methods to monitor, prevent, reduce, and clean up air emissions, wastewater discharges, and hazardous wastes
  - Obtaining permits or exemptions for air, water, and hazardous waste activities.
- Ensure environmental compliance through environmental monitoring, risk assessment, and analysis of LLNL activities. Specifically, EPD evaluates the impact of ongoing LLNL operations on the surrounding environment by sample collection, analysis, data reduction, and simulation modeling.
- Develop and conduct cost-effective environmental restoration and remediation.
- Design and apply appropriate, cost-effective treatment technologies to manage hazardous and nonhazardous waste streams.
- Develop and implement waste minimization and pollution abatement strategies.
- Coordinate Laboratory-wide decontamination and decommissioning activities.

LLNL programs are supported by EPD's five Environmental Support Teams (ESTs). Each EST includes representatives from environmental specialties within the Department. These teams evaluate operations, determine potential environmental impacts, and provide guidance on environmental regulations and DOE orders for existing and proposed projects. ESTs assist programs in planning, implementing, and operating projects and in understanding and meeting

their environmental obligations. When permits are obtained from regulatory agencies, ESTs aid the program in evaluating the permit conditions and implementing recordkeeping requirements.

With respect to environmental monitoring, EPD performs all environmental surveillance monitoring; Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)-related monitoring; and liquid effluent monitoring. EPD also oversees and reports on all air effluent monitoring.

Environmental monitoring is important in an overall environmental protection program. The monitoring of effluents and environmental media provides an understanding of the impact of LLNL's activities on its surroundings and confirms whether pollution prevention activities are effective. EPD's environmental monitoring and environmental occurrences information and data are collected, evaluated, reported, and maintained in accordance with established procedures and protocols.

EPD is composed of three divisions.

- Radioactive and Hazardous Waste Management (RHWM) Division
- Environmental Restoration Division (ERD)
- Operations and Regulatory Affairs Division (ORAD)

Figure 1-1 identifies the organizational structure of EPD.

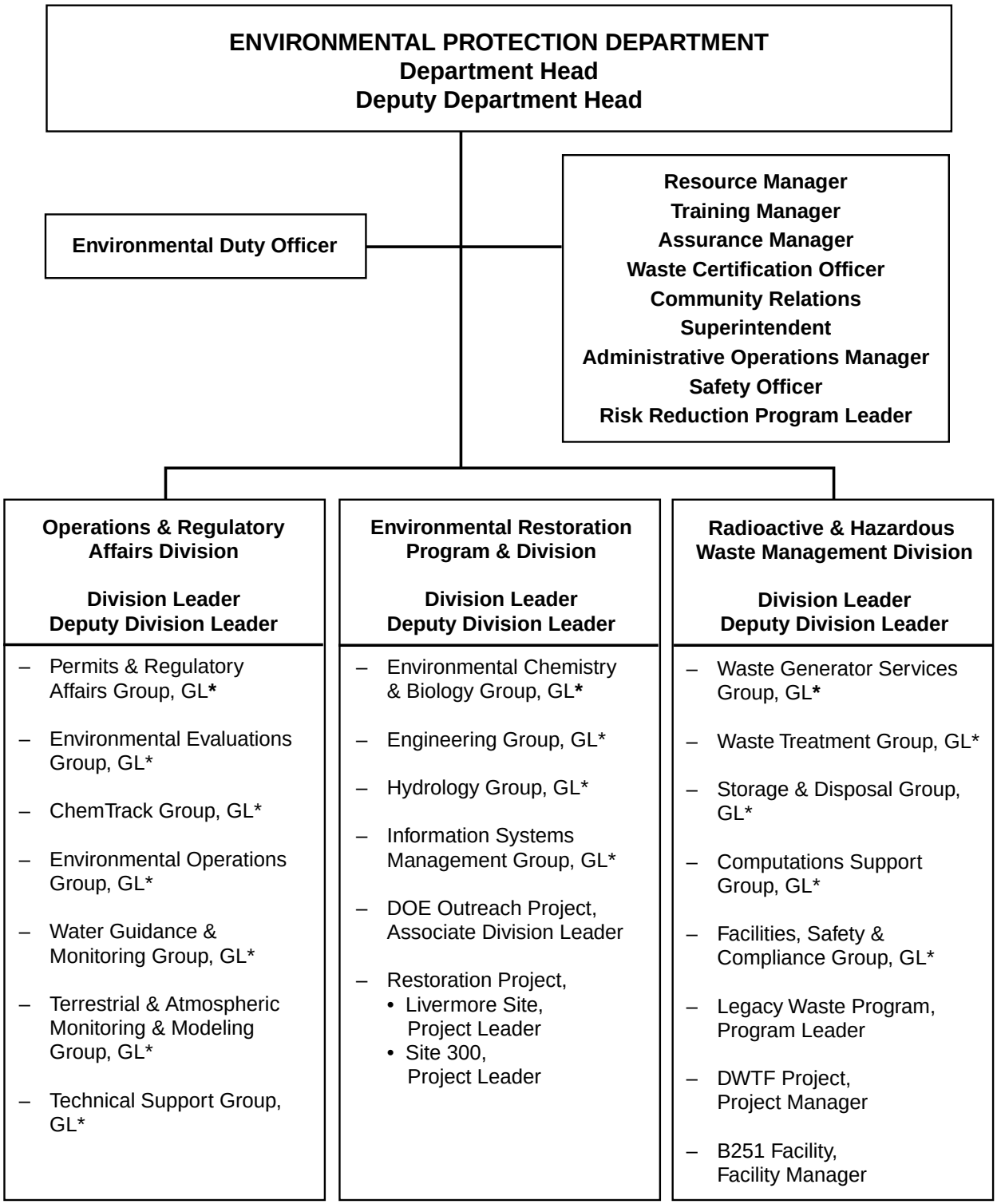
1.3.1.1 Radioactive and Hazardous Waste Management Division (RHWM)

Even with rigorous waste minimization efforts, LLNL cannot entirely avoid the production of some hazardous waste and must deal with "legacy waste" from past activities. The RHWM Division implements the technologies necessary to manage all hazardous, radioactive, and mixed wastes generated at LLNL facilities. This responsibility includes the design and acquisition of new facilities as well as the investigation of new and more cost-effective methodologies for hazardous waste handling, stabilization, treatment, certification, and disposal.

To carry out its responsibilities, RHWM Division:

- Tracks and documents hazardous, radioactive, and mixed wastes for LLNL facilities
- Processes, stores, packages, treats, and prepares waste for shipment to licensed off-site treatment, storage, and recycling facilities

- Ensures that LLNL meets local, state, and federal regulations regarding the permitting and compliance of RHWM facilities



*GL = Group Leader

Figure 1-1. Organizational Structure of the LLNL Environmental Protection Department

- Administers the LLNL Waste Certification Program, which manages sampling and analysis for all low-level radioactive waste streams to ensure requirements for offsite shipment are met
- Responds to emergencies and participates in the cleanup of hazardous and radioactive spills at LLNL facilities.

1.3.1.2 Environmental Restoration Division (ERD)

ERD was formed to protect the public health and the environment by investigating and remediating contamination of soil and groundwater from past activities of LLNL and its predecessors at the Livermore site and Site 300 facilities. The Division evaluates, selects, and implements appropriate, innovative, state-of-the-art environmental restoration technologies. ERD is responsible for:

- Conducting restoration of soil and groundwater to comply with state and federal regulations and to protect public health and the environment
- Utilizing state-of-the-art contaminant hydrogeology and restoration methods for groundwater and soils
- Providing and managing a series of well-characterized and instrumented test beds to assist in development of a broad array of investigation and remediation technologies and approaches.

ERD directs groundwater and soil monitoring efforts associated with CERCLA compliance. The Division monitors more than 600 wells and conducts soils sampling at the well sites in conjunction with remedial activities performed at both the Livermore site and Site 300.

1.3.1.3 Operations and Regulatory Affairs Division (ORAD)

ORAD helps Laboratory programs to operate in an environmentally sound manner and to meet environmental compliance requirements. It is responsible for obtaining the environmental permits that allow LLNL to operate its facilities. Evaluating environmental laws and regulations, it drafts environmental guidelines for personnel working in Laboratory facilities and in the field. Serving as internal consultants, ORAD staff also advises Laboratory personnel concerning interactions and inspections involving federal, state, and local environmental regulatory agencies.

ORAD personnel develop and apply monitoring techniques, source evaluations, and computer modeling to evaluate the effect of LLNL operations on human health and the environment at both the Livermore site and Site 300. By monitoring radiological air emissions, sewer effluent discharges, and storm water runoff, ORAD staff helps to identify new contamination that result

from current Laboratory activities. Monitoring results are also used to help focus cleanup activities on existing contamination.

ORAD's responsibilities include:

- Helping Laboratory programs comply with environmental regulations
- Providing regulatory guidance and acting as the interface between regulatory agencies and LLNL organizations
- Writing environmental evaluations, permit applications, environmental reports, and other documents for submittal to DOE or regulatory agencies
- Conducting natural resource and cultural surveys and monitoring the air, meteorological conditions, groundwater, wastewater, surface water, storm water runoff, rain, vegetation and foodstuffs, soils and sediments, and direct radiation to verify that the Laboratory is complying with all federal, state, and local regulations, and to determine the Laboratory's impact, if any, on the local environment.

1.3.2 Other Environmental Support Organizations

ORAD is the Laboratory organization with primary responsibility for sampling environmental media, but other organizations also perform activities related to environmental monitoring. For example, non-EPD staff, under the direction of ORAD, handle some air effluent monitoring activities, such as sample collection, as well as the calibration and maintenance of the equipment, in the facilities being monitored (see Chapter 3).

Sample analyses associated with monitoring efforts are provided by both external contract analytical laboratories and in-house analytical laboratories (See Chapters 3-11 and Chapter 13). The choice of which analytical laboratory to use is dependent on the analysis, detection limits needed, laboratory certification requirements, turnaround time requirements, cost, and precedent. Individual chapters of this document indicate whether an on-site or off-site analytical laboratory provides analyses for the medium under discussion.

1.4 Environmental Monitoring Activities

The current ORAD environmental monitoring program has two major components. First, the program monitors effluents, such as stack emissions, and storm and sanitary sewer discharges. Second, the program conducts surveillance monitoring of all environmental media that could be impacted by LLNL, including air, surface water, groundwater, rainwater, surface runoff, wastewater and sewage, vegetation and foodstuffs, soils and sediments, and direct radiation. This existing program involves a staff of Laboratory scientists and technicians as well as

contractors; the collection of more than 24,000 samples from a variety of environmental media; and the performance of more than 260,000 analyses per year.

Funding for both air and liquid effluent monitoring, as well as environmental surveillance monitoring, is provided from general and administrative funds collected from scientific research programs in operation at LLNL.

The following ORAD organizations have major environmental monitoring responsibilities:

- The Terrestrial and Atmospheric Monitoring and Modeling (TAMM) Group is responsible for the planning, data analysis, regulatory compliance, dose assessments, and reporting for all radiological air effluent and nonwater environmental surveillance monitoring, including soils and sediments, vegetation and foodstuffs, ambient air, meteorology and climatology, and direct radiation, both on and off LLNL property (Chapters 3, 4, 5, 9, 10, 11).
- The Water Guidance and Monitoring Group (WGMG) is responsible for planning, data analysis, regulatory compliance, and reporting for all nonhazardous wastewater, storm water, non-CERCLA groundwater, and surface water monitoring (Chapters 6, 7, 8).
- The Technical Support Group (TSG) provides field and data-management support for environmental monitoring and surveillance for a variety of environmental media. TSG support includes:
  - Sample collection and management
  - Design, fabrication, installation, testing, maintenance, modification, repair, and calibration of sampling and monitoring equipment
  - Management of related data for reporting and data archiving.

1.5 Emergency Response

Emergency response activities at LLNL are performed according to the LLNL *Emergency Response Plan* (Volume I; LLNL 2000) and its Emergency Response Implementing Procedures (EPIPS, Volumes II and III; LLNL 2000). The objectives of emergency response are to respond to and mitigate potential consequence of credible onsite emergencies and significant nearby emergencies that could threaten Laboratory workers, the public, national security, or the environment. The *Emergency Response Plan* further specifies methods to be employed for emergency response including the organizational structure, response procedures, and functional roles of responding personnel.

The Laboratory organization responsible for the initial and ongoing response to an actual operational emergency, and for the mitigation of it, is the Emergency Management Team (EMT). During an emergency, the EMT may be supported by the Operation Support Centers within the Environmental Protection Department, Hazards Control Department, Health Services, Plant Engineering, Public Affairs, Safeguards and Security, and Site 300.

EPD is one of the Laboratory's important resources during certain emergencies. In the event of a large emergency requiring the involvement of EPD, it will support emergency response efforts by sending a senior member of EPD management to serve as a member of the EMT. For smaller incidents, an EPD Environmental Duty Officer (EDO), on call 24 hours a day to support environmental emergency response needs, may report directly to the scene of the emergency.

EPD provides necessary expertise and equipment to ensure that releases of radiological or hazardous materials are assessed for possible environmental impacts. EPD is responsible for identification and implementation of environmental mitigation and corrective actions, containment, clean-up, disposal, environmental monitoring and modeling, notification of regulatory agencies, and preparation of required reports.

1.6 Document Organization

This 2002 LLNL *Environmental Monitoring Plan* is structured to provide the environmental professional who is familiar with environmental monitoring at DOE facilities with an understanding of how LLNL fulfills its monitoring obligations. This 2002 EMP describes and explains LLNL' s environmental monitoring networks; sampling methods, locations, and frequencies; and measured parameters as well as methods and procedures for data collection, analysis, maintenance, reporting, and archiving. It addresses quality assurance and verification issues for monitoring data and the specifics of sampling and data collection.

The mission of LLNL and EPD and the organizational framework of the Laboratory's environmental monitoring program are described in Chapter 1. Chapter 2 describes the setting of environmental monitoring at the Livermore site, Site 300, and the surrounding environs.

Chapters 3 through 11 address subjects that encompass all environmental media (air effluent, meteorology, air surveillance, sewer, surface water monitoring [i.e., storm water, rain, drainage retention basin, cooling towers, and other waters], groundwater, soil, vegetation, foodstuffs, and direct radiation). Each chapter specific to a medium contains a discussion of the rationale and design criteria, the extent and frequency of monitoring and measurements, quality assurance requirements, program implementation procedures, preparation and disposition of reports, and future plans. All future plans are contingent, however, on the allocation of funding

and the approval of LLNL management. Short-term plans have a high likelihood of implementation; long-term plans are more likely to be subject to revision.

Chapter 12 describes major aspects of the QA program including analytical capabilities of the analytical labs, the lab certification process, the sample identification system, the performance evaluation program, record handling, and audit procedures.

Chapter 13 describes data management and analysis of routine monitoring data and data storage. Chapter 14 describes radiation dose and risk assessment calculations.

The acronyms used throughout this volume are defined in Appendix A. The environmental Work Smart Standards are listed in Appendix B. The actual procedures for conducting monitoring are filed in an electronic document system and are available to personnel as needed.

1.7 References

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2 Setting

Arthur H. Biermann

2.1 Introduction

Meteorology and geography play primary roles in determining how human actions affect the environment. Geographical characteristics, for example, influence wind patterns, surface heating and cooling, and precipitation, which, in turn, influence dispersal of particles in the air. Similarly, the particular geology of a site constrains the flow and the hydrodynamic dispersion of groundwater. Thus, the environmental monitoring program at Lawrence Livermore National Laboratory (LLNL) collects and analyzes data on wind, precipitation, and geological and geographical characteristics to help determine the effects of LLNL's operations on the surrounding environment. Some background and a description of these data help to explain the relationship of the Laboratory to its meteorological and geographic setting.

2.2 Location

LLNL consists of two main facilities **(Figure 2-1)**—the main laboratory site located in Livermore, California (Livermore site), and the Experimental Test Facility (Site 300) located near Tracy, California. Each site is unique, requiring a different approach for environmental monitoring and protection.

2.2.1 Livermore Site

LLNL was founded at the Livermore site in 1952 at the site of a former U.S. Navy air station. At that time, the location was relatively isolated, being approximately 1.6 km from the Livermore city limits. Over the years, Livermore evolved from a small town of fewer than 7,000 people to its present population which, based on the 2000 census, is 73,345. The area's economy diversified from primarily agricultural to include light industrial and business parks. Within the last few years, low-density, single-family residential developments have begun to fill formerly vacant fields, bringing the city limits of Livermore up to LLNL's western boundary.

LLNL's Livermore site occupies an area of 3.28 km^2. Immediately to the south is Sandia National Laboratories, California (Sandia/CA), operated by Lockheed-Martin Corporation under a U.S. Department of Energy (DOE) contract. Sandia/CA provides research and development associated with nuclear weapons systems engineering, as well as related national security and environmental tasks. Although their primary missions are similar, LLNL and

Sandia/CA are separate DOE facilities, each with its own management and each reporting to a different DOE operations office. Sandia/CA maintains its own on-site environmental monitoring but relies on LLNL for off-site environmental surveillance monitoring. Potential off-site environmental impacts of Sandia/CA operations are considered in LLNL's monitoring plans.

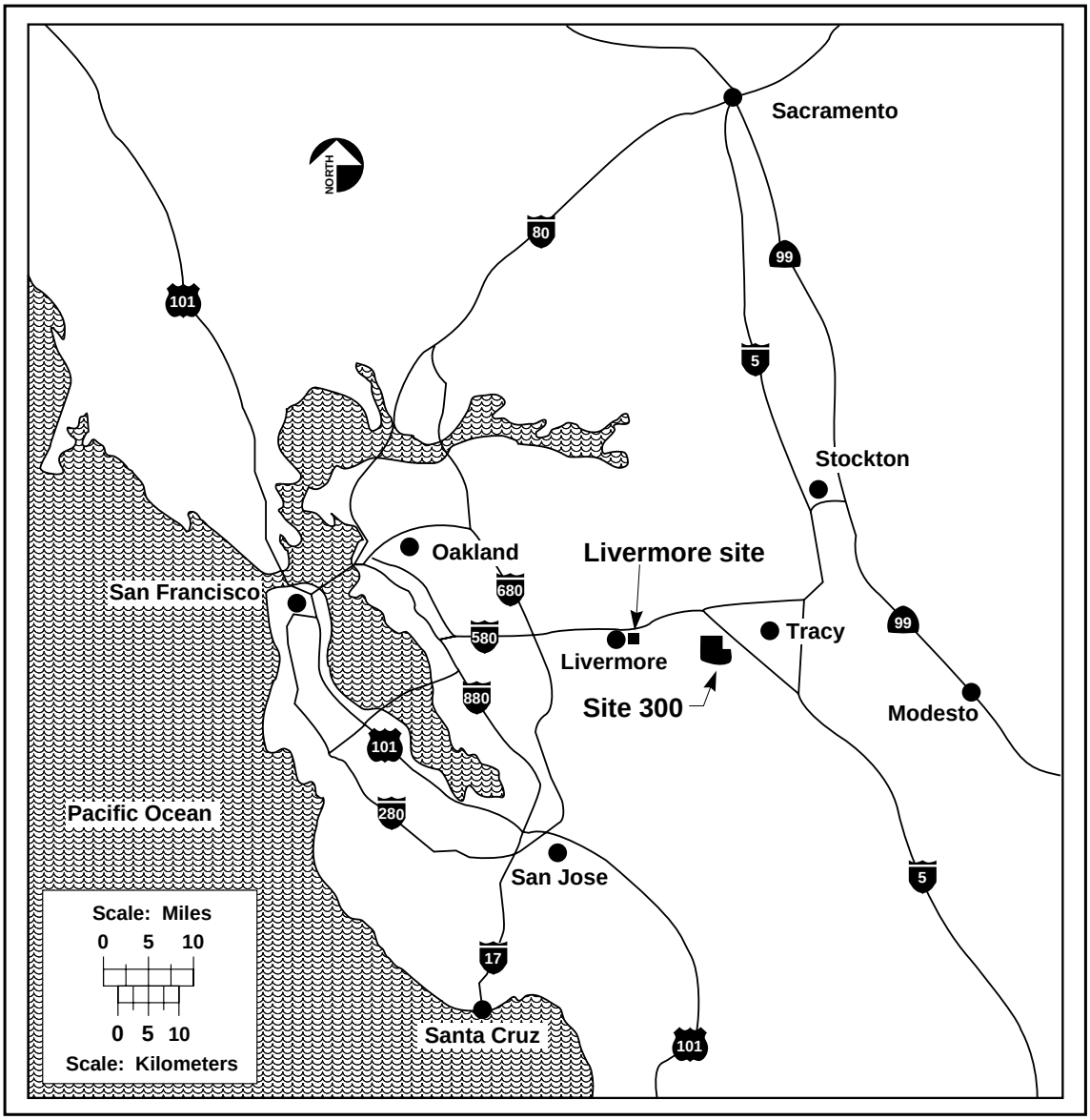

Figure 2-1. Location of LLNL Livermore site and Site 300

South of LLNL and SNL/CA are low-density residential areas and agricultural areas devoted to grazing, orchards, and vineyards. Southwest of the Laboratories is a business park. Farther south, the land is primarily open space, rural ranchettes, or agriculture. Immediately to the

west, low-density residential areas have been recently developed. A very small amount of low-density residential development lies east of the Livermore site, and agricultural land extends to the foothills of the Diablo Range, the intercoastal range that defines the eastern margin of the Livermore Valley. A business park is north of the Laboratories. Major population centers near Livermore include Pleasanton and Tracy, and the more distant metropolitan areas of Oakland, San Jose, San Francisco, and Stockton. There are 6.9 million residents within an 80-km radius of the Livermore site.

2.2.2 Site 300

Site 300, LLNL's Experimental Test Site, is located 20 km east of the Livermore site in San Joaquin and Alameda counties in the Altamont Hills of the Diablo Range. The site occupies an area of 30.3 km^2. Another testing facility owned by Primex Physics International and located east of Site 300 is no longer in operation. The Carnegie State Vehicular Recreation Area is south of the western portion of Site 300, and wind turbine generators line the hills northwest of the site. The remainder of the surrounding area is in agricultural use, primarily as grazing land for cattle and sheep, although there are plans for future residential development to the northeast of the site.

Currently, the nearest residential area is the town of Tracy (population 56,529), located 10 km to the northeast. Within 80 km of Site 300, there are 6 million residents, many of whom are located in the metropolitan areas of Oakland, San Jose, and Stockton.

2.3 Meteorology

2.3.1 Livermore Site

Mild, rainy winters and warm, dry summers characterize the climate of the Livermore Valley. The mean annual temperature is 15 °C. Temperatures range from –5 °C during predawn winter mornings to 40 °C during summer afternoons.

For approximately 50 percent of the year, prevailing winds are from the west and southwest. These wind patterns are controlled by the thermal draw caused by rising air in the warm Central Valley of California, which results in wind blowing from the cool ocean toward the warm valley, increasing in intensity as the valley heats up. This is the predominant wind direction during the summer. The wind blows from the northeast primarily during the winter storm season. The annual wind pattern for 2000 is depicted by the wind rose in **Figure 2-2** (Biermann et al. 2001).

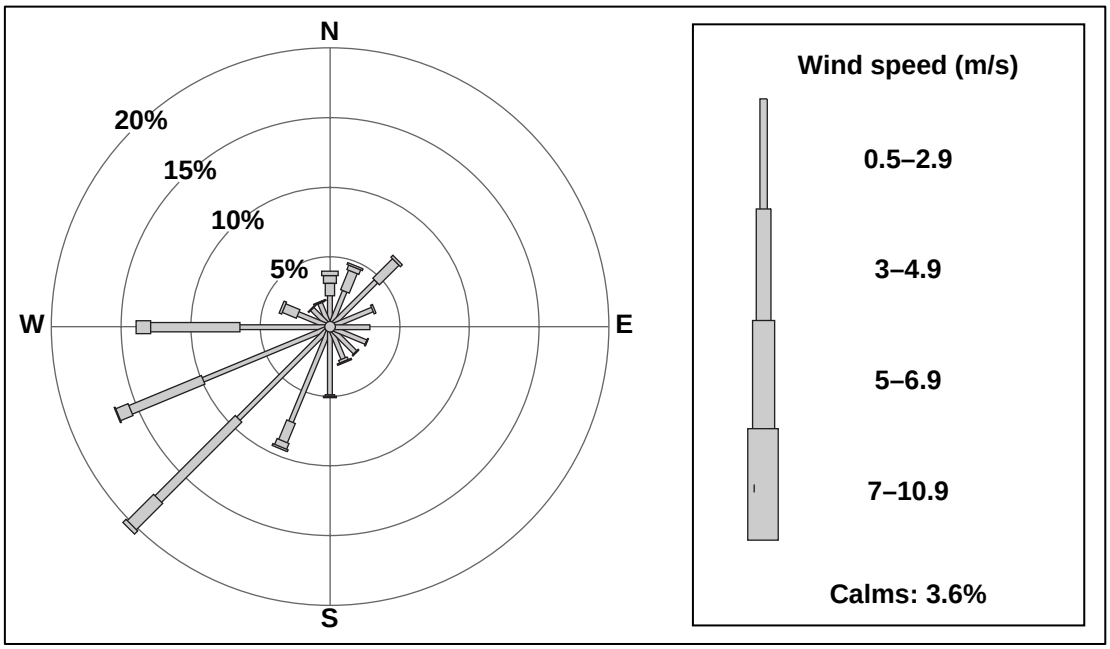

Figure 2-2. Wind rose showing the frequency of occurrence for wind speed and direction at the Livermore site, 2000

Precipitation also exhibits a strong seasonal pattern with most of it occurring between October and April but very little during the warmer months. Snow is uncommon in the Livermore Valley. Based on a 10-year record, the highest and lowest annual rainfalls were 541 and 211 mm. The average annual rainfall was 360 mm.

2.3.2 Site 300

The climate at Site 300, while generally similar to that at the Livermore site, is modified by the higher elevation and more pronounced topographical relief, which significantly influences local wind and temperature patterns. The temperature range is slightly more extreme than at the Livermore site, and surface winds are generally greater. At Site 300, the prevailing winds come more consistently from the west-southwest and reach greater speeds than at the Livermore site. The wind rose for the year 2000 is shown in **Figure 2-3** (Biermann et al. 2001).

For the past 9 year period, the annual average rainfall for Site 300 was 303 mm. The highest and lowest annual rainfalls were 475 and 193 mm.

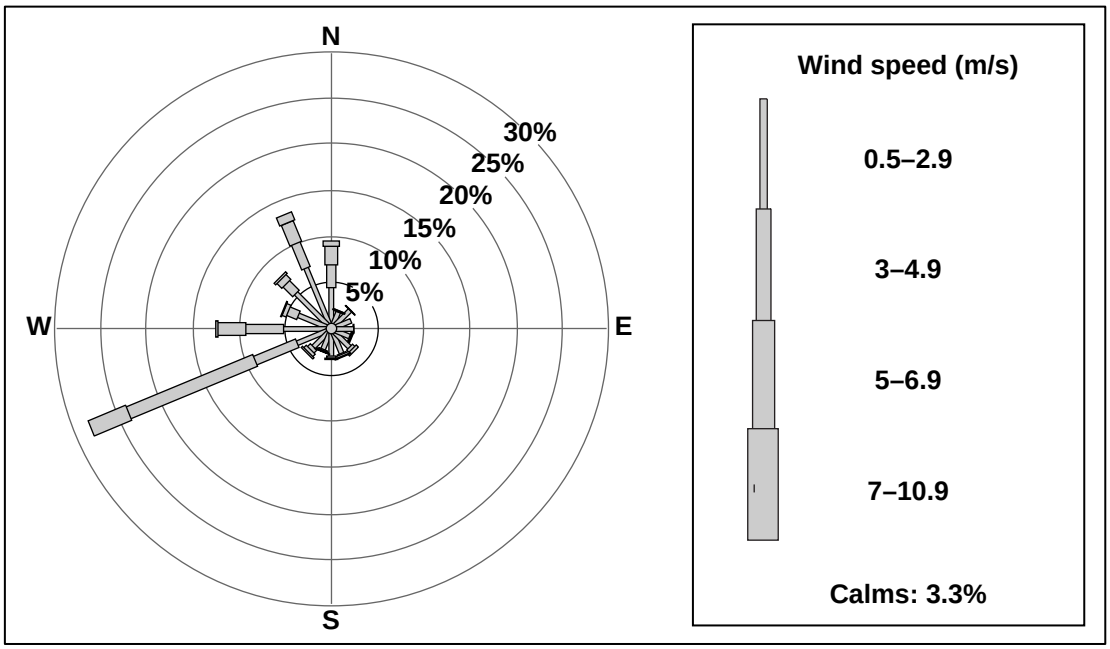

Figure 2-3. Wind rose showing the frequency of occurrence for wind speed and direction at Site 300, 2000

2.4 Geology

2.4.1 Topography

2.4.1.1 Livermore Site

The Livermore site is located in the southeastern portion of the Livermore Valley, a topographic and structural depression oriented east–west within the Diablo Range of the California Coast Range Province. The Livermore Valley, the most prominent valley within the Diablo Range, is an east-west trending structural and topographic trough that is bounded on the west by Pleasanton ridge and on the east by the Altamont Hills. The valley is approximately 25 km long and averages 11 km in width. The valley floor is covered by alluvial, lake, and swamp deposits consisting of gravels, sands, silts, and clays, with an average thickness of about 100 m. The valley floor is at its highest elevation of 220 m above sea level along the eastern margin and gradually dips to 92 m at the southwest corner. The valley's major streams, Arroyo del Valle and Arroyo Mocho, drain the southern highlands and flow mostly during the rainy season.

2.4.1.2 Site 300

The topography of Site 300 is much more irregular than that of the Livermore site. It consists of a series of steep hills and ridges oriented along a generally northwest-southeast trend and separated by intervening ravines. The Altamont Hills, where Site 300 is located, are part of the

California Coast Range Province and separate the Livermore Valley to the west from the San Joaquin Valley to the east. The elevation ranges from approximately 150 m above sea level at the southeast corner of the site to approximately 540 m in the northwestern portion.

2.4.2 Hydrogeology

2.4.2.1 Livermore Site

The hydrogeology and the movement of groundwater in the vicinity of the Livermore site have been the subjects of several recent and continuing investigations (Stone and Ruggieri 1983; Carpenter et al. 1984; Webster-Scholten and Hall 1988; Thorpe et al. 1990). This section has been summarized from these reports and from data supplied by Alameda County Flood Control and Water Conservation District, Zone 7, which is the agency responsible for groundwater management in the Livermore Valley basin (CRWQCB 1995).

The Livermore Formation (and overlying alluvial deposits) contains the aquifers of the Livermore Valley groundwater basin and is an important water-bearing formation. Natural recharge occurs primarily along the fringes of the basin and through the arroyos during periods of winter flow. Artificial recharge, if needed to maintain groundwater levels, is accomplished by releasing water from Lake Del Valle or from the South Bay Aqueduct into arroyo channels in the east. Groundwater flow in the valley generally moves toward the central east-west axis of the valley and then westward through the central basin. Groundwater flow in the basin is assumed to be primarily horizontal although a significant vertical component probably exists in fringe areas, under localized sources of recharge, and in the vicinity of heavily used extraction (production) wells.

Beneath the Livermore site, the depth to the water table varies from about 10 to 40 m. **Figure 2-4** shows a contour map of water table elevations (meters above mean sea level) for the Livermore site area. Although water table elevations vary slightly with seasonal and year-to-year differences in both natural and artificial recharge, the qualitative patterns shown in **Figure 2-4** are generally maintained. At the eastern edge of the Livermore site, groundwater gradients (change in vertical elevation per unit of horizontal distance) are relatively steep; but under most of the site and farther to the west, the contours flatten to a gradient of approximately 0.003. Groundwater flow under most of the site is southwesterly. This flow direction diverges from the generally westward regional flow and from flow patterns demonstrated for the site in the 1980s. This shift in flow direction is a consequence of groundwater recovery and remediation in the southwest portion of the site and agricultural pumping. Aquifer tests on monitoring wells in the vicinity of the Livermore site indicate that the hydraulic conductivity of the permeable sediments ranges from 1 to 16 m per day (Isherwood et al. 1991). This, in combination with the observed water table gradients, yields an average groundwater velocity estimate of 20 m/y

(Thorpe et al. 1990). The range in these values reflects the heterogeneity typical of the more permeable of the alluvial sediments that underlie the area.

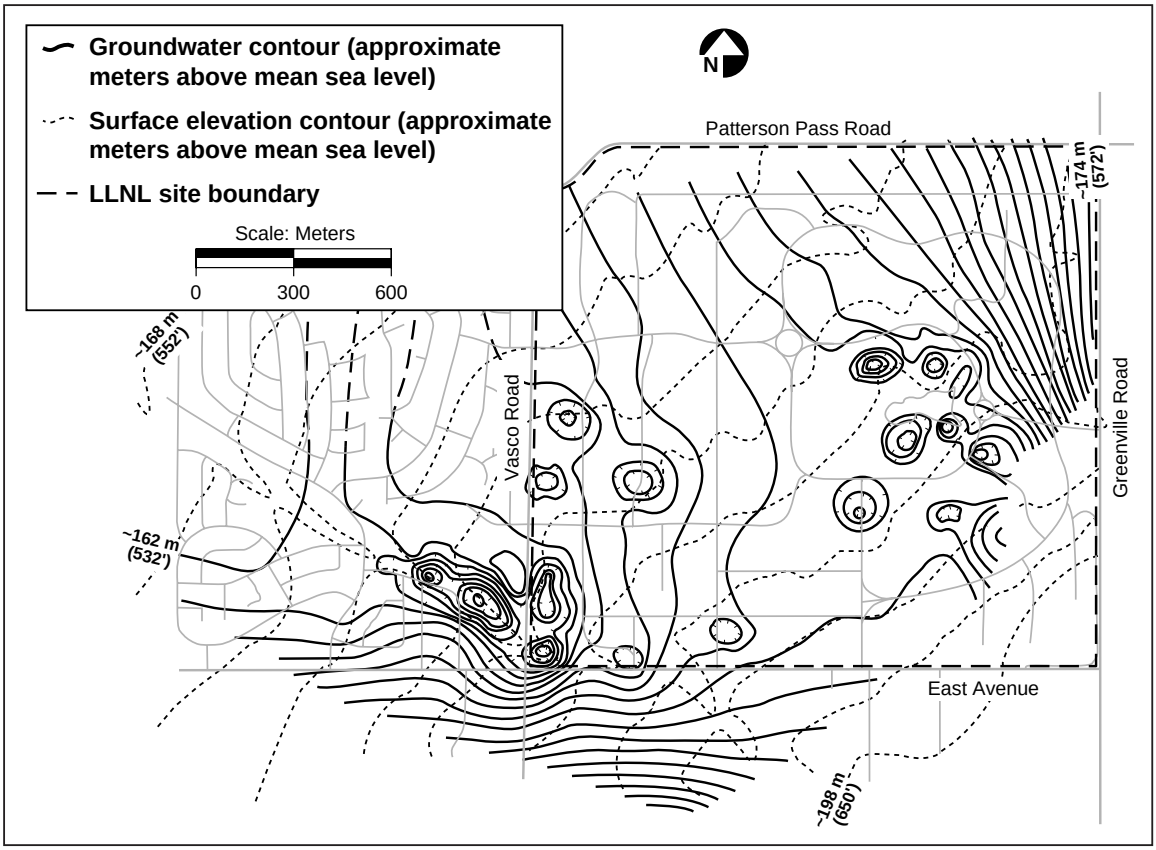

Figure 2-4. Approximate groundwater and surface elevation contours, Livermore site and vicinity, 2000

2.4.2.2 Site 300

Site 300 is generally underlain by gently dipping sedimentary bedrock dissected by steep ravines. The bedrock consists primarily of interbedded sandstone, siltstone, and claystone. Most groundwater occurs in the Neroly Formation upper and lower blue sandstone aquifers. Significant groundwater is also locally present in permeable, Quaternary alluvium valley fill. Much less groundwater is present within perched aquifers in the unnamed Pliocene nonmarine unit.

Perched aquifers contain unconfined water separated from an underlying main body of water by impermeable and permeable layers; normally, they are discontinuous and highly localized. Because water quality is generally poor and yields are low, these perched water-bearing zones do not meet criteria of the state of California for aquifers that are potential drinking water sources.

Fine-grained siltstone and claystone interbeds may confine the groundwater and act as aquitards, or perching horizons. Groundwater is present under confined conditions in parts of the deeper bedrock aquifers but is generally unconfined elsewhere.

Groundwater flow in most aquifers follows the attitude of the bedrock. In the northwest part of Site 300, groundwater in bedrock generally flows northeast except where it is locally influenced by the geometry of alluvium-filled ravines. In the southern half of Site 300, groundwater in bedrock flows roughly south–southeast, approximately coincident with the attitude of bedrock strata. The thick Neroly lower blue sandstone, stratigraphically near the base of the formation, generally contains confined water. Wells located in the western part of the General Services Area, near the southeast border of Site 300, are completed in this aquifer and are used to supply drinking and process water.

Figure 2-5 shows the elevation contours for water in the regional aquifer at Site 300. This map of the piezometric surface (the elevation to which water rises in a well that penetrates a confined or unconfined aquifer) is based primarily on water levels in the Neroly lower blue sandstone aquifer.

Recharge occurs predominantly in locations where saturated alluvial valley fill is in contact with underlying permeable bedrock, or where permeable bedrock strata crop out because of structure or topography. Local recharge also occurs on hilltops, creating some perched water-bearing zones. Low rainfall, high evapotranspiration, steep topography, and intervening aquitards generally preclude direct vertical recharge of the bedrock aquifers.

2.5 Conclusion

LLNL recognizes the importance of its geology, hydrogeology, climate, and geographical relationship with its neighbors in assessing potential impacts of operations at the Livermore site and Site 300. The environmental scientists at LLNL take into account the unique locations of the Livermore site and Site 300 to tailor sampling and analysis programs for each medium—air, soil, water, vegetation, foodstuff, and direct radiation—used to monitor the environment. LLNL recognizes that its operations may affect each of these environmental media differently. Each year, gathering additional monitoring data allows better predictions and interpretations of potential impacts and helps to ensure that LLNL complies with regulatory standards.

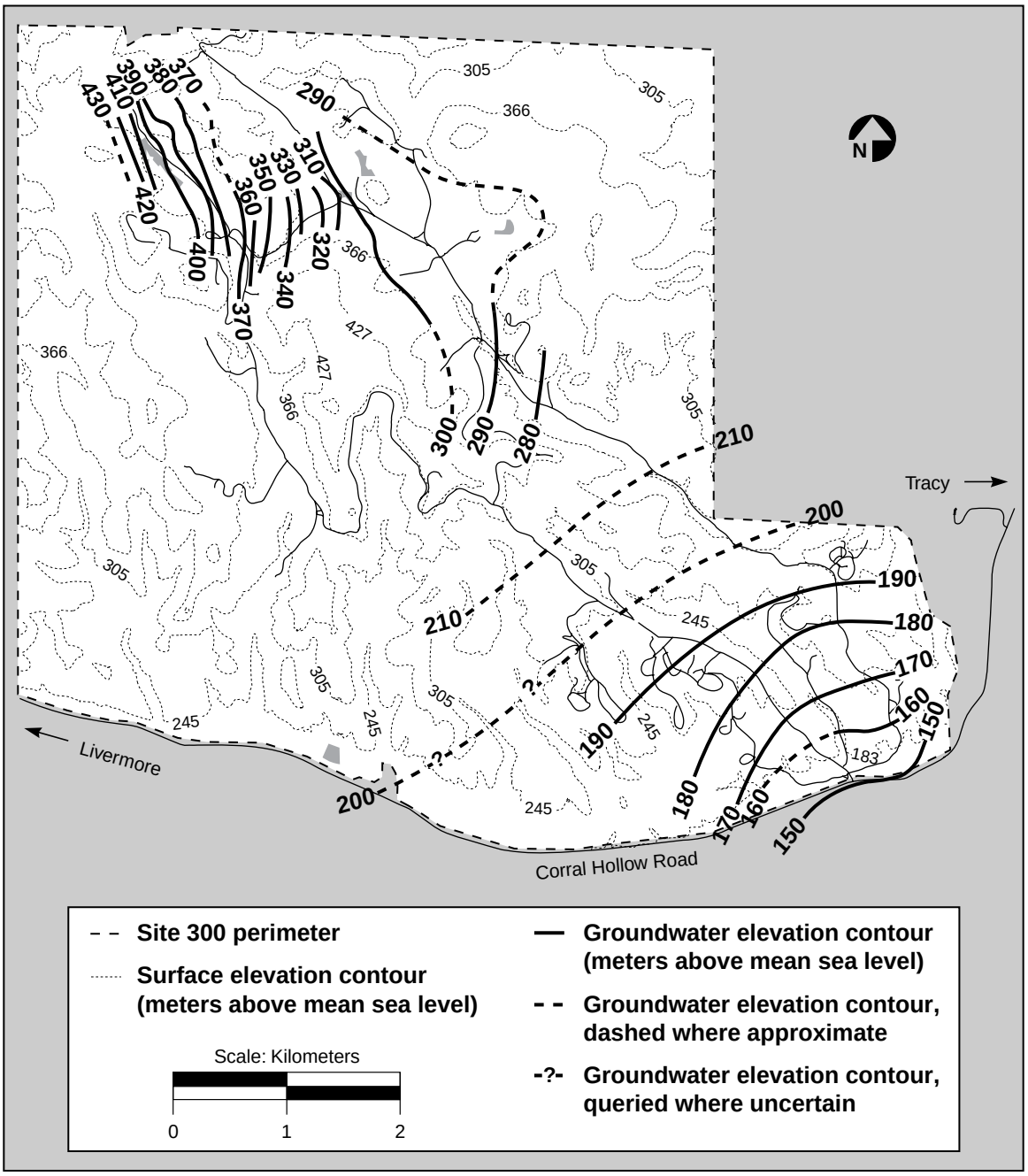

Figure 2-5. **Approximate groundwater elevations in principal continuous water-bearing zone aquifer at Site 300, 2000**

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3 Air Effluent Monitoring

Paula J. Tate

3.1 Introduction

A key monitoring method for evaluation of environmental impacts from facilities having discharges to the atmosphere is the measurement of pollutants at their point of emission. LLNL performs continuous air effluent sampling of atmospheric discharge points at several facilities that complies with U.S. Department of Energy (DOE) orders, federal laws, and industry standards. DOE monitoring guidance specifies that emissions from facilities with radionuclides should be monitored. The LLNL air effluent monitoring program complements the environmental air surveillance monitoring effort (Chapter 5); it can confirm or discount specific source locations as being contributors to any release that environmental surveillance monitoring might detect. It can also provide source term information for regulatory compliance or emergency response and dispersion and dose assessment modeling.

3.2 Rationale and Design Criteria

3.2.1 Regulatory Drivers

The applicable portions of DOE Orders 5400.1 (WSS B93) and 5400.5 (WSS B94 and B95) define standards for controlling exposures to the public from operations at DOE facilities. Applicable portions of 40 CFR 61 (WSS A12), a regulation promulgated under the Clean Air Act, set requirements for continuous monitoring of radiological discharges and the estimation of radiological dose to the public (Chapter 14) resulting from operations at DOE facilities.

Historically, monitoring of radionuclide air effluents at LLNL has been implemented according to the DOE as low as reasonably achievable (ALARA) policy. The more recent 40 CFR 61 Subpart H National Emission Standards for Hazardous Air Pollutants (NESHAPs) regulations require that monitoring of radionuclide air effluents must be performed if the potential offsite effective dose equivalent (EDE) from a specific emission point is greater than 1 μSv/y (0.1 mrem/y), as calculated using the air dispersion dose models mandated by the U.S. Environmental Protection Agency (EPA) and assuming no emission control devices. Where air monitoring is not required, periodic confirmatory measurements are to be performed.

All LLNL operations having the potential for radiological air emissions are evaluated to determine the need for continuous monitoring. At discharge points having air effluent

monitoring, the monitoring results provide the actual source term for evaluating that the radiological NESHAPs standard, 100 μSv/y (10 mrem/y) effective dose equivalent (EDE) from all site operations, is not exceeded.

3.2.2 Monitoring Objectives

The primary purpose of LLNL's air effluent sampling program is to measure radiological emissions at the point of release. In doing so, LLNL can demonstrate compliance with regulatory requirements and ensure protection of the public and the environment. In addition, sampling provides confirmation of the performance of emission control systems in place at facilities.

3.2.3 Potential Sources and Contaminants

Researchers at LLNL use a wide variety of radioisotopes for experimental purposes, including uranium and transuranic elements, biomedical tracers, tritium, mixed fission products, and others. The major radionuclide released to the atmosphere from the Livermore site is tritium. In addition to effluent sampling for tritium, a number of other facilities at the Livermore site have air effluent samplers to detect the release of uranium and transuranic aerosols. The air effluent sampling systems described in this chapter apply to stationary point source discharges. Sampling methods to evaluate LLNL diffuse sources are described in Chapter 5.

3.2.3.1 Radiological Sources

To assess the need for monitoring air effluent discharge points, LLNL conducts evaluations of all operations having the potential to release radionuclides to the atmosphere. The evaluation demonstrates that LLNL is in compliance with 40 CFR 61 Subpart H section (b)(4) for the regulation of radionuclide emissions from DOE-owned or -operated facilities. Internal to LLNL, the Terrestrial and Atmospheric Monitoring and Modeling (TAMM) Group in the Environmental Protection Department (EPD) is responsible for radiological NESHAPs evaluations and reporting. Results for the most recent evaluation are contained in the *LLNL NESHAPs 2000 Annual Report* (Gallegos et al. 2001).

As a result of annual NESHAPs evaluations and the DOE ALARA policy, LLNL now operates 72 continuous samplers in seven facilities at the Livermore site. Site 300 was also evaluated as part of this process and LLNL now operates one continuous sampler in one facility at Site 300. Implementation guidance on air effluent sampling is provided in the NESHAPs-cited American National Standards Institute (ANSI) N13.1-1969 (WSS B81) and the

Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance (DOE 1991).

3.2.3.2 Nonradiological Sources

LLNL operations that have the potential to release nonradiological pollutants are currently not required to be monitored. Moreover, LLNL is not considered a major source of nonradiological pollutant emissions. Emissions from LLNL are fewer than 25 tons per year of precursor organic compounds and nitrogen oxides; these emission levels qualify LLNL to be considered a small facility by local air quality management districts. However, permits for such operations must be obtained from the local air districts responsible for enforcement, which are the Bay Area Air Quality Management District (BAAQMD) for the Livermore site and the San Joaquin Valley Unified Air Pollution Control District (SJVUAPCD) for Site 300. Applicable regulations and permitting requirements are contained in the BAAQMD Regulations 1-12 (WSS A27) for the Livermore site and the SJVUAPCD Regulations Rules 1010-9120 (WSS A37) for Site 300. Verification of emissions from sources may be performed in accordance with *Standards of Performance for New Stationary Sources* in 40 CFR 60 (WSS A23). The TAMM group of EPD is responsible for obtaining necessary permits and exemptions, maintaining permit records, and coordinating inspections.

3.3 Extent and Frequency of Monitoring and Measurements

3.3.1 Air Effluent Sampling Locations

The locations of facilities or buildings at the Livermore site and Site 300 that have radionuclide air monitoring systems are shown in **Figures 3-1** and **3-2**. **Table 3-1** lists these buildings along with the number of samplers, the types of samplers, and the analytes of interest. The following sections describe the sampling systems for each facility. Because emission estimates depend on both sampled pollutant concentrations and stack exhaust volume, determinations of both are made for all stacks. Stack flow measurements and calculations are discussed separately in **Section 3.3.2**.

3.3.3.1 Buildings 175, 177, and 491 – Laser Isotope Separation

In the past, operations performed in Buildings 175, 177, and 491 have supported research and development activities for the separation of uranium isotopes under the Advanced Vapor Laser Isotope Separation (AVLIS) Program. In 1999, the AVLIS Program was shut down and a comprehensive plan addressing the shutdown, surveillance, and maintenance of the facilities was developed. Air effluent sampling systems at Buildings 175 and 491 remain active as part of the shutdown activities to render the equipment and facility safe and preserve basic

functionality and operational potential. At Building 175, the effluent exhausts of four ventilation systems are currently sampled for particles through six individual sampling probes (the two larger ventilation systems are each driven by two blowers, with each blower having a monitored release point).

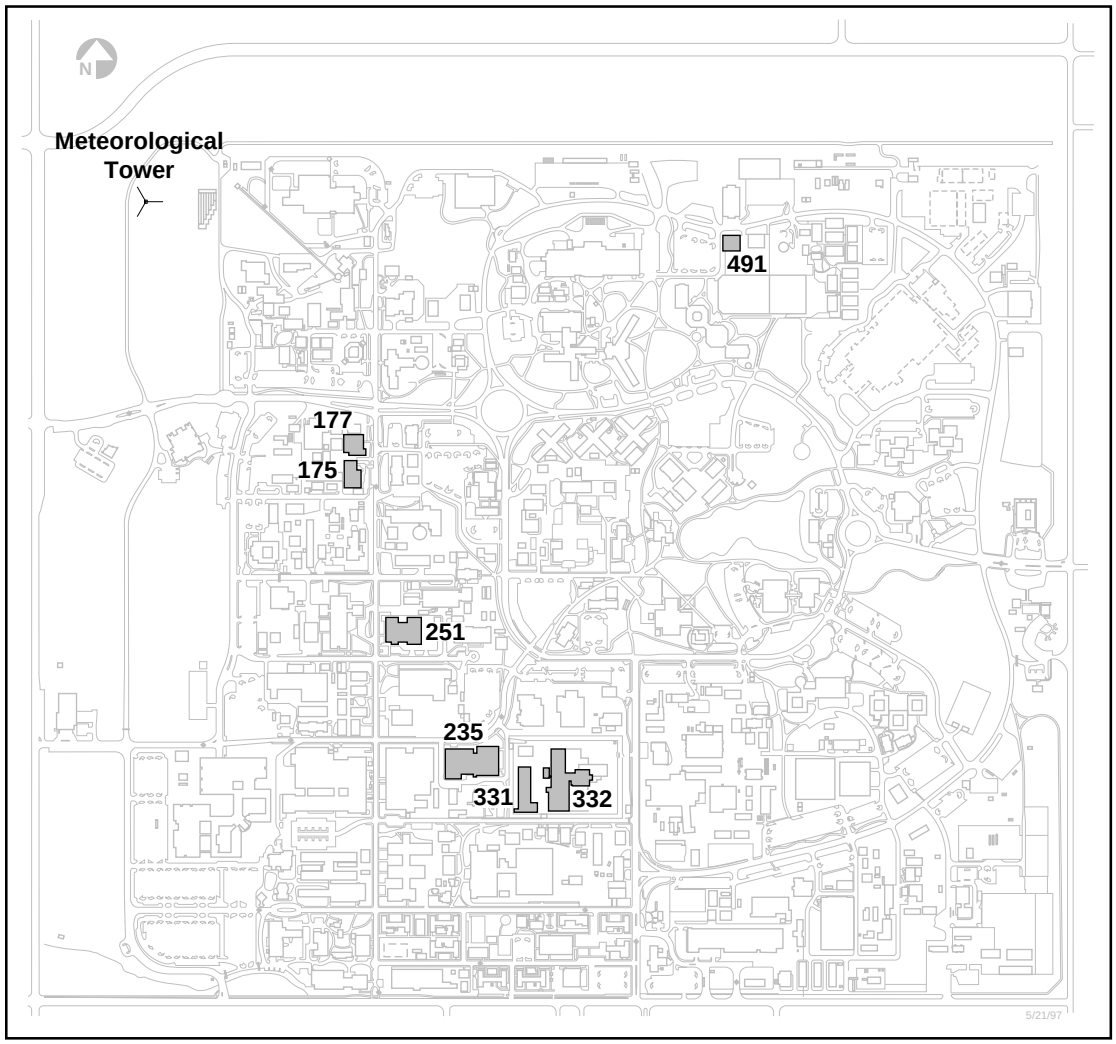

Figure 3-1. LLNL buildings at the Livermore site that have air monitoring systems for effluent gas streams

In early 2002, Building 177 underwent decontamination and decommissioning, and the sampling system was removed when the process was completed. At Building 491, exhausts from operations are routed through a single stack where a single four-nozzle probe is used to withdraw an air sample. All samplers are located downstream of high-efficiency particulate air (HEPA) filters and immediately before discharge to the atmosphere. The sample filters, 47-mm-diameter mixed cellulose membranes, collect particles continuously and are removed weekly for analysis of gross alpha and gross beta activity.

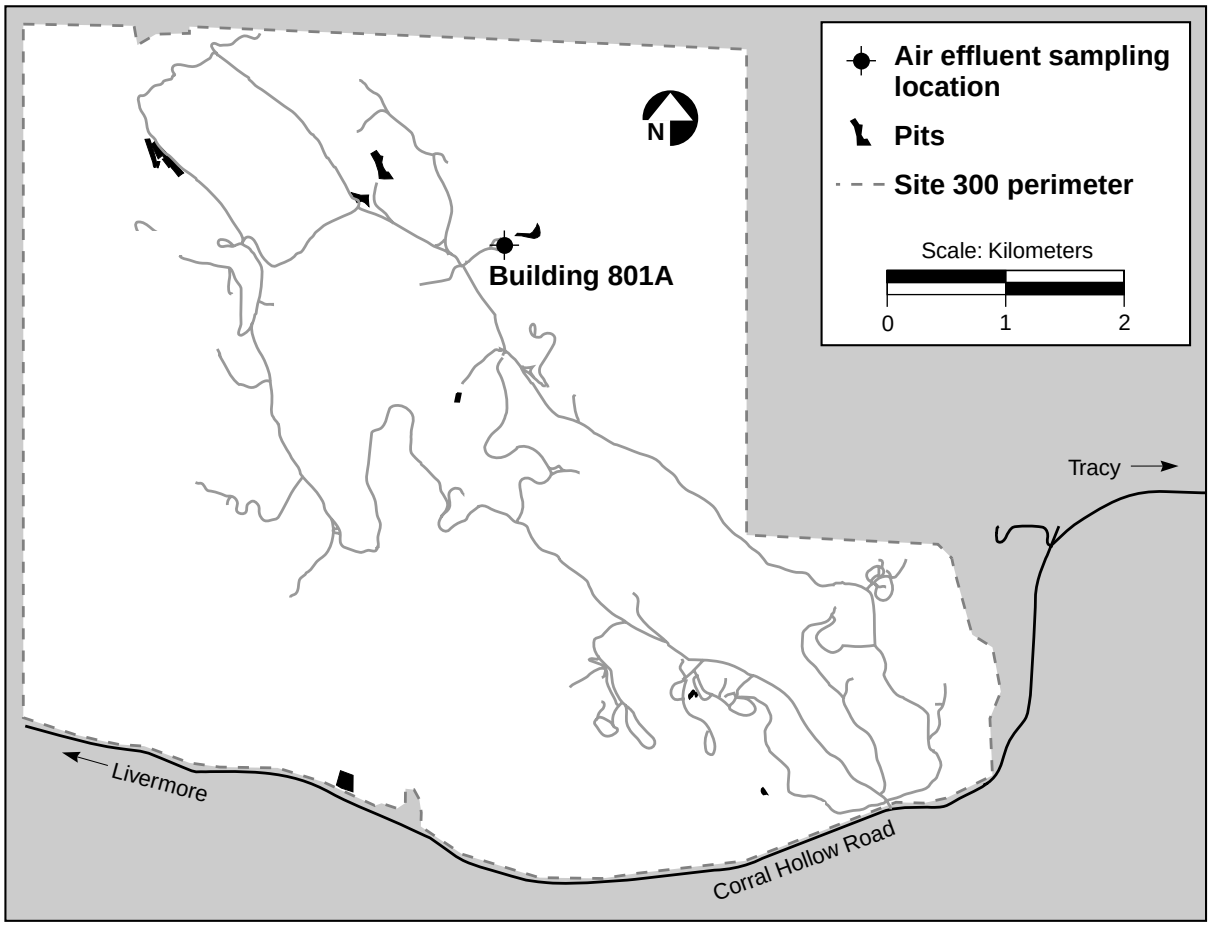

Figure 3-2. Site 300 Building 801A, which has an air monitoring system for effluent gas streams

Table 3-1. Air effluent sampling locations and systems

Building	Facility/Project	Analytes	Sample type	Number of samplers
175	MARS	Gross α, β on particles	Filters	6
235	Chemistry and Materials Science	Gross α, β on particles	Filters	1
251	Heavy Elements	Gross α, β on particles	Filters	27
331	Tritium	Tritium	Ionization chamber[a]	4
		Gaseous tritium/tritiated water vapor	Molecular sieves	4
332	Plutonium	Gross α, β on particles	CAM[a,b]	12
		Gross α, β on particles	Filters	16
491	Laser Isotope Separation	Gross α, β on particles	Filters	1
801A	Contained Firing Facility	Gross α, β on particles	Filters	1

a Alarmed systems

b CAM = continuous air monitors (Eberline)

3.3.3.2 Building 235 – Chemistry and Materials Science

Building 235 houses operations that include the examination of material structure, surface, and subsurface. Only one laboratory conducts experiments requiring effluent monitoring. This laboratory performs characterization of the microstructure of plutonium and plutonium alloy samples. The sampler is located downstream of HEPA filters and before discharge to the atmosphere. The 47-mm-diameter sample filters are exchanged weekly and analyzed for gross alpha and gross beta activity.

3.3.3.3 Building 251 – Heavy Element Facility

Building 251, the Heavy Element Facility, has operations limited to the storage of radioactive material from previous operations, clean up and decontamination of facility work areas and equipment, removal of contaminated systems and enclosures, facility maintenance, repackaging and removal of radioactive materials from the facility, and characterization of waste generated by these activities. This facility is currently undergoing decontamination and decommissioning activities. The facility has 27 filter-type continuous sampling systems on exhausts throughout the facility. All samplers are placed downstream of air filtration systems. The filter-type systems sample individual emission points from either glove boxes, fume hoods, or rooms. Particles in the exhaust are collected onto 47-mm-diameter membrane filters. Sample filters are changed every two weeks for gross alpha and gross beta analysis.

3.3.3.4 Building 331 – Tritium Facility

The Building 331 Tritium Facility houses laboratories for conducting experiments involving radioactive gases and their compounds. All air effluent from the facility is exhausted through two stacks. Each stack is monitored for tritium release by both a continuous monitoring alarm system and continuous molecular sieve samplers; all are on the emergency power system. The alarmed samplers provide real-time total tritium concentration release levels (combination of both molecular tritium gas and tritiated water vapor), while the sieve samplers, which can discriminate between tritiated water (HTO) vapor and molecular tritium (HT), provide the values used for environmental reporting. The continuous alarm monitors consist of two Overhoff ion chambers in parallel—one to monitor high tritium concentrations and the other to detect lower levels. Routine inspections of ion chamber operation include a weekly source check for the ion chamber and alarm set points, a quarterly check of the alarmed monitor electronics, and semiannual electronic checks and detector calibration. The ion chambers satisfy the DOE/EH-0173T (DOE 1991) requirement that alarm monitors be in use at discharge points having the potential to give an offsite EDE greater than 1 μSv/y (0.1 mrem/y).

Each continuous tritium sampler (unalarmed) is placed in parallel with the alarmed monitors and consists of two molecular sieves placed in series. The first sieve collects

tritiated water vapor; in the second sieve, palladium-coated sieve material catalytically oxidizes molecular tritium to tritiated water and collects the vapor. Molecular sieves are collected weekly and analyzed for tritium content.

3.3.3.5 Building 332 – Plutonium Facility

The Plutonium Facility has supported research and development in the chemical, metallurgical, and physical properties of plutonium. Currently, the facility supports programs addressing weapon dismantlement and plutonium disposition, research in the metallurgy and chemistry of actinides, and development of pyrochemical processing methods. The facility has 11 air effluent discharge points, including both building and glove box ventilation systems. The discharge points are monitored by alarmed Eberline CAMs and also by simple filter-type aerosol collection systems. The latter are also continuous collection systems but are not alarm systems. The Eberline CAMs provide the alarm capability for the facility and meet the DOE/EH-0173T (DOE 1991) requirement of alarm-type samplers, as noted in **Section 3.3.3.4.** The filter-type sampling system provides more representative sampling of the air effluent streams by better placement of the sample extraction probes and minimization of particle losses in the aerosol transport lines. Alarms from the Eberline monitors are automatically routed to the facility's control room and also to the LLNL Sitewide Alarm System Emergency Dispatch Center. Both the CAMs and the filter aerosol systems operate from the facility's emergency power system. Sampling locations are downstream of HEPA filtration. The 47-mm-diameter cellulose filters from both the CAM and simple filter-type systems are changed weekly and analyzed for gross alpha and gross beta activity.

3.3.3.6 Building 801A – Contained Firing Facility

The Contained Firing Facility (CFF) at Site 300 supports the LLNL stockpile stewardship program. This is a new facility constructed to complete high explosives testing indoors and will reduce the emissions to the environment and minimize noise, blast pressures, and the generation of hazardous waste. At Building 801A, exhausts from operations are routed through a single stack where a single six-nozzle probe is used to withdraw an air sample. The sampler is located downstream of HEPA filters and immediately before discharge to the atmosphere. The sample filter, a 47-mm cellulose membrane, collects particles continuously and is exchanged weekly for analysis of gross alpha and gross beta activity.

3.3.3.7 Low-Volume Ambient Air Samplers

Two special low-volume ambient air sampling systems support the air effluent sampling network. These samplers are co-located with high-volume environmental surveillance air samplers at the FCC and HOSP sampling locations shown in **Figure 5-2**. These locations are

generally upwind of the Livermore site. The results from the low-volume samplers are used to establish background levels of gross alpha and beta activity for comparison to results from the air effluent samplers monitoring facility discharge points. These special sampling systems are very similar to the air effluent samplers, including sampling system design, sampler operation, sample tracking, sample analysis, and processing of results.

3.3.3.8 Periodic Confirmatory Measurements

In addition to the continuous air effluent monitoring effort, LLNL conducts periodic sampling measurements at selected potential radiological effluent locations where continuous sampling is not specifically required by the radiological NESHAPs regulations. However, this periodic sampling is required by the regulations to confirm that alternative methods used to evaluate emissions and calculate resultant doses are conservative. The extent and frequency of these measurements are not specified in the regulations. The TAMM Group in EPD annually reviews candidate operations for this type of sampling, makes arrangements with LLNL program personnel, and samples exhausts during active operations on a case by case basis. The method for determining which discharge points will be measured and the techniques used to carry out the measurements can be found in EMP-AE-PCM, *Air Effluent Periodic Confirmatory Measurements*. Data are reported in the annual NESHAPs report (e.g., Gallegos et al. 2001).

3.3.2 Effluent Flow Rate Measurement

Along with the concentration of radiological constituents in the discharge as determined by the continuous sampling systems, the effluent volume from a discharge point must be known to determine the annual emissions. The effluent flow rate from all discharge points having continuous sampling systems is determined by EPA-approved methods (CFR 1994). At most facilities, periodic measurements of stack flow velocity are made using hot-wire anemometers or pitot tubes. Effluent volume is then calculated based on the periodic flow rate measurements. At the other facilities, continuous measurements of stack flow rate are made using permanent electronic velocity, or mass flow, probes. These locations are the seismically strengthened area of Building 251, Building 331, Building 332, and Building 801A exhausts. Stack flow rate is measured every few seconds and the average rate is calculated and recorded every two hours. Effluent volume is calculated by integration of these data over time.

3.4 Procedures for Laboratory Analysis

Air effluent samples are processed and analyzed by the Hazards Control Department (HCD) Radiological Measurements Laboratory (RML) and Hazards Control Analytical Laboratory (HCAL).

3.4.1 Sample Preservation and Handling

Filter samples submitted to HCAL are stored in glassine bags. No special preservation techniques are necessary for air effluent samples.

Before samples are submitted to the HCD safety laboratories (HCAL and RML), they are logged into the HCD sample tracking and receiving (STAR) computer system by the EPD sampling technologists or by the ES&H technicians. Information provided at login includes field identification number, origin, sample type, and the required analyses. The HCD safety laboratories are locked at all times. Samples received by HCAL are stored in a specially designated area that includes separate storage for incompatible samples and for volatile or unstable compounds. All personnel delivering samples to the RML are trained in contamination control and taught to segregate any samples with potentially unusual activity.

3.4.2 Analytical Methods and Calibration

3.4.2.1 Gross Alpha and Gross Beta on Air Effluent Filter Samples

Methods used for the analysis of air effluent filter samples conform to the requirements of 40 CFR 61, Method 114, specifically:

- 3.1.4–Method A-4 for gross alpha determination
- 3.3.2–Method B-4 for gross beta determination
- 3.5.1 for alpha counting using gas flow proportional counters
- 3.5.2 for beta counting by scintillation counters

Gross alpha and gross beta activity from particles collected on the air filters is detected with gas flow proportional counters. Samples are not analyzed until at least 4 days after sampling to allow for the decay of naturally occurring radon daughters. To verify the operation of the counting system, calibration sources as well as background samples are intermixed with the sample filters for analysis. Laboratory blanks constitute at least 10 percent of analyses and serve as indicators of cross-contamination within the counters. Sample handling, equipment operation, and calibration are performed according to RML procedures documented in the *Radiological Measurements Laboratory Gross Alpha-Beta Procedures Manual* (HCD 2000a).

3.4.2.2 Molecular Sieve Samplers for Tritium

Molecular sieves are prepared for counting by the HCAL. The sieves are installed in a recovery system where tritiated water is baked out and collected in cold traps according to a written procedure, *Recovery of Tritiated Water from Molecular Sieve Stack Samples* (HCD 2000c). The water

collected is forwarded to the RML, where the samples are counted by liquid scintillation techniques (*Liquid Scintillation Counting Procedures Manual* [HCD 2000b]).

3.4.2.3 Calibration

Equipment in the HCAL and the RML is calibrated with sources that are traceable to National Institute for Standards and Technology (NIST). Calibration follows a variety of methods from calibration by a certified third party (as is done for laboratory balances), to calibration with known standards that are made from traceable materials (as is done for metals and most radiological analyses). Calibration practices are in accordance with standard procedures and are evaluated during audits required for maintenance of certifications.

The HCD Safety Laboratory Division laboratories are part of LLNL's calibration program. Calibration records are maintained for each piece of calibrated equipment, including CAMs.

LLNL uses Eberline Alpha 3, Alpha 5/5A, and Alpha 6 CAMs for the detection of alpha activity in the form of aerosols both in the workplace and at stack locations. A membrane filter is used to collect particles from the air stream and alpha activity is detected by a 490-mm^2, solid-state detector. The instruments have pulse height discriminators for the detection of alpha activity with specific energies. Thus, much of the activity from radon progeny can be rejected, resulting in increased alarm sensitivity for radionuclides having energies near those of the radon progeny. The Hazards Control Instrument Calibration Team performs calibration of these instruments according to written procedures, including the setting of alarm points, adjustment of energy discrimination ranges, flow calibration, and leak checking for the Alpha 3, Alpha 5/5A, and Alpha 6 instruments. Instruments are tagged with stickers indicating the most recent calibration date and the next due date for calibration.

3.5 Quality Assurance

3.5.1 Quality Assurance Program

The radiological NESHAPs regulation specifies a rigorous quality assurance (QA) program for radionuclide emission measurements at DOE facilities. The *LLNL NESHAPs Quality Assurance Project Plan* (QAPP) (Hall and Biermann 2000) is a comprehensive document written specifically to address the NESHAPs requirements in Appendix B, Method 114, Section 4 of 40 CFR 61.

The air effluent quality assurance program at LLNL is a multi-organizational effort that relies on the EPD and HCD support organizations and LLNL facilities that have air effluent monitoring systems. The QAPP describes the organizational structure of the air effluent monitoring program as well as sample collection and analysis procedures, sampling site locations, sampling rationale, sampling systems, effluent flow rate measurements, sample

tracking system, and reporting. Documents relevant to the monitoring program, such as facility safety plans (FSPs), safety analysis reports (SARs), QA manuals, and laboratory and analysis procedures have been collected and are appropriately referenced in the QAPP. Because the sampling program is multi-organizational, several NESHAPs Agreement of Roles and Responsibilities (NARRs) between EPD, HCD, and the facilities and/or programs have been implemented to specify the responsibilities of the organizations regarding air effluent sampling. These responsibilities include provisions for guidance and review of air sampling system design, sampling procedures and schedules; the installation of new air effluent sampling systems (when required); fiscal support for sampling efforts; maintenance and repair of sampling systems; sampling and calibration activities; sample tracking and analysis; data management and review; and reporting.

FSPs, SARs, and QA manuals for each monitored facility describe its organizational structure, responsibilities for sampling locations used for continuous air monitoring, and procedures to be followed in the case of unplanned radionuclide releases. For example, the FSP for the Plutonium Facility describes in detail the procedure for responding to detection of radioactive materials in a release from the stacks. These documents also describe the sampling collection systems for both CAM alarm and simple filter-type air monitoring systems, including sampling probes, procedures to be used on measuring flow rates, and sampling and calibration procedures.

HCD's Radiation Measurements Laboratory QA program describes laboratory analysis procedures; precision, accuracy and completeness objectives; sample tracking procedures; quality control sampling; sample handling; and data reporting. For example, its *Radiological Measurements Laboratory Gross Alpha-Beta Procedures Manual* (HCD 2000a) describes operational procedures for analyzing the air sample filters for radioactivity. RML participates in the EPA Environmental Radioactivity Laboratory Intercomparison Studies Program on a quarterly basis as well as in comparison studies with the DOE Environmental Measurements Laboratory and Oak Ridge National Laboratory.

EPD, under whose auspices radiological NESHAPs modeling and reporting are conducted, also operates under a quality assurance management plan (QAMP) and associated procedures. Specifically, the TAMM Group, which operates under the *Environmental Protection Department Quality Assurance Management Plan* (Merrigan 2001), is responsible for modeling and reporting radionuclide emissions for the purpose of evaluating radiological NESHAPs compliance. Detailed records are kept of all measurements and radiological usage inventory forms, as well as dispersion and dose assessment modeling results. Selected modeling results are validated by having a separate individual re-evaluate sources, beginning with the inventory process and finishing with the modeling process. All NESHAPs calculations are archived with the

supporting information used to make them. Air effluent sampling results are maintained in an electronic database (see Chapter 14).

3.5.2 Data Quality Objectives

The NESHAPs QAPP (Hall and Biermann 2000) specifies required levels of sample completeness and analytical lower limits of detection. Within the context of NESHAPs, completeness applies both to sampling systems and to laboratory analyses of environmental samples. For the continuous stack samplers (simple filter-type and molecular sieves), TAMM requires 80 percent completeness of sample collection. That is, over all monitored facilities, samplers must be operational for at least 80 percent of the sampling period. With respect to laboratory analyses, TAMM requires that 90 percent of the samples submitted to, and analyzed by, the HCD laboratories yield valid data. The QAPP also specifies that the radionuclide sampling collection systems and analyses have lower limits of detection meeting the levels of the derived concentration guides (DCGs) in DOE Order 5400.5.

3.6 Program Implementation Procedures

EPD is responsible for the LLNL air effluent monitoring program; however, implementation of the program relies strongly on participation by facilities, programs, and HCD.

3.6.1 Evaluation of the Need for Air Effluent Sampling

LLNL complies with radiological NESHAPs requirements by performing annual assessments on the need for new sampling locations. These evaluations are performed by the TAMM Group in EPD. Each assessment addresses LLNL air emission points and diffuse sources that have the potential to discharge radionuclides to the atmosphere. To update radionuclide inventories and operations, as well as stack information, inventory forms and appropriate guidance are sent to Livermore site facilities and Site 300. These forms are completed by experimenters, certified by facility managers, and returned to EPD for dispersion and dose-assessment modeling with EPA-mandated codes. The potential EDEs to members of the public are calculated and indicate if any additional discharge points require monitoring.

In addition to the annual assessment process, EPD is notified when new or modified operations or facilities are planned. Currently, the Environmental Evaluations Group (EEG) of EPD, which conducts reviews for compliance with the National Environmental Policy Act, notifies the TAMM Group of proposed new or modified operations. In addition, TAMM has representatives on the Environmental Support Teams (ESTs) (see Chapter 1) that routinely discuss environmental issues and are integrated with the HCD Environment, Safety and Health Teams. TAMM continues to refine mechanisms to ensure that it is informed whenever new

operations are proposed, significant changes in radionuclide inventories occur, or existing operations are modified so that a NESHAPs evaluation can be performed and appropriate action taken. These actions may include installation of effluent monitoring systems in stack exhausts and the establishment of memoranda of understanding with LLNL facilities and/or programs.

3.6.2 Air Sampling

Collection and replacement of air filters for the sampling of particulate radionuclides is performed by the HCD environment, safety, and health (ES&H) technician assigned to the facility. After removing each air sample filter from its sample holder, the ES&H technician places each air sample filter in a glassine bag for subsequent handling and routing to RML. Care is taken to avoid cross-contamination between samples. The ES&H technician labels each sample bag with the sample location, tags the bag with a unique bar code, and logs the sample into the HCD sample tracking and receiving (STAR) computer system. The STAR system follows the samples through the submittal, receipt, and analysis processes. Air filter samples are submitted to RML where they are analyzed for gross alpha and gross beta activity. Because air effluent monitoring is the joint responsibility of EPD, HCD, and the programs/facilities, procedures for its implementation are found as field instructions in the Environmental Section of the facility *Environmental, Safety, and Health Discipline Action Plans* (DAPs). These procedures specify the frequency of filter exchange for the filter-type stack samplers and calibration of sampler flow rate. TAMM environmental analysts are responsible for the drafting and revision of procedures, and EPD's Environmental Operations Group (EOG) analyst for the facility places the DAPs in the facility DAP and ensures that they are implemented.

Collection and replacement of the molecular sieves from the tritium samplers in Building 331 are also performed by a HCD ES&H technician. Instructions in the Building 331 DAP specify the change frequency of the molecular sieve samplers and call for the verification of flow rates and operating pressures on a daily basis to ensure proper operation of the HT/HTO sampling system. As with the filter samples, the sieve samplers are labeled, identified with a bar code, and logged into the STAR system. The molecular sieves are then submitted to the HCAL for water extraction and then passed to RML for scintillation counting.

Operation and maintenance of the two special low-volume ambient air samplers (**Section 3.3.3.7**) is performed by the Technical Support Group (TSG) of EPD's Operational and Regulatory Affairs Division (ORAD). The procedure that describes the operation is EMP-AP-LV, *Low-Volume Radiological Air Particulate Sampling*.

Analytical results of the air effluent samples are reported by the analytical labs to the HCD health physicist assigned to the facility and the responsible environmental analyst in TAMM. Air effluent results are also retained in the air effluent database in ORAD. Results for the two special low-volume ambient air samplers are only reported to the TAMM environmental analyst. The procedure EMP-AE-DAM, *Air Effluent Data Analysis and Management*, describes the methods used to manage and analyze the data.

3.6.3 Effluent Flow Measurement

Effluent flow is determined by measurement of the velocity of the effluent exiting from a discharge point and its cross-sectional area. The procedure EMP-AE-SF, *Air Effluent Stack Flow Measurement,* describes the methods used to measure gas velocity and the calculation of flow rate from a discharge point. At exhaust points having permanent mass flow probes, calibration of the probes is performed in accordance with the procedure EMP-AE-MFC, *Air Effluent Stack Mass Flow Probe Calibration*. Data from the mass flow probes are recorded on electronic data cards in the field. The procedure EMP-AE-SFDR, *Air Effluent Stack Flow Data Retrieval,* provides detailed instructions for downloading data from the electronic data cards. Effluent flow measurement, probe calibration, and data retrieval from the mass flow probes is the responsibility of EPD's TAMM Group.

3.7 Action Levels

3.7.1 Air Filter Samples

For particulate monitoring, the HCD health physicist for the affected facility is notified immediately by RML in cases where gross alpha activity concentration in the air effluent from a discharge point exceeds 3.7×10^{-3} Bq/m^3 (1×10^{-13} μCi/mL) or where the gross beta activity exceeds 3.7×10^{-1} Bq/m^3 (1×10^{-11} μCi/mL). Such cases may warrant further investigation of the sample, such as verification of location, sample volume, comparison with past data, reanalysis, and identification of the specific radionuclides present.

In addition, the EPD TAMM Group has established a notification level for the gross alpha and beta activity concentration as measured by the air filter samplers. The level is based on a dose to a member of the public receiving 1 mrem/y, or 10 percent of the NESHAPs regulatory standard, assuming that the level was released throughout the entire year. Since the estimation of dose is dependent on many parameters, not the least of which is the radiological material having the potential for emission, conservative assumptions were made and resulted in a notification level for gross alpha and beta activity of 3.7×10^{-1} Bq/m^3 (1×10^{-11} μCi/mL). For air filter samples having confirmed results greater than these concentrations, EPD and the facility management are notified. If consecutive results continue to be above the notification

level, EPD works with the facility to determine the source and possibly implement better controls.

3.7.2 Building 331 Tritium Monitoring

The ion chambers monitoring the stack exhausts of the Tritium Facility (Building 331) have both low and high alarm settings. High alarm conditions, corresponding to either an instantaneous release having a concentration greater than 6×10^{-3} TBq/m^3 (10 Ci/m^3) or an integrated release greater than of 33 TBq (900 Ci) in 15 minutes, are reported at the facility and the LLNL Sitewide Alarm System Emergency Dispatch Center. Low alarm conditions, corresponding to either an instantaneous release having a concentration greater than 6×10^{-4} TBq/m^3 (1 Ci/m^3) or an integrated release greater than of 3.3 TBq (90 Ci) in 15 minutes, are reported at the facility. Responses by facility personnel to these alarms, as well as to room alarms, are detailed in the Building 331 FSP. In addition to the alarm conditions, the Facility Manager is notified if there is a planned, unplanned, or suspected tritium release of 5 Ci or more in a 24 hour period.

In addition to the action levels in place at the facility, the EPD TAMM Group notifies EPD and Building 331 management if stack emissions exceed 3.7×10^5 Bq/m^3 (1×10^{-5} μCi/mL) as measured by the molecular sieve samplers. This action level is based on a dose to a member of the public receiving 1 mrem/y or more, assuming emissions at or above the notification level continued for the entire year. As with particulate emissions, if results continue to be above the action level, EPD works with the facility to determine the source.

3.8 Preparation and Disposition of Reports

The TAMM Group is responsible for the reporting of air effluent radionuclide emissions. Radionuclide emissions are reported in the annual *Environmental Report* (e.g., Biermann et al. 2001) and in the *LLNL NESHAPs Annual Report* (e.g., Gallegos et al. 2001) to DOE and EPA, respectively. Additionally, the *LLNL NESHAPs Annual Report* includes the estimated potential emissions from all facilities whose operations have the potential to release radionuclides to the atmosphere; and hence, it documents if there is need for additional effluent sampling systems. Because tritium emissions from the Tritium Facility are the major source of atmospheric radionuclide releases, a summary report of emissions is provided to the Tritium Facility manager quarterly.

3.9 Future Plans

In the near future, the EPD TAMM Group will focus on improvements in the quality assurance area. The group will update the radiological *NESHAPs Quality Assurance Project Plan* (QAPP) (Hall and Biermann 2000). The QAPP addresses NESHAPs (40 CFR 61 Subpart H) requirements and provides details of the air effluent sampling systems with regard to the regulations.

Secondly, the group will establish additional data quality objectives (DQOs) by setting precision and accuracy values for the air effluent sampling network.

In the Heavy Element Facility (Building 251), TAMM deactivated 16 sampling systems in 1999. In 2001, four more sampling systems were deactivated and one was deactivated in early 2002. Nine systems are scheduled to be deactivated in early 2003. Air samplers to be deactivated are currently sampling from ventilation systems that are no longer in use or that exhaust work areas where radiological materials are no longer used.

TAMM also intends to deactivate the air effluent sampling system in Building 177 when the decontamination and decommissioning of the facility is complete. This is currently scheduled for early 2002.

TAMM will continue to review the need for air effluent sampling from all facilities including new facilities and existing facilities having new and/or modified operations.

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4 Meteorological Monitoring

Brent M. Bowen

4.1 Introduction

Meteorological data are used to demonstrate compliance with federal, state, and local laws, regulations, and orders. U.S. Department of Energy (DOE) directives require Lawrence Livermore National Laboratory (LLNL) to collect sufficient meteorological data to assess the impact of hazardous and radiological material releases on the environment and the public. Onsite meteorological monitoring is required to accurately assess the transport and diffusion of airborne materials and the impacts of planned and unplanned airborne releases on the public health. In addition, Laboratory personnel use meteorological data in the design of new facilities and in scheduling experiments and operations.

4.2 Rationale and Design Criteria

4.2.1 Regulatory Drivers

The regulatory drivers for meteorological monitoring are the applicable portions of DOE Orders 5400.1 and 5400.5. These orders and the associated regulatory guide, EH-0173T (DOE 1991a) require each DOE site to have a meteorological program that is appropriate to the site's activities, topography, and distance to critical receptors. Meteorological measurements must be representative of the conditions that determine transport and dispersion at the site. Furthermore, in accordance with WSS B180, LLNL will comply with DOE Order 151.1 Chg 2 (DOE 1996), whereby real-time meteorological data must be available to assess adequately the actual or potential onsite and offsite consequences of an emergency.

DOE Order 5400.1 requires DOE sites to have onsite programs that can provide the data used to perform the required dose calculations specified in Title 40 of the *Code of Federal Regulations* (CFR), Part 61 Subpart H, *National Emission Standards for Hazardous Air Pollutants (NESHAPs), Standards for Radionuclides*, which states:

> Compliance with this standard will be determined by calculating the dose to members of the public at the point of maximum annual air concentration in an unrestricted area where any member of the public resides or abides.

The U.S. Environmental Protection Agency (EPA) requires the use of mandated computer models (CFR 1998) to demonstrate compliance with 40 CFR Part 61 Subpart H. LLNL's primary calculation tool for the estimation of dose and risk is the computer model CAP88-PC, developed by EPA's Office of Radiation Programs (Parks 1992). The meteorological input to CAP88-PC consists of:

- Joint-frequency distribution of wind direction and atmospheric stability class
- Average wind speed for each combination of wind direction and stability class
- Mixing-layer depth
- Annual-average ambient air temperature
- Annual rainfall

Meteorological information can also be used to assess the potential consequences of projected airborne releases of contaminants from new or modified facilities as well as the consequences of actual accidental releases. Data from both the Livermore site and Site 300 are continuously made available to the LLNL Emergency Operations Center (EOC) and the Environmental and Hazards Control Operation Support Centers (OSCs) for input to local and LLNL's Atmospheric Release Advisory Capability (ARAC; Sullivan et al. 1993) transport and dispersion models.

Offsite meteorological data, such as the data collected at National Weather Service (NWS) stations, may be used if the meteorological conditions at the NWS station are similar to onsite conditions. However, meteorological conditions at the NWS station closest to LLNL (i.e., the Oakland Airport) do not accurately represent dispersion conditions at the Livermore site or Site 300. Moreover, retrieving data in a timely manner from offsite meteorological stations may be difficult during emergencies. For these reasons among others, LLNL employs meteorological monitoring systems at both the Livermore site and Site 300.

LLNL maintains a quality assurance (QA) program for its meteorological stations that meets the performance requirements set by DOE and EPA (Chapter 13).

LLNL's meteorological monitoring also reflects the guidance for assessing the validity of meteorological data and the accuracy of meteorological measurement systems contained in Volume IV of EPA's *Quality Assurance Handbook for Air Pollution Measurements* (EPA 1990).

4.2.2 Uses of Onsite Meteorological Data

The legitimate uses of meteorological data go beyond support of environmental monitoring activities as described in the Work Smart Standards. Various projects require meteorological

monitoring and they should not be expected to recreate the monitoring systems currently in place at LLNL. Therefore, it is good business practice for LLNL to centralize ambient meteorological monitoring and make the data available to all. Several DOE orders suggest some of the possible uses for meteorological data.

DOE Order 6430.1 (DOE 1989), describes the use of meteorological data to aid in identifying conditions that may influence the design and operation of a facility. Temperature and humidity data can be used to plan efficient air conditioning and space heating of proposed facilities. Hood exhaust re-entrainment and building-wake effects can be modeled using wind-flow data provided by onsite monitoring. Designers often use meteorological data when they plan air handling systems and exhausts for new facilities. EPA also provides guidance for exhaust stack design in its *Guideline for Determination of Good Engineering Practice Stack Height* (EPA 1985).

Onsite programs and offsite groups frequently request meteorological data for various projects. For example, the local air regulatory agency, Bay Area Air Quality Management District (BAAQMD), has requested LLNL's meteorological data to use in its regional models of airflow. Meteorological data are also used to support fire-fighting operations and to estimate the electrical load of individual buildings and the site as a whole. Discomfort indexes based on measured temperature and humidity are used to manage or limit physical work outside during the summer season.

DOE Order 4320.1 (DOE 1991b) encourages facility personnel to utilize onsite meteorological data in site development planning, including data on such conditions as winds, temperature, probabilities and intensities of severe storms, tornadoes, and prolonged rainy and dry seasons. In its site planning, LLNL considers natural hazards, such as strong winds, hurricanes, tornadoes, hail, lightning, and snow. LLNL's meteorological database includes expected annual ranges and distributions of wind direction and wind speed, temperature, stability, joint frequency of wind direction and speed and stability, water vapor, and joint frequency of temperature and specific humidity in accordance with DOE Order 1324.2 (DOE 1987).

All uses of the meteorological database comply with EPA guidance established in *Guideline for Fluid Modeling of Atmospheric Diffusion* (EPA 1981), *Ambient Air Monitoring Guidelines for Prevention of Significant Deterioration* (EPA 1987), and *Meteorological Monitoring Guidance for Regulatory Modeling Applications* (EPA 2000).

4.2.3 Atmospheric Dispersion Modeling

Atmospheric dispersion calculations range in complexity from very simple analytical expressions that require little or no meteorological data, to complex supercomputer models that accept extensive data sets. EPA describes its preferred computer models in *Guideline on Air*

Quality Models (EPA 1997). *Handbook on Atmospheric Diffusion* (Hanna et al. 1982) is another good source of dispersion models. The dispersion model selected should be appropriate for the site and the application. In addition, the assumptions upon which a dispersion model is based should be reasonable, completely documented, and scientifically defensible. The dispersion model should be realistic and be appropriate for the scale of problem.

All data used in these models should be from the appropriate time period. For example, if a proposed experiment has the potential for a release during the daytime, then the probability tables and wind roses that are to be used with the model should include meteorological data taken exclusively during the daytime.

4.3 Extent and Frequency of Monitoring and Measurements

4.3.1 General Pattern of Wind

The wind at LLNL is strongly influenced by the land/sea breeze and the orientation of the Livermore Valley (Gouveia and Chapman 1989). The wind comes from the southwest quadrant more than 50 percent of the time. This surface flow pattern can be enhanced or weakened by large-scale, upper-air circulation. The meteorology at Site 300, while generally similar to the Livermore site, is modified by the higher elevation, the greater distance from the ocean, and the greater topographical relief.

During the summer, differential heating between the ocean and land produces afternoon winds that generally are stronger than morning and nighttime winds. A strong, upper-air, high-pressure circulation frequently occurs, suppressing the advection and formation of high clouds. The result is warm, dry weather during the summers with a persistent diurnal cycle of winds.

Because differential heating is less during winter than in summer, the sea breeze in winter is less pronounced. The winters commonly feature long periods of weak winds separated by short episodes of strong winds that are associated with winter storms. The winds are generally from the south to southwest during a storm and from the northwest to north after the storm passes. During the periods of weak, synoptic-scale winds, cold air drainage may occur during the night. The cold air that reaches the Livermore site is drained from the hills to the east.

4.3.2 Required Meteorological Measurements

Meteorological data are used as input to dispersion models (e.g., CAP88-PC). Measurements of the local meteorological conditions must include horizontal wind speed and direction, atmospheric stability, air temperature, and rainfall rate. Atmospheric stability can be estimated, following a procedure in Section 6 of *Meteorological Monitoring Guidance for Regulatory Modeling Applications* (EPA 2000), using time of day, wind speed, and sigma theta (the standard deviation

of the wind-vane position). Another approved stability algorithm, solar radiation delta T (SRDT), uses data from a pyranometer (which measures incoming solar radiation) and thermistors at two tower heights (which measure temperature [delta T]). LLNL will start using the preferred SRDT method to estimate stability after tower upgrades are completed in 2003. Upgrades include the installation of a pyranometer and lower-level thermistor at Site 300 and more accurate thermistors at both the Livermore site and Site 300.

Data provided by the wind direction vane are used to determine sigma theta using the algorithm presented in Yamartino (1984). The calculation of sigma theta requires a minimum of 180 samples of the wind-vane position.

4.3.3 Accuracy of Monitoring Measurements

The accuracies of the monitoring measurements should be consistent with the specifications set forth in either:

- American National Standard for Determining Meteorological Information at Nuclear Power Sites, ANSI-2.5-1984, published by the American National Standards Institute (ANSI 1984)
- Guidance provided by EPA if it recommends more stringent specifications

Table 4-1 shows the pertinent standards of accuracy for meteorological systems.

Table 4-1. Standards of accuracy of meteorological parameters

Parameter	Standard of accuracy
Wind direction	±5° azimuth with a starting threshold of 0.5 m/s. The delay distance[a] must not exceed 2 m, and the damping ratio must be between 0.4 and 0.6.
Wind speed	±0.2 m/s for speeds less than 2.2 m/s; within 5 percent for speeds of 2.2 m/s or greater; the starting speed must be 0.5 m/s or less.
Temperature	±0.5°C
Delta temperature	±0.1°C
Relative humidity	±10 percent
Dew point temperature	±1.5°C
Solar radiation	±5 percent of observed
Precipitation	±10 percent of observed
Pressure	±3 mb
Time	±5 min

a The delay distance is the length of air, at any wind speed, that must pass through a wind vane during the time it takes the vane to return to 50% of the initial displacement.

Because of EPA guidance and the large frequency of wind speeds below 0.5 m/s at the Livermore site, a more stringent anemometer specification for starting speed of less than 0.25 m/s is used. Low wind speed threshold wind instruments (vane and anemometer) will also be installed at Site 300 during 2003.

All meteorological instruments must be capable of continuous operation in the expected range of atmospheric conditions at the Livermore site and Site 300. Because of the relatively mild weather conditions in the Livermore area, most meteorological instruments that are designed for routine measurement meet this requirement. Sensors installed at Site 300, especially anemometers, must be checked frequently because of more frequent strong winds at the site.

4.3.4 Locations of Monitoring Sites

Important considerations in choosing a meteorological monitoring site include siting and exposure of meteorological instruments and towers (EPA 2000), local conditions, and obstructions. Meteorological monitoring sites should be located in areas that have atmospheric conditions similar to those into which any material potentially would be released. The monitoring location should be away from the influence of manmade and natural obstructions, such as buildings and trees. The onsite meteorological towers at the Livermore site and at Site 300 have been located with these considerations in mind. The location of the Livermore site meteorological tower is shown on **Figure 3-1**. The location of the Site 300 meteorological tower is the same as the air sampling location ECP shown in **Figure 5-3**.

To minimize the tower's influence on wind measurements, wind and temperature instruments have been mounted on booms extending more than two tower widths from the side of the meteorological tower. They are mounted on the west side of the tower, facing the prevailing wind. Wind and temperature measurements are made at the standard height of 10 m, and additional measurements are made at a height of 40 m to evaluate potential releases from 30-m stacks at the Livermore site. A hygrometer at the 10-m level measures relative humidity and allows calculations of other humidity variables (dew point, absolute humidity, etc.) using simultaneous temperature measurements. An additional temperature sensor is on the Livermore site tower at the standard 2-m height.

Solar radiation is measured at the Livermore site in a location that is free of any obstruction to the measurement and away from light-colored walls or artificial sources of radiation.

Both the Livermore site and Site 300 systems include rain gauges. These gauges are mounted on stable platforms and are adjusted so that their openings are horizontal. They are at least 30 cm above the ground to prevent surface water splash into the gauges and are shielded from the wind.

A barometer is currently deployed at Site 300. The inlet port of the barometer is protected from wind effects. The barometer reading is reduced to sea level (RSL) to be consistent with regional RSL reports. However, starting in 2003, actual atmospheric pressure will be measured, with estimates of RSL available on the LLNL weather website. Actual pressure is preferred to allow LLNL personnel to directly use pressure data without conversion. The installation of a barometer is also planned at the Livermore site in 2003.

4.3.5 Frequency of Sampling

LLNL's data loggers poll all meteorological instruments at the shortest, practical time interval. This interval is 10 seconds or less for the anemometers, and 1 minute or less for the thermistors and pyranometer. The time period represented by the averages should not be less than 10 minutes (EPA 2000); the LLNL data loggers collect 15-minute averages of all meteorological parameters. The loggers' averaged values are saved for automatic retrieval, which is conducted minutes after the sampling period (**Section 4.5.2**).

4.4 Quality Assurance Requirements

Regulatory drivers for quality assurance of LLNL's monitoring programs come from DOE Order 414.1A (WSS B89). The primary guidance for quality assurance of LLNL's meteorological monitoring program is contained in the comprehensive EPA document prepared by Thomas Lockhart (EPA 1990).

A meteorologist reviews the meteorological data at least once every working day. Periods of missing data are noted and investigated. The EPD database automatically checks the reported values for reasonableness and proper format, and compares captured values with expected values or a range of values. The limits used in the screening test are based upon historical data or physically realistic values. Another screening test, called the rate of change test, compares the difference between data of adjacent time periods. **Table 4-2** lists meteorological data screening criteria.

Selected data are compared to other available, reliable data. In addition, monthly averages are compared with climatological norms.

Major problems with the meteorological instruments or data are noted in nonconformance reports (NCRs) as specified in Chapter 13. Appropriate procedures are followed to alleviate the problem, and the NCR is concluded with an explanation of the corrective action taken.

Replacement of questionable data is done carefully and only when large blocks of contiguous data are involved. When available, data from another level of the same tower may be used with the proper adjustments for the magnitude of the wind speed or temperature. When data from

the same tower are not available or reliable, representative offsite meteorological data from a nearby tower may be used. This approach works best for temperature, relative humidity, and solar radiation. Wind speed and direction can vary greatly with increasing distance, so offsite data may not be suitable for replacement.

Table 4-2. Meteorological data screening criteria

Meteorological variable	Screening criteria: flag the data if the value
Wind speed	• is less than zero or greater than 20 m/s • does not vary by more than 0.1 m/s for 3 consecutive hours • does not vary by more than 0.5 m/s for 12 consecutive hours
Wind direction	• is less than zero or greater than 360° • does not vary by more than 1° for more than 3 consecutive hours • does not vary by more than 10° for more than 18 consecutive hours
Temperature	• is greater than the record high • is less than the record low • is greater than a 5°C change from the previous hour • does not vary by more than 0.5°C for more than 12 consecutive hours
Vertical temperature difference	• is greater than 0.1°C/m during the daytime • is less than –0.1°C/m during the nighttime
Precipitation	• is greater than 2.5 mm (0.1 in.) in 15 minutes • is greater than 25 mm (1 in.) in 1 hour • is greater than 100 mm (4 in.) in 24 hours • is less than 50 mm (2 in.) in the rainy months
Solar radiation	• is greater than zero at night • is less than zero • is greater than the maximum possible for the date and latitude

4.5 Program Implementation

4.5.1 System Description

Meteorological instruments in use at LLNL are specified in procedure EMP-M-MCA, *Meteorological System Maintenance and Sensor Calibration*. The anemometers currently used are cup-and-vane style, the temperature sensors are precision thermistors, the relative humidity instruments are variable capacitance units, the pyranometer is a photocell, and the rain gauges are tipping buckets.

The instruments currently on the Livermore site meteorological towers meet or exceed the performance standards of accuracy identified in **Table 4-1.** The instruments at Site 300 meet or

exceed the standards except for starting speed and wind-vane damping distance. A new wind vane and anemometer that exceed the performance standards will be installed at Site 300 in 2003.

The temperature sensors are currently placed in fan-aspirated radiation shields. These shields are adequate for measuring absolute temperature and vertical temperature differences, provided a sufficiently accurate sensor is used.

Routine inspection, scheduled maintenance, and calibration of the meteorological instrumentation and data acquisition system meet the manufacturer's recommendations and are conducted in accordance with LLNL procedure EMP-M-MCA, *Meteorological System Maintenance and Sensor Calibration*. Calibrations and audits are performed at least annually, alternating between calibrations and audits. Calibrations are also performed when problems are found or instruments switched out. The logs of inspections, maintenance, and calibrations are maintained as permanent records, allowing routine inspection of current data.

Regular and frequent routine operational checks of the monitoring system are performed to ensure high data-retrieval rates. These include visual inspections of the instruments for signs of damage or wear, inspections of the recording devices to ensure correct operation and reasonableness of data, and periodic preventive maintenance measures. The latter includes periodic checks of wind speed and direction bearing assemblies, cleaning of aspirated shield screen in temperature systems, clearing the precipitation-gauge funnel of any obstructing debris, and frequent cleaning of the optical surface of the radiometer.

A 48-hour battery backup ensures continuous operation of the ARAC site system computer so that it will download data from the meteorological towers even if AC power is lost. Although lightning storms are infrequent at LLNL, the meteorological tower and associated systems are protected from lightning strikes with grounding spikes. Other phenomena that may deteriorate performance, such as icing and sea spray, are not problems at either the Livermore site or Site 300.

4.5.2 Data Inspection and Transfer

LLNL's meteorological system is designed to provide data recovery of at least 90 percent on an annual basis. Based on guidance in meteorological data collection, processing, and archiving (Crutcher 1984; EPA 1990), LLNL's meteorological system provides 15-minute averages of all measured quantities to dispersion models used in response to emergency situations. Instruments are polled more than 30 times over the 15-minute averaging period to provide adequate statistical representation of conditions.

A Laboratory meteorologist or environmental analyst reviews the data every working day. Files of 15-minute averages are saved in the ARAC site system computer. Each file contains an entire day's data. Each file is uniquely identified with the site name, year, month, and date. Each month, meteorological data are electronically transferred from the web page database to a desktop computer. Further data inspection, reduction, and analyses are performed on the PC.

The 15-minute averages are combined into hourly averages, following guidelines in Section 6 of *Meteorological Monitoring Guidance* (EPA 2000). The hourly averages are used to establish local climatology data, detect problems with the instrumentation and data acquisition, and provide frequency of occurrence tables of dispersion parameters for input to dose models. One-hour averages of all measured quantities are generally considered adequate to assess the consequences of potential releases and to demonstrate compliance with regulatory requirements.

4.5.3 Computed Parameters

Several useful parameters can be computed from the meteorological data, including diffusion coefficients and boundary-layer parameters. Diffusion coefficients (sigma y and sigma z) are used to quantify the spread of plumes in Gaussian and trajectory models. These coefficients can be estimated from the atmospheric stability class and from the time that has elapsed since a release. Gifford (1976) and Hanna et al. (1977) discuss various methods for determining diffusion coefficients. Section 6 of *Meteorological Monitoring Guidance* (EPA 2000) describes the computation of atmospheric stability by EPA's alternate algorithm based on sigma theta, wind speed, and time of day. This algorithm is called the Modified Sigma Theta method and is completely described in Mitchell and Timbre (1979) and Mitchell (1982).

EPA has adopted another stability calculation scheme (SRDT) that is based on incoming solar radiation, wind speed, and vertical temperature difference. Instruments will be installed in 2003 to allow routine use of the SRDT method.

Calculating boundary-layer parameters, such as sensible and latent heat flux, require accurate temperature and wind speed measurements taken at multiple levels. These parameters are related to atmospheric stability, temperature tendency, soil moisture flux, and mixing depth among others. Installation of a sonic anemometer and two levels of accurate hygrometers in 2003 will allow estimation of sensible and latent heat flux, respectively, at LLNL. A ground heat flux plate and soil moisture sensor will also be installed just under the soil surface at LLNL in order to estimate ground heat flux.

Other hygrometric parameters can be calculated from LLNL meteorological data on absolute temperature and relative humidity. These parameters are useful when planning efficient air conditioning and space heating of proposed facilities.

4.5.4 Wind-Rose Diagram

The wind-rose diagram displays the frequency of winds coming from 16 compass directions and also retains information on the frequency of wind speed in each sector. Often at low winds, especially at night, wind direction becomes highly variable. At wind speeds lower than the starting threshold of the wind vane, the wind direction value is meaningless. At that time, the wind is considered to be calm, and the wind direction is undefined. The upper limit of the calm wind category should be no greater than the starting threshold of the anemometer. Winds at Site 300 are much greater than at the Livermore site, and there are very few winds below the starting threshold of the less-responsive anemometer. The wind rose derived from Site 300 data will have a higher upper limit for calm winds, but less than 2 percent of the data from this site are normally below this higher threshold.

4.5.5 Meteorological Data on the Internet

Every 15 minutes, LLNL meteorological data from the ARAC site system are added to a parallel database on a fileserver. An HTML script developed by LLNL makes the information available to end users on the World Wide Web at the address http://www-metdat.llnl.gov. Although this information is available to anyone in the world with access to the Web, the primary users are LLNL personnel. In addition, the database stores and offers access to historical meteorological data.

4.6 Preparation and Disposition of Reports

A wind rose, which is a common graphical display showing the character of winds recorded by a weather station, is generated for the Livermore site and Site 300. Reports requiring the annual wind rose include the annual *Environmental Report* [e.g., Biermann et al. 2001]) and the *LLNL NESHAPs Annual Report* (e.g., Gallegos et al. 2001).

The regulatory model, CAP88-PC, requires joint-frequency tables of wind direction, wind speed, and stability. LLNL has computer programs that transform a year of data from the archive into the tables that are used as meteorological input to the CAP88-PC code. These programs are described in procedure EMP-M-D *Meteorological Data Management and Analysis*.

4.7 Future Plans

Future meteorological monitoring includes an expanded program of internal comparisons of measured and computed parameters, and comparisons with LLNL's climatology to other sources of meteorological data. For example, guidance related to meteorological measurements and meteorological data processing in the *Quality Assurance Handbook for Air Pollution Measurements Systems* (EPA 1990), will be the basis for determining and examining appropriate comparison data and computations.

LLNL's meteorological monitoring will be evaluated for enhancement by the addition of supplementary locations for additional meteorological instruments at the Livermore site and Site 300. The distance from a potential source to the site boundary and the topographic setting of the site are factors that will be considered when making this evaluation.

LLNL's current meteorological system does not directly measure vertical (or convective) turbulence. Vertical propellers will be installed at both levels at the Livermore site and at Site 300 during 2003 in order to measure vertical wind and the standard deviation of vertical velocity.

New data loggers will be installed at both the Livermore site and Site 300 tower sites. Two redundant PCs will be installed and located with TAMM and the Hazards Control OSC order to continuously poll tower data and forward them to the EPD server and website. This will relieve the current single-point-of-failure potential of having only one workstation and maintain access of data by the EOC in case of a power or LAN outage.

Mixing height is another common parameter used in many dispersion models and is often measured with an acoustic sounder. Adding an acoustic sounder to the monitoring system would provide data for comparison of mixing height to measured meteorological parameters, such as wind speed and vertical temperature difference. Evaluations of this technology for potential use at LLNL will be conducted.

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5 Ambient Air Monitoring

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5.1 Introduction

At a research facility like Lawrence Livermore National Laboratory (LLNL), there is a potential for emissions to the atmosphere. If released in significant amounts, various types of emissions are considered air pollutants. In general, over 100 varieties of air emissions have been identified as pollutants. Typically, air pollutants can be categorized as either particulate matter or gases. Potential air pollutants that can contribute to radiological dose or inhalation hazard from LLNL operations include radioactive particulate, tritium (radioactive, nonparticulate), and beryllium. Air can be a primary exposure pathway for human and ecological impact. In an effort to protect human health and the environment from hazardous air emissions, many federal and state environmental air quality laws, as well as U.S. Department of Energy (DOE) orders and local agency regulations, have been promulgated.

To reduce, control, and eliminate air pollutants from its operations, LLNL employs an array of engineering and administrative controls. LLNL conducts air surveillance monitoring in the environment to assess the adequacy of these controls and to determine the impact, if any, of its air pollutants on the environment. Using data obtained from air effluent monitoring (see Chapter 3) and air surveillance, LLNL-induced human-health and environmental impacts can be assessed accurately.

LLNL is not considered a major source of nonradiological pollutants that are defined under The Clean Air Act as of major concern to the environment. These pollutants, known as criteria air pollutants, include nitrogen oxides, carbon monoxide, photochemical oxidants (such as ozone), sulfur oxides, particulate matter (particles with a diameter less than or equal to 10 µm; PM_{10}) and lead. The sources of criteria pollutants from the Livermore site are surface coating operations, internal combustion engines, solvent operations, and oil- and natural-gas-fired boilers when grouped together. Sources at Site 300 include internal combustion engines, boilers, a gasoline dispensing operation, open burning, paint spray booths, drying ovens, and soil vapor extraction. Similarly, LLNL uses a variety of chemicals that are considered air toxics. In accordance with the regulatory authority of the local air districts, monitoring for both criteria pollutants and air toxics is not required. Instead, these emissions are managed through permits issued by the air districts. Periodic review of LLNL operations is performed to identify nonradiological air contaminants.

5.2 Air Particulate Monitoring Program

5.2.1 Rationale And Design Criteria

5.2.1.1 Regulatory Drivers

DOE Order 5400.1, Chapter IV, paragraph 1.a. and paragraph 5 (see WSS B93 in Appendix B) state that environmental surveillance shall be conducted to monitor the effects, if any, of DOE activities on environmental and natural resources both onsite and offsite.

Guidance for air monitoring is provided in DOE/EH-0173T (DOE 1991). This document states that it is a DOE objective that all its operations properly and accurately measure radionuclides in their effluents and in ambient environmental media. The guidance document specifies that the surveillance program should characterize the radiological conditions of the offsite environment, estimate public doses, confirm predictions of public dose based on effluent monitoring data and modeling, and provide compliance data for all applicable environmental regulations. It also states that surveillance may be necessary for legal reasons, public concerns, and state or local commitments, and "provisions *should* be made for the detection and quantification of unplanned releases of radionuclides to the environment" (DOE 1991).

According to DOE/EH-0173T, environmental monitoring during an emergency situation *should* be considered (DOE 1991). LLNL's surveillance air monitoring network is part of the EPD emergency response program (see Chapter 1). In addition, battery operated portable emergency air samplers are available for deployment. The surveillance and portable air sampling units do not provide data in real-time, but they are available if emergency sampling is needed. The sample results may be used to validate dispersion models and calculations, determine offsite effects, and determine future courses of action.

The primary radiation protection standard for members of the public, 1 mSv/y (100 mrem/y) EDE for prolonged exposure from all sources, including air emissions is established in DOE Order 5400.5 Chg. 2, Chapter II, Paragraph 1 (except 1.a.3.c. and 1.c) (see WSS B94 in Appendix B). The concentrations of radionuclides that can be inhaled continuously 365 days a year without exceeding the DOE primary radiation protection standard for the public is specified in DOE Order 5400.5 Chg. 2, Chapter III (see WSS B95 in Appendix B). Order 5400.5 also states that DOE facilities should have the capabilities, consistent with the types of operations conducted, to monitor routine and nonroutine releases and to assess doses to members of the public.

EPA has established a radiation dose standard for all radiological air emissions of 100 μSv/y (10 mrem/y)[1] effective dose equivalent (EDE) for members of the public in Code of Federal Regulations (CFR), Title 40, Part 61, Subpart (see WSS A12 in Appendix B). This dose standard is based on emissions that can contribute to human radiation doses via all pathways once released to the air. Air effluent monitoring and air surveillance monitoring can provide the actual source terms for modeling to ensure that the NESHAPs standard of 100 μSv/y (10 mrem/y) total-site EDE is not exceeded.

Bay Area Air Quality Management District (BAAQMD) Regulation 11, Rule 3, (see WSS A27 in Appendix B) establishes an ambient air concentration limit for beryllium of 0.01 $\mu g/m^3$, averaged over a 30-day period. It also requires monitoring and reporting of beryllium concentrations in air. LLNL has an agreement with BAAQMD to notify them should any location exceed the limit.

5.2.1.2 Monitoring Objectives for Air Particulates

The configuration of an air quality monitoring network involves several elements: the number of sampling/monitoring sites, their geographical location, historical wind patterns, effects of topography, and access logistics. The configuration of LLNL's air monitoring network relies on the guidance provided by DOE/EH-0173T (DOE 1991), which deals with monitoring, siting, and overall ambient air quality monitoring criteria. DOE/EH-0173T states that an air sampling network should include:

- Background or control locations (10-15 km from the site)
- Locations sited in areas where the maximum, predicted ground-level concentration from stack releases are anticipated
- Locations in the nearest community within a 15-km radius (DOE 1991)

The number of sampling locations is determined by meteorology, demography, and the magnitude of the projected doses (DOE 1991). Finally, the overall configuration of the LLNL air sampling networks are determined by monitoring objectives and the typical spatial distribution of the pollutants being monitored.

The factors (primarily climatological and topographic) typically considered in estimating an adequate network size are also involved in designing an optimum network configuration. These siting factors are discussed by Ludwig (1976). Because meteorological factors have the

[1] Doses are commonly expressed in units of millirem per year (mrem/y), millisievert per year (mSv/y), or microsievert per year (μSv/y), where 1 mrem = 0.01 mSv = 10 μSv.

greatest effects on ambient concentrations, LLNL's placement of samplers has primarily been based on the location of main emission sources, horizontal wind speed and direction, vertical distribution and mixing structure, stability, and mixing heights. Air-sampling dilution climatology—i.e., the long-term average combination of meteorological conditions that affect the interchange and dispersion of pollutants—can change over relatively large areas and long intervals of time. The details of atmospheric dispersion, mixing dilution, and geographical terrain effects are described by Pasquill (1979) and Slade (1968). These factors have influenced the selection of air sampler locations at sites near emission sources and at facility boundaries. In addition, offsite samplers are placed both upwind and downwind from LLNL. Resources, manpower, and logistics (such as availability of electrical power, access, and security) must also be considered and have often affected the selection of locations.

Air sampling should also provide adequate temporal and spatial resolution. In addition, DOE has stated that air sampling locations should be selected to represent radionuclide concentrations in the air breathed by the population surrounding LLNL (DOE 1991).

5.2.1.3 Sources and Contaminants

Plutonium and uranium are the primary particulate radionuclides of concern at the Livermore site. The major potential source for plutonium is Building 332, the Plutonium Facility. The potential source of uranium is the Building 321 Complex, where milling, shaping, and machining of depleted uranium (uranium-238) as well as other related operations occur. Other sources include:

- Many buildings in the Chemistry and Material Sciences Directorate where uranium is used or stored
- Hazardous Waste Management operations at Buildings 514 and 612 where a wide variety of radionuclides are handled
- The southeast quadrant of the Livermore site which has elevated levels of plutonium-239 in the surface soil and air (presumably from resuspension). This area is considered a diffuse source of plutonium.

At Site 300, depleted uranium (mostly uranium-238), which is used in explosive tests, is the primary particulate radionuclide of concern. Explosive tests are conducted on open-air firing tables located at Bunkers 801, 850, and 851 and at the newly constructed Contained Firing Facility (CFF). Small amounts of uranium-235 and uranium-234 that are minor components of depleted uranium are also potentially released during open-air explosive tests.

A comprehensive listing of all potential radiological emission sources can be found in any LLNL NESHAPs Annual Report (e.g., Gallegos et al. 2001).

The primary nonradiological particulate of concern is beryllium. Beryllium is mostly used in Buildings 231, 235, 241, and 321 at the Livermore site. Other buildings using small quantities of beryllium include Buildings 298, 329, and 391. Site 300 test shots may also include beryllium.

DOE defines background/control locations as 10-15 kilometers from the site, however, selecting a location that far from Site 300 places the background location in a completely different geologic formation. The Neroly geologic formation at Site 300 contains variable uranium levels that subsequently may result in variability in airborne uranium activity from resuspended soil particulate. Therefore, the background activity for Site 300 is determined from several Site 300 locations that are not likely to be affected by explosive test shots.

5.2.2 Extent and Frequency of Air Particulate Monitoring and Measurements

5.2.2.1 Collection Methods

The LLNL high-volume air particulate sampling units use 8 in. × 10 in. cellulose filter media to collect particulates. To allow continuous circulation of ambient air over the filter paper, the samplers are housed in an outdoor aluminum shelter with a peaked roof overhang. Air samples are collected at a constant flow rate of 425 liters per minute (15 CFM). The collection area of the sheet media, 406.45 cm^2, at this flow rate results a face velocity of 17.4 cm/s. This is the highest flow rate that can be maintained as the filter becomes loaded with the collected particulate material during the sampling period.

To provide and maintain the flow, the sampling units employ a brushless, variable-speed motor controlled by an electronic mass-flow sensor. The sensor adjusts motor speed/flow rate to compensate for particulate loading and barometric and temperature variations. Additionally, the units are supplied with a liquid crystal display (LCD) indicating total flow, instantaneous flow rate, and total running hours.

All sampling performed is done in accordance with the LLNL Environment, Safety, and Health Manual. Any required training and/or special concerns associated with performing this sampling are identified in the Operations and Regulatory Affairs Division (ORAD) Integration Worksheet (IWS) 2271, Technical Support Group (TSG) Environmental Monitoring Activities. Specific hazards associated with this activity and required ES&H controls are also identified in the standard operating procedure (SOP) supplement EMP-HAZ-SUP, *Hazards and Controls for Environmental Sampling*.

5.2.2.2 Radiological Particulate Monitoring

The air monitoring program at LLNL is designed to identify a problem at the lowest possible level, therefore all total suspended particles are analyzed. Particle-size distributions (PM 2.5 or PM10 analysis) are not determined because the EDE to the maximally exposed individual (MEI), using a conservative approach and measuring the total particulate material, is well below the threshold limit requiring such analyses set in DOE/EH-0173T (DOE 1991).

To monitor radiological particulates, LLNL maintains seven continuously operating hi-vol samplers on the Livermore site (**Figure 5-1**), nine in the Livermore Valley (**Figure 5-2**), eight at Site 300 and one in the City of Tracy (**Figure 5-3**). The samplers are positioned to ensure reasonable probability that any significant concentration of radiological particulate effluents of concern from LLNL operations will be detected.

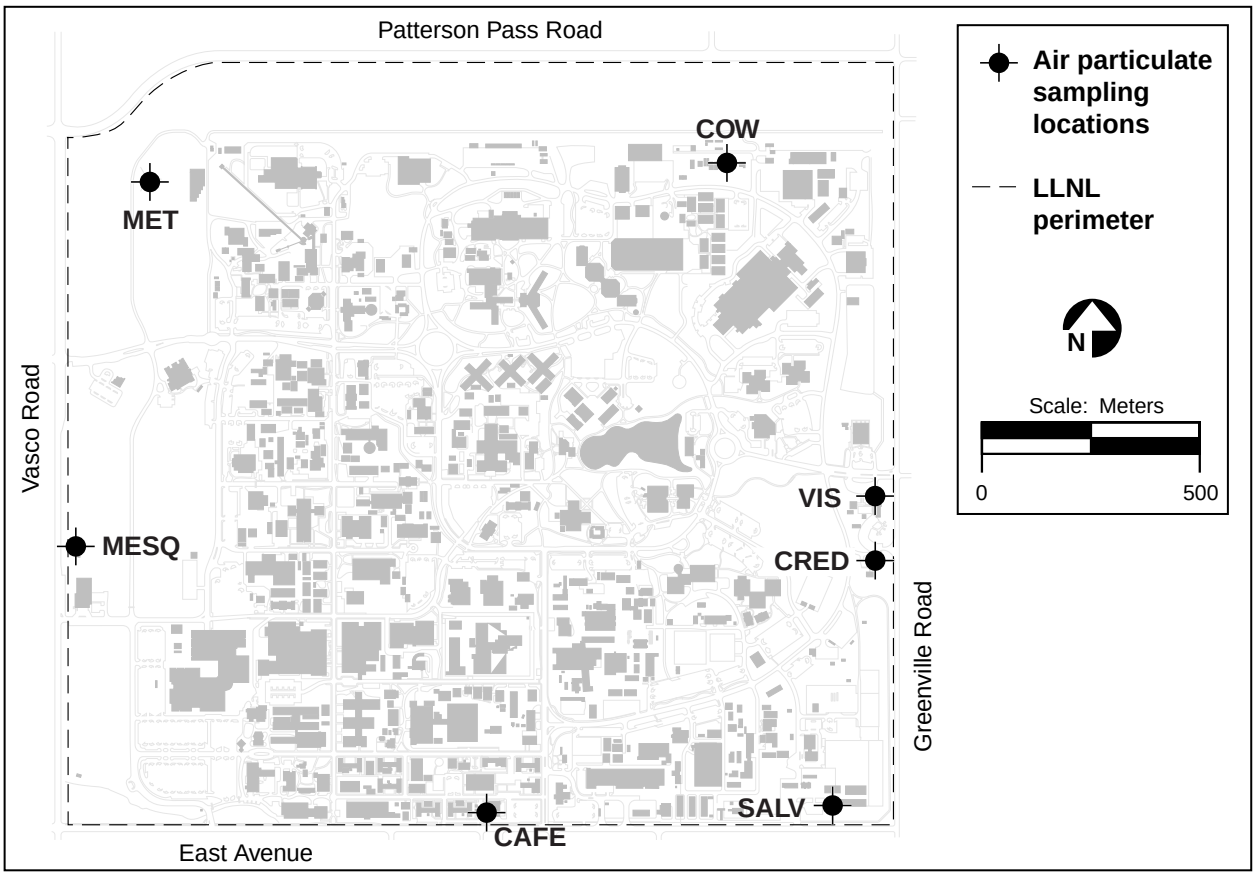

Figure 5-1. Air particulate sampling locations, Livermore site

High volume air particulate samplers run continuously and filters are collected weekly. New filters are identified and placed on the sampling units, and the "on" airflow is verified and, if necessary, set to the desired flow rate.

Samples are submitted to the analytical laboratory after a 4-day delay to allow for decay of the radon-thoron daughters. Portions of all weekly air particulate samples (including those from Site 300 locations) are analyzed for gross alpha and non-volatile beta emitting isotopes by a gas-flow proportional counting system. In addition, portions of the weekly filters from all of the Livermore site perimeter locations (except CRED) (shown in **Figure 5-1**) are combined to form a monthly site composite sample. Location CRED is not included in perimeter composites because it is located at a diffuse source and in the same general direction as location VIS. Including both in a composite would bias the sample. This monthly site composite is digested and counted for

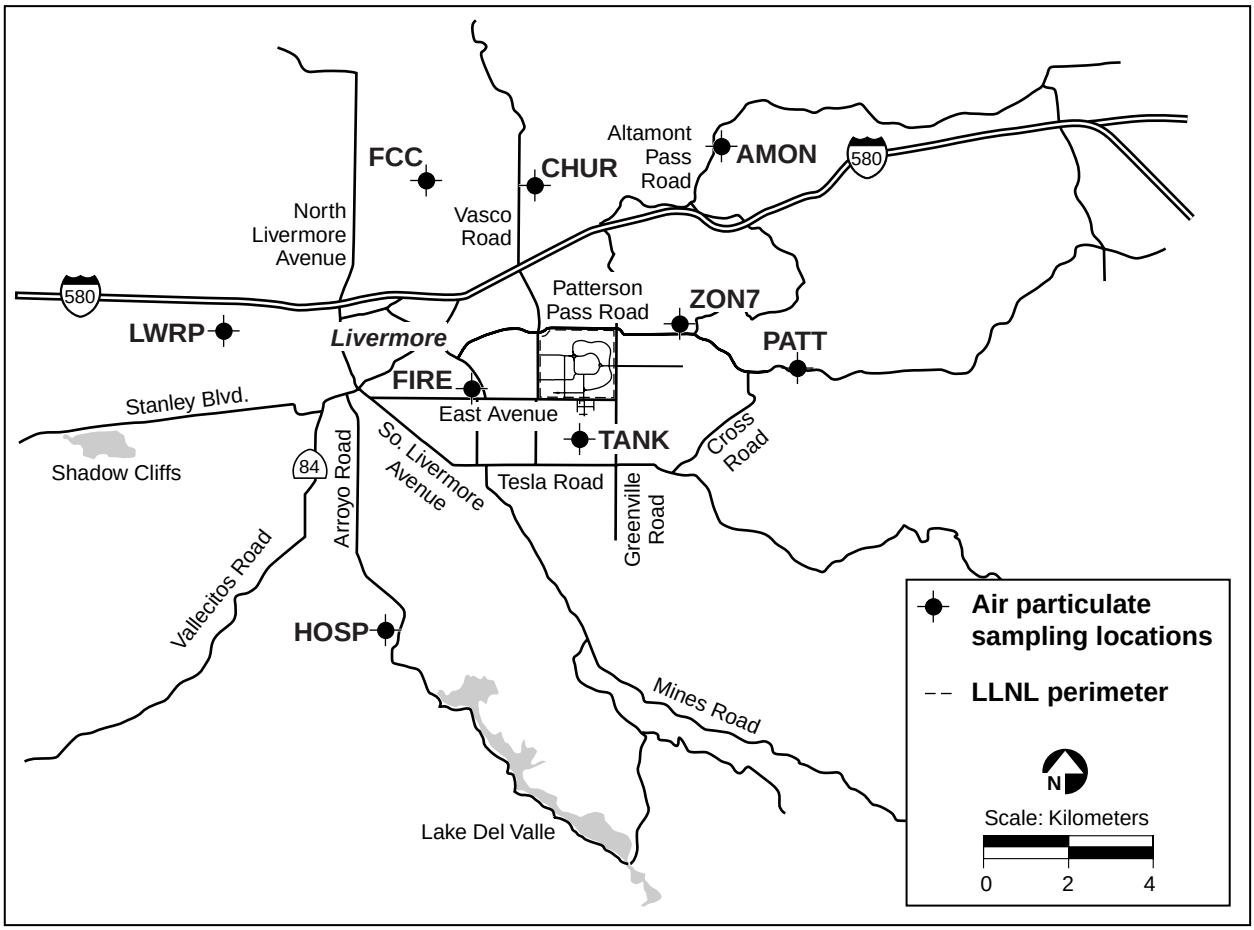

Figure 5-2. Air particulate sampling locations, Livermore valley

gamma-emitting radionuclides. The remaining portion of the weekly filters is combined to form a monthly composite at each location which is analyzed for plutonium 239+240 by alpha spectrometry.

Weekly Site 300 perimeter samples are also combined to form a monthly site composite which is digested and counted for gamma emitting isotopes. The remaining portion of the weekly filters from Site 300 locations are combined to form a monthly composite at each location which is analyzed for uranium-235 and uranium-238 by alpha spectrometry.

5.2.2.3 Beryllium Particulate Monitoring

To monitor for potential emissions from LLNL's beryllium operations, LLNL monitors for beryllium at six locations along the perimeter fence line (all locations except CRED in **Figure 5-1**). Although under no regulatory requirement to monitor for beryllium at Site 300, as a best management practice, LLNL monitors for beryllium at three locations within the Site 300

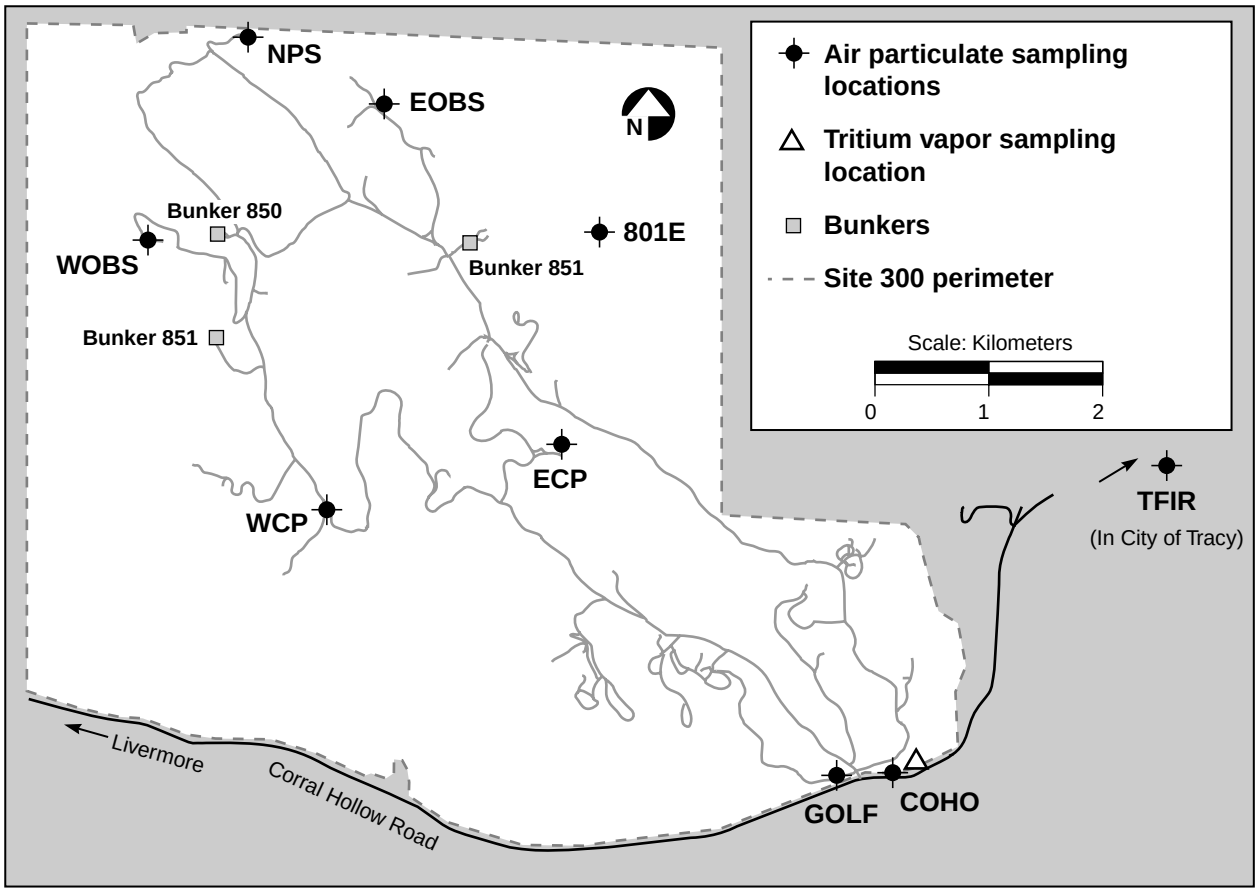

Figure 5-3. Air particulate and tritium sampling locations, Site 300

perimeter (EOBS, 801E and GOLF; see **Figure 5-3**) and at one location in Tracy (TFIR; see **Figure 5-3**). Portions of the weekly perimeter location samples are combined to create a location specific composite which is then analyzed by the same analytical laboratory as the radiological samples.

5.2.2.4 Network Changes

One location, (L-B531), was removed in 1999 after 8 1/2 years of investigation. The purpose of this location was to investigate the plutonium contribution to air from soil contamination near the sampler. During 1998 and 1999, the soil in the vicinity of the sampler was almost completely covered by either a parking lot or ground cover. Monthly data for B531 showed a steady decline in activity because of a decrease in the resuspension of these soil particles.

In mid 1999, TAMM was notified of a change in ownership for the SWMEI location at Site 300 (PRIM). A suitable replacement was established and named COHO. This site is just inside the perimeter fence within 100 yards of the closest neighbor from the site.

As a cost saving measure, the analysis for isotopic uranium, plutonium, and gamma scanning was moved from an onsite laboratory to an offsite commercial laboratory in January 2000. This change subsequently resulted in an increase in the minimum detectable concentration (MDC), though the MDC for all analysis remains far below any derived concentration guideline.

In 1999, the AVLIS Program was shutdown. Although there are still some uranium sources at LLNL, the specific location analysis for uranium-235 and uranium-238 was replaced by a composite consisting of all the perimeter locations. Historically, a composite of all Site 300 perimeter locations received plutonium, uranium and gamma analysis. To better evaluate the airborne contribution of explosive tests using depleted uranium, each location at Site 300 now receives uranium analysis. A composite of the Site 300 perimeter location continues to be analyzed for gamma and plutonium activity and weekly samples are submitted for gross alpha and gross beta activity. This change took place January 2000.

Before 1997, LLNL used cellulose filters for both radiological and beryllium analysis. During an audit, DOE suggested that LLNL sample using glass-fiber media, which has greater particle collection efficiency. LLNL changed to the glass-fiber filter media in April 1997 for radiological analysis only. Beryllium analysis continued with cellulose filters because of the variable and often high background levels of beryllium inherent in blank glass-fiber filters. In 2001, TAMM thoroughly evaluated the past radiological data collected from cellulose and compared it to recent data collected with glass-fiber filters. While the efficiency of glass-fiber filters appeared to be greater than cellulose filters for some particle sizes (which is consistent with literature), the activity detected in glass-fiber filters was not necessarily greater. TAMM determined that glass-fiber filters are not suitable for low-level uranium air monitoring because of the high uranium activity contained in a blank filter (Althouse 1999). In fact, the amount of activity in the blank glass-fiber filter was greater than what was detected in the air at the location with the highest activity at Site 300 or the Livermore site. In order to report accurate airborne levels of uranium, a filter blank activity had to be subtracted (EPA 1976). This subtraction added error to the

reported uranium data making the ratios of uranium-235 to uranium-238 unrealistic. (The uranium-235/uranium-238 ratio is a common way to distinguish natural from enriched or depleted uranium.) In addition to the uranium issues, during the three years of sampling with glass-fiber filters, less plutonium was detected on samples submitted for analysis. The lack of detected plutonium may be the result of changes in sampling, flow rate, or analytical methodology. This will be further investigated. However, less plutonium detection coupled with the fact that the uranium levels from the filters were greater than those in the air, makes glass-fiber filters a poor medium for low-level radioactivity detection at LLNL. LLNL switched back to using cellulose filters for radiological air sampling in January 2002. LLNL will continue to search for a more efficient filter with low beryllium and radiological background activities.

5.2.3 Procedures for Laboratory Analysis

A certified offsite commercial laboratory performs the air particulate analysis. **Table 5-1** describes the analysis required, method of analysis, and the reporting limit.

Table 5-1. Air particulate analysis methodology and reporting limits

Requested Analysis	Method	Reporting Limit
Gross alpha & beta emitters	Gas-flow proportional counting	0.5 pCi/cm^2
Beryllium metal	Inductively Coupled Plasma- Mass Spectrometry	50 pgm/cm^2
Plutonium 239+240	Alpha Spectrometry	0.05 pCi/ sample
Uranium 235, 238	Alpha Spectrometry	0.05 pCi/ sample
Gamma emitters	Gamma Spectroscopy	Depends on isotope

Gross alpha and beta activity is determined through the direct reading of a 47 mm punch-out from each sampled filter. The punch-out is placed in the gas-flow proportional counter where quantification is determined. The analytical laboratory uses americium-241 and cesium-137 as calibration sources to determine alpha and beta counting efficiencies, respectively. Cross checks utilizing thorium-230 and strontium-90 are also completed periodically.

For plutonium-239+240, uranium-235, and uranium-238 isotopic determination, sampled filters are ashed and then digested in a series of heated acid baths. The solution is then diluted to the appropriate volume and counted by alpha spectrometry. The tracer for plutonium analysis is plutonium-242, and uranium-232 is used as the tracer for the uranium analysis. Quality control samples are run with each batch of samples and include a method blank, matrix spike, sample duplicate and laboratory control spike.

Gamma emitting isotopes from site-wide composites are determined after samples are digested, weighed, and then counted for 8 hours. Quality control for gamma samples includes method blanks, matrix spikes, and laboratory control spikes.

For beryllium analyses, the analytical laboratory adds acid to each monthly composite, heats and evaporates the solution several times. The samples are diluted with de-ionized water and quantification is accomplished by inductively coupled plasma mass spectrometry. Quality control samples are also run for beryllium analysis and include initial calibration verification, interference check standards, matrix spike, laboratory control spike and duplicates.

5.2.4 Quality Assurance Procedures

A QA/QC sampler is operated in parallel with a permanent sampler at a given location for 2 months. The QA/QC samplers are rotated randomly among onsite locations on a bimonthly basis. Each site has a duplicate sampling unit (one for Site 300 and one for Livermore). In addition, two trip blank filters, one for the Livermore site and one for Site 300, are also taken on the routine during filter exchange each week.

All QA/QC samples are submitted to the analytical laboratory as blind samples and the results of QC duplicates are compared to results from the routine samples at the locations where they were collected.

Self assessments of the air particulate documentation and monitoring activities are performed every three years as described in ORAD-QA-SA, *Self Assessments*.

5.2.4.1 Data Quality Objectives

The analytical laboratory performs in-house quality control tests to determine the accuracy and precision of their data. This includes method blanks, matrix spikes, duplicates, and laboratory control samples.

All data reported from the analytical laboratory also undergoes a data validation process. Data that falls outside the established guidelines is identified as "rejected: in the database and not typically reported unless justified.

5.2.5 Program Implementation Procedures

The primary responsibility for activities related to the air particulate monitoring networks is assigned to an environmental analyst within the TAMM Group of the Operations and Regulatory Affairs Division (ORAD). The analyst is responsible for the network design,

implementation, and correct operation of the network; the analysis and evaluation of all monitoring results; data trending; documentation; and result reporting.

Details of sampling, processing, and documentation for radiological and beryllium air particulates is described in EMP-AP-S, *Air Particulate Sampling* and its supplemental instructions.

Details of calibration protocol are described EMP-AP-CA, *Air Particulate Sampler Calibration*, and its supplemental instructions.

Geographical details of sampling locations are described in the Location Database. Details for accessing the database are available in EMP-QAS-LOC, *Locations Database SOP Supplement*.

5.2.5.1 Prevention of Cross-Contamination

To reduce the risk of cross-contamination among air particulate samples, the sampling technologists follow established procedures, including avoidance of the contaminants of concern. Vehicles used to collect samples are kept clean and free of known contaminants.

Sampling technologists wear clean, disposable gloves while performing the weekly filter exchange and while preparing the samples for delivery to the analytical laboratories. New gloves are worn at each sample location. The filters are placed in glassine bags after removal from the sampling units. The glassine bags containing the filters kept in a field storage folder while the route is being performed.

Nonconformance reports are completed according to procedure ORAD-QA-NCR, *Nonconformance Reporting and Tracking* when samples are lost, damaged, or potentially cross-contaminated.

5.2.5.2 Sample Preservation and Handling

There are no sample preservation requirements for air filters. All filters awaiting delivery to the analytical laboratory are stored in locked offices until the end of the month when they are further prepared for laboratory analysis. At this time, a technologist wearing clean gloves and working in a clean environment processes the samples. Filters are stored in ziplock or glassine bags and then placed in an enclosed box until they are delivered to the analytical laboratory.

5.2.5.3 Flow Verification and Calibration Procedures

The air-particulate hi-vol sampling units have automatic, mass-flow correction capabilities that are designed to maintain constant flow throughout the sampling period. This system

incorporates a two-staged centrifugal blower powered by a brushless motor. An electronic sensor automatically adjusts the motor speed. This feature, along with the LCD readout, provides real-time flow rates, continuous flow volume, and total running time.

DOE/EH-0173T (DOE 1991) states that the "air sampling rate *should* not vary by more than ±20 percent, and the total air flow or total running time *should* be indicated." The 10 percent tolerance established in the ORAD calibration procedure is well within DOE standards.

The TAMM Group utilizes two types of calibration units for verifying hi-vol flow rates:

- Flow rate verification is done primarily in the field using the Venturi unit.
- For bench-test calibrations, the hi-vol flow rate is calibrated using a variable-resistance calibrator.

The flow rate and accuracy of the internally operated flow sensor are verified using a secondary calibration source. This secondary source, a Venturi with an attached magnehelic, is placed on each hi-vol every week, and the instantaneous flow rate displayed on the hi-vol is compared with the known Venturi flow rate (after correction to standard temperature and pressure). A TAMM analyst reviews flow rates and Venturi readings quarterly to ensure accuracy. If the flow rates as indicated by the Venturi and the LCD differ by more than 10 percent (after applying the temperature and pressure corrections), an internal bench-test calibration is performed on the hi-vol. This calibration (further described EMP-AP-CA, *Air Particulate Sampler Calibration*, and its supplemental instructions), involves the electronic adjustment and flow verification using a primary calibration source.

Because all calibration units have their own identification number with their own calibration curve, the technologist must ensure that the correct calibration curve for the unit is used. When performing weekly flow verification, the technologist logs the Venturi unit identification number on the FTF. The Venturi and all other calibration equipment are stored in the lead technologist's office, and spare calibration units are stored at TSG's repair facility (Building 195).

All calibration activities are documented on flow calibration worksheets and maintained by TSG technologists. Dates of hi-vol calibrations are also logged on the FTFs.

The Hazards Control Instrument Laboratory calibrates both the Venturi and variable-resistance calibrator annually. Hazards Control Department personnel maintain documentation of these activities.

5.2.5.4 Data Analysis

There are five main goals for analyzing surveillance data:

- Estimation of concentrations at each sampling point
- Comparison of current concentrations to previous concentrations in order to identify changes or inconsistencies
- Comparison of concentrations to established DCGs
- Comparison of concentrations at a single location, or a group of locations, to control or background locations and evaluation of the reliability of the comparisons
- Review of quality assurance data to ensure validity

5.2.6 Action Levels

Recent changes in the filter media and analytical detection limit have caused large variations in the arithmetic means for most air particulate data. The mean value and standard deviation of these means are normally used to set action limits. However, using these large variable statistics sets the action limit at an unrealistic range for these data. Therefore, action limits for air particulate sample data are determined by the previous year's median value (as reported in the site annual environmental report) with a consideration of the historical values. If a value is determined to be significantly high (two standard deviations from the median), it is investigated.

The investigation involves checking sampling operations by contacting the technologist who performed the sampling and reviewing the appropriate FTFs. Field operations can greatly impact the data; for example, excessive particulate buildup on air filters (caused by soil resuspension) from construction activities may result in higher sample results. If the sample results that exceeded warning levels are not the result of sampling or field activities, further investigation is required. The data are checked for transcription errors, and the analytical lab is contacted to determine if any problems occurred during analysis. In some cases, reanalysis may be performed. Any results outside three standard deviations (the action level) are also subject to the same investigation as warning levels. If the activity is high and no transcription, analytical or other problems are found, the environmental analyst notifies EPD management, and further action is taken with EPD management concurrence.

Specific action levels will be determined when more data with one filter media are available.

5.2.7 Preparation and Disposition of Reports

The air monitoring results based on these data are reported in the annual *Environmental Report* (e.g., Biermann et al. 2000). Results from diffuse source locations are also reported in the *LLNL NESHAPs Annual Report* (e.g., Gallegos et al. 2000).

The requirement for quarterly beryllium reporting to the BAAQMD was lifted in January 2002. Instead, LLNL provides the BAAQMD with the annual environmental report and will notify them within 24 hours should the ambient beryllium concentration exceed 10,000 pg/m^3.

5.2.8 Future Plans

TAMM continues to investigate the suitability of new filters that possess low background activity yet have a high particle collection efficiency. Current investigations involve commercially available synthetic filters.

TAMM is also working on improving the emergency air monitoring capabilities for the routine analysis such as radioactivity, metals, and volatile organic compounds.

The long-term plan is to keep current with changes in LLNL operations and to add and remove sampling locations as these operational activities change.

As always, periodic technical assessments of the air monitoring networks will be performed.

5.3 Air Tritium Monitoring Program

5.3.1 Rationale and Design Criteria

5.3.1.1 Regulatory Drivers

The regulatory drivers for air tritium monitoring are the applicable portions of DOE Order 5400.1 and DOE Order 5400.5 (see WSS B93 and B94 in Appendix B). These state that environmental surveillance shall be conducted to predict the effects, if any, of DOE activities on environmental and natural resources both onsite and offsite.

Guidance for monitoring tritium in air is provided in DOE/EH-0173T (DOE 1991). This document advises that air sampling techniques *should* employ methods that extract moisture from the air. It also states that, for facilities that release tritium to the air, air sampling is an important medium, but not the only one (see Chapter 3). Guidance on choice of sampling method and precautions associated with sampling is provided.

5.3.1.2 Monitoring Objectives for Air Tritium

Data collected from the surveillance program should characterize the radiological conditions of the offsite environment and should be used to estimate inhalation doses to the public and provide compliance data for all applicable environmental regulations. To do this, estimations of concentrations at each sampling point are needed. To identify changes or inconsistencies, current concentrations must be compared to historical concentrations. Furthermore, concentrations at a single location or group of locations must be compared with control or background locations to evaluate the effect of LLNL operations on the environment.

Tritium in air monitoring data may be used to test predictions by dispersion/dose models of concentrations in air to assess whether the model predictions are sufficiently higher than the measurements to be health-protective. Measured air concentrations of tritium from monitors located near diffuse sources (e.g., B612 yard, B331 outside) are used to estimate the tritium released from these areas of waste storage to estimate dose (Gallegos et al. 2001), which otherwise would go unreported.

According to DOE/EH-0173T, environmental monitoring during an emergency situation *should* be considered (DOE 1991). LLNL's routine air monitoring network is part of EPD's emergency response program (see Chapter 1). The air sampling units do not provide data in real-time, but they are available if sampling is needed to confirm elevated concentrations due to an accidental release.

5.3.1.3 Sources and Analytes

Tritium is currently the only nonparticulate radionuclide from LLNL operations that warrants monitoring. Tritium is released as tritiated water (HTO) and tritiated hydrogen gas (HT) from the Tritium Facility (Building 331). Because the potential inhalation dose from HT is approximately 10,000 times lower than an inhalation dose from a comparable release of HTO, the tritiated hydrogen gas does not contribute significantly in calculations of the overall dose. However, because HT is converted to HTO in the environment, LLNL monitors both forms of tritium in effluents from the Tritium Facility stacks (Chapter 3).

From start-up of operations in 1953, to 1999, releases from the Tritium Facility have dominated total dose to the public from operations at the Livermore site. Approximately 3.0×10^{16} Bq (810,000 Ci) have been released as both HTO and HT. Of this amount, 1.3×10^{16} Bq (36,000 Ci) were released in 1965, and 1.1×10^{16} Bq (287,000 Ci) were released in 1970 in separate, unplanned HT releases of extremely short durations. In 2000 and 2001, however, operations at the Tritium Facility had been cut back so severely that the estimated dose to the site-wide maximally exposed individual from the Tritium Facility was less than that from diffuse sources (Biermann et al. 2001). Important diffuse sources of tritium in recent years have been the

Building 612 Yard and the Building 331 Waste Accumulation Area (WAA). The Building 612 Yard consists of several areas where containers holding radioactive wastes are stacked outdoors. These containers are not airtight and may release tritium. The Building 331 WAA provides temporary storage for tritium-contaminated equipment slated for disposal. Diffuse sources that are monitored but have minimal contribution to dose to the public include the Building 514 Yard, where liquid and solid radioactive and/or mixed wastes are stored and treated in tanks, and the pine tree near Building 292 that is rooted in tritium-contaminated soil water.

Environmental monitoring is conducted routinely by LLNL for HTO only. Monitored HTO accounts for tritium released to the environment both as HTO and as HT that has been converted to HTO in the environment. HTO, as an isotope of water, can be incorporated into all biological systems and is readily mobile. It can enter the human body through respiration, ingestion, and absorption through the skin (Okada and Momoshima 1993). If air concentrations of HTO are measured, conservative doses from inhalation and skin absorption of HTO and ingestion of HTO and OBT[2] can be calculated quite accurately by means of the specific activity model (see Appendix A, Biermann et al. 2001). The specific activity model assumes that the tritium to hydrogen ratio in every environmental compartment is the same as the tritium to hydrogen ratio in air.

Tritiated organics (e.g., tritiated methane) may also be released to the environment. The operations at LLNL are such that the likelihood of such releases is minimal, and the potential dose to the public would be far below any level of concern.

At Site 300, both past and current activities influence emissions and environmental impacts. Historically, tritium-contaminated material from explosive tests at Site 300 was disposed of in the Site's landfills. The groundwater at Site 300 has locally elevated levels of tritium (see Chapter 8), and tritium purge water from routine monitoring of groundwater wells in areas where elevated tritium levels occur also represents a diffuse source of tritium emissions at Site 300.

A study performed at Site 300 during 1996 and 1997 determined that atmospheric tritium levels detected at locations of known tritium contamination were generally at background levels. Based on the results of the study, no surveillance air monitoring for tritium is currently being conducted at Site 300. However, one sampler was placed at a location (COHO) that represents

[2] Organically bound tritium (OBT) is formed during plant photosynthesis from HTO. It is tritium bound to the organic matter of plants. When animals eat these plants, OBT is transferred to the organic matter of the animal.

the Site Wide Maximally Exposed Individual to fulfill NESHAP's reporting requirements (Gallegos et al. 2001)

5.3.1.4 Collection Methods for HTO

A suitable collection technique for tritium must remove moisture from the air. This is done by pumping a known volume of air through a desiccant that absorbs all the moisture from the air. The length of the sampling period depends on the amount of desiccant used, average absolute humidity, and air-flow rate. DOE/EH-0173T (DOE 1991) recommends the use of silica gel as a desiccant, as is done by LLNL.

The LLNL tritium samplers, operating at a flow rate of 500 mL/min, use about 700 g of silica gel in a cylindrical flask to trap the tritiated water vapor. The silica-gel flasks are changed every two weeks. Data collected includes location, date on, date off, elapsed sampling time, instantaneous and total flow rates, empty flask weight, flask weight with dry silica gel, and flask weight with wet silica gel. Each sample has a sample identifier that accompanies it through the analysis.

The sample collection for tritium is a simple exchange process (EMP-AT-S Instructions #2, *Air Tritium Sampling Activities*). The sampling technologist determines the existing flow rate, removes the exposed flask, and places it in the special transport carrier. Then, a replacement flask containing fresh silica gel is placed on the sampling unit. The flow rate is checked, and if necessary, adjusted. The technologist then completes the field tracking form (FTF) in the logbook. About 70 g of moisture is extracted from the air during the sampling period, but the exact quantity will depend upon the average absolute humidity. No break-through occurs, indicating that all moisture is removed from the air as it passes through the silica gel. A complete, detailed procedure for tritium sample collection is found in procedure EMP-AT-S, *Air Tritium Sampling* and its three sets of instructions (#1 *Air Tritium Pre-Sampling Activities*, #2 *Air Tritium Sampling Activities*, #3 *Annual Rotameter Calibration Check*, and #4 *Air Tritium Electronic Flow Meter Calibration*).

There are very few cross-contamination concerns with air tritium samples because the field technologists never come in physical contact with the silica gel samples. Special care is taken to minimize the possibility of breaking a flask containing an air tritium sample. Each flask is wrapped in plastic mesh to reduce the chance of breakage. The sample flasks are transported in a Plexiglas transport carrier specifically designed to hold them.

All sampling performed is done in accordance with the LLNL *Environment, Safety, and Health Manual*. Any required training and/or special concerns associated with performing this sampling are identified in the Operations and Regulatory Affairs Division (ORAD) integration worksheets

IWS 2271, "Technical Support Group (TSG) Environmental Monitoring Activities"; IWS 540, "Air Tritium Environmental Surveillance and Maintenance (B514 Yard and B612 Yard)"; and IWS 305, "Flask Preparation for Airborne Tritium Sampling." Specific hazards associated with this activity and required ES&H controls are also identified in the SOP supplement, EMP-HAZ-SUP, *Hazards and Controls for Environmental Sampling*.

5.3.2 Extent and Frequency of Tritium Monitoring and Measurements

5.3.2.1 Routine Monitoring Requirements

The configuration of LLNL's air tritium monitoring network is based on the guidance provided by DOE/EH-0173T (DOE 1991). Using the EPA- and DOE-approved Gaussian plume dispersion model CAP88-PC, air concentrations and dose at the perimeter fence and in the vicinity of the Livermore site were modeled in 1993 using actual emissions from the Tritium Facility at LLNL and the Tritium Facility (since closed) at Sandia National Laboratory, Livermore. Concentration contours were created from the CAP88-PC output. These results confirmed that the perimeter sampling locations being used then (and now) adequately assessed areas of potentially elevated tritium concentrations. In addition to perimeter locations, off-site tritium monitors are situated in the areas with the potential for the highest air concentrations.

Currently, tritium air samplers operate continuously at twelve locations on the Livermore site (**Figure 5-4**), at six locations in the Livermore Valley (**Figure 5-5**), and at one location near the southeast boundary of Site 300 (COHO; **Figure 5-3**). In accordance with DOE/EH-0173T (DOE 1991), the tritium sampling network includes:

- HOSP (**Figure 5-5**), the background or control location 7.2 km from the site in an upwind direction. Although 7.2 km is not the 10-15 km recommended for a background location, concentrations of tritium at HOSP are consistently at or below detection limits because of low tritium emissions during the last few years.

- VIS (**Figure 5-4**), the location where the maximum, predicted ground-level concentrations from stack releases are anticipated at the perimeter.

- FIRE (**Figure 5-5**), the location in the nearest community (Livermore) within a 15 km radius.

Offsite samplers are placed both upwind (VET) and downwind (ZON7, also the site of a water treatment plant) from LLNL. The tritium sampling network provides a comprehensive assessment of where tritium is most likely to be found in the Livermore Valley. A few changes in sampling locations have occurred since the last *Environmental Monitoring Plan* (Tate et al. 1999). In March 2000, the location XRDS was discontinued, but PATT (**Figure 5-5**) was added in

January 2001. The location DWTF (**Figure 5-4**), a new sampling location near Building 694, was added in October 2001. Four of the Livermore site locations (B331, B292, B514, and B624) monitor diffuse source emissions of tritium.

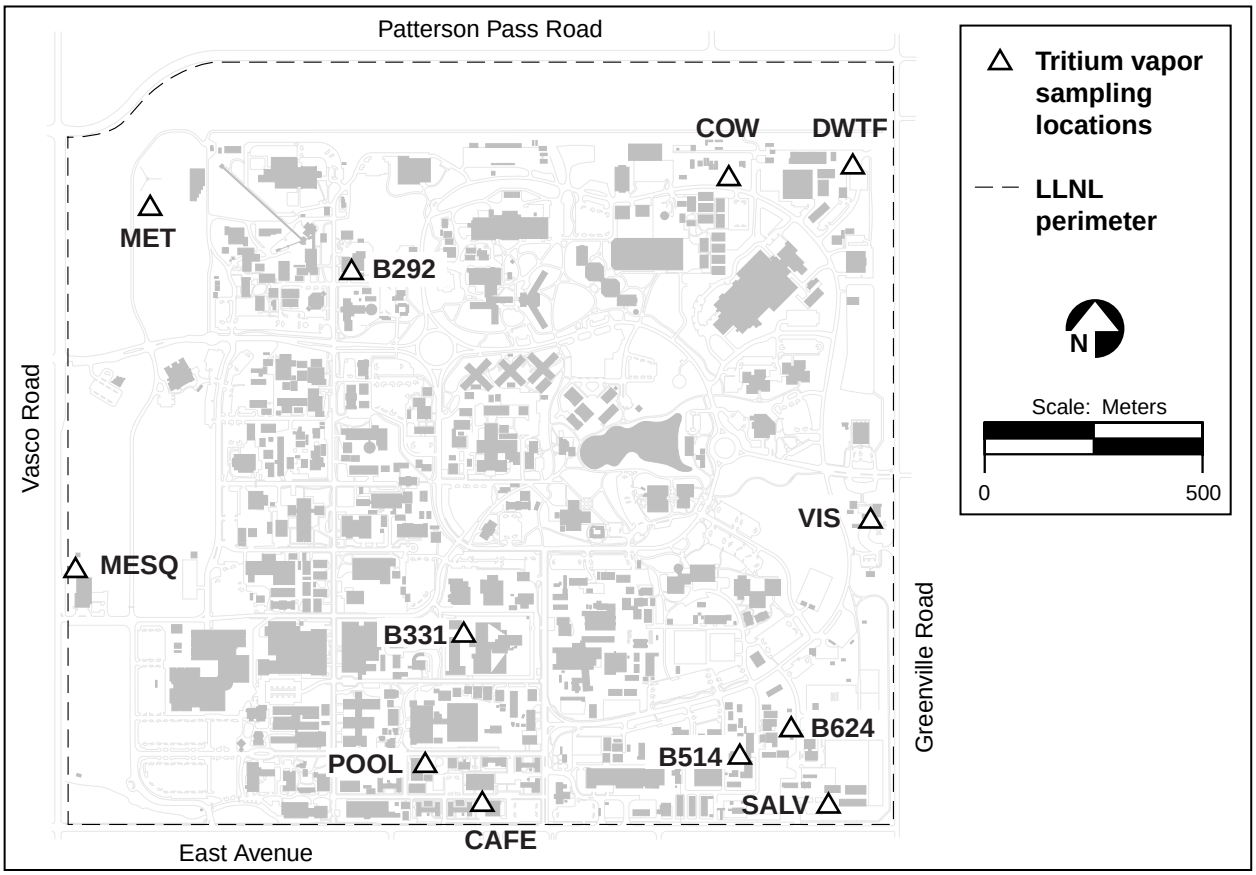

Figure 5-4. Air tritium sampling locations, Livermore site

Resources, manpower, and logistics (such as the availability of electrical power, access and security) are also considered when selecting a sampling location.

A detailed description of all sampling locations may be found in the Locations Database. The Locations Database includes directions to the sampling location, the environmental medium sampled at the location, safety concerns and other pertinent information. EMP-QAS LOC, *Locations Database, SOP Supplement*, describes the process to be used for defining, documenting and approving sampling locations. In addition, a hardcopy of all current sampling locations is maintained by the TSG Coordinator in ORAD.

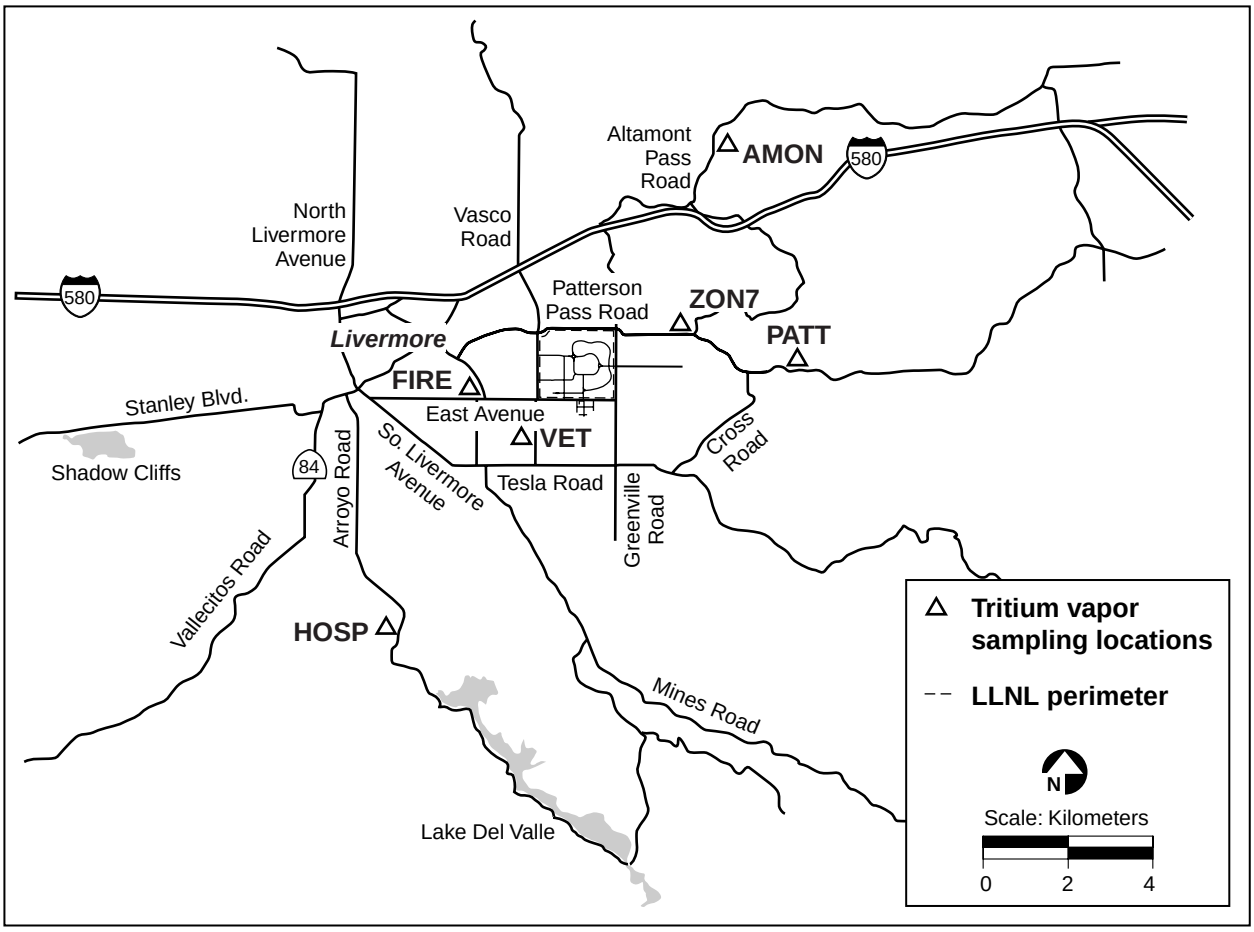

Figure 5-5. Air tritium sampling locations, Livermore Valley

A new operation releasing tritium may require that a tritium monitor be installed downwind at such a distance that the plume will have come to ground. This location will be chosen after modeling the dispersion of a unit release of tritium using CAP88-PC. For example, in anticipation of the start-up of the Decontamination and Waste Treatment Facility (DWTF), a tritium sampler was installed for the fourth quarter 2001. Background concentrations are being monitored in advance of the activation of the DWTF.

Many factors must be considered to determine sampling frequency. These factors include limitations of the sampling units themselves, amounts of moisture required for analysis, flow rates, and sample retrieval time. Typical sampling frequency for tritium is biweekly at LLNL. All air tritium sampling, regardless of location, is conducted according to the LLNL procedure EMP-AT-S, *Air Tritium Sampling*.

5.3.2.2 *Special Studies*

At the request of the National Tritium Labeling Facility (NTLF) at Lawrence Berkeley National Laboratory (LBNL), LLNL installed an air tritium sampler next to the LBNL sampler on the hillside above the NTLF. To match the LBNL sampling period of one month, the flow rate of the LLNL sampler was reduced to 350 mL/min. The first sample was taken off March 7, 2000. Sampling was discontinued April 2, 2002, three months after the closure of the NTLF. LBNL was interested in finding out whether two different sampling set-ups and two different analytical methods (azeotropic distillation compared with freeze-drying) would yield the same tritium concentrations. This is being investigated.

A similar sampling protocol was established at LLNL at T5475 at the request of the Environmental Restoration Division, as part of the Livermore Site Groundwater Project (Chapter 2, Biermann et al. 2001). A groundwater treatment facility that extracts groundwater and removes volatile organic compounds is running next to T5475. Because levels of tritium are known to be elevated in the groundwater, knowledge of the ground level air concentrations of tritium need to be monitored. This project is ongoing.

5.3.3 Procedures for Laboratory Analysis

Flasks of silica gel that have been in the field for two weeks with an indicated total flow greater than half that expected for the sampling period are taken to the Chemistry and Materials Science Division. After the sampling technician weighs a flask on properly maintained and calibrated balances (SOP-CES-P542, *CES Balances*) the flask is then placed in the fume hood of the Chemistry Environmental Services (CES) laboratory, and CES assumes responsibility for the air tritium samples. All silica gel from each flask is emptied into a jar for freeze-drying The water extracted by freeze-drying (CES-EM-P542, *Low-Level Tritium Analysis- Freeze Dry*) is counted for HTO by liquid scintillation (SOP-EM-P552, *Operation of Packard Tri-Carb LSC for Environmental Sample*s). About 5 mL of extract is needed for each liquid scintillation sample. Based on a study carried out at CES in mid-2001 that confirmed reports in several publications in the open literature, (Baumgärtner and Kim 1990; Rosson et al. 1998; Rosson et al. 2000), the following equation is now used to correct the measured concentration:

$$C = 1.0309\ C_m'\ [(0.0512 + W)/W]$$

where

C = corrected concentration (to equal the HTO in air moisture)

C_m' = HTO measured in the extracted water

W = fraction adsorbed water in silica gel = (wet weight of silica gel – dry weight of silica gel)/dry weight of silica gel

This correction is necessary because about 5% of the "dry" silica gel is water that cannot be removed unless the silica gel is destroyed. When the tritiated air moisture comes in contact with this residual water in the silica gel, exchange occurs. As a result, the tritium concentration of the ambient air moisture will be diluted by the water in the silica gel. This effect is greater when less water is extracted from the air relative to the mass of dry silica gel.

Concentrations are reported for the extracted water as the measured value in pCi/L and as a calculated value of pCi/m^3 based on the volume of air that has passed through the sample.

5.3.4 Quality Assurance Procedures

5.3.4.1 Data Quality Objectives

5.3.4.1.1 Precision. The reporting limits for tritium in extracted air moisture are about 2.0 to 3.0 Bq/L (~ 50 to 80 pCi/L). Typically this means that the reporting limits per cubic meter (a derived value) are usually between 0.011 and 0.019 Bq/m^3 (0.3 to 0.5 pCi/m^3).

Two air tritium duplicate samples (one onsite and one offsite) are taken during each sampling period. The sampling locations of field duplicate samples are not identified on the silica gel flasks, so the analytical laboratory does not know where the samples originated (procedure EMP-QA-DM, *Sample and Data Management*). This information is recorded on FTFs that are filled out in the field by the sampling technologist. The tritium air samplers for duplicate QA/QC samples are rotated among the locations at bimonthly intervals.

After the laboratory results are obtained by the analyst, the concentrations of duplicates are compared. Different concentrations can be explained by analytical error and natural variability. In most cases historically, the difference between duplicates can be explained exclusively by analytical error. This is invariably true when concentrations are near the detection limits, which occur much of the time in the air tritium network. When one of the results in a pair is a nondetection, then the other result should be less than two times the detection limit (Chapter 14, Biermann et al. 2001). Natural variability becomes important at higher concentrations. Nevertheless, if all parts of the sampling system are working properly and no human error is involved, the mean ratio should be between 0.7 and 1.3 (Chapter 14, Biermann et al. 2001). If a larger difference is detected, the reason should be investigated by checking the information contained on the FTF. Specifically, the total flow rates and grams of water extracted should be compared. If the total flow rates are similar, the quantity of water extracted should also be similar for all locations during a sampling period. If it is not, the reason for the inconsistency in

the duplicate concentrations has been found. If the magnitude of the differences cannot be explained, the analytical laboratory is contacted to discuss any problems that may have occurred during analysis.

Laboratory duplicates (or splits), taken from the field samples, are created at a rate of about 10 percent of samples and are introduced blind into sample processing. The relative error ratio is calculated and reported for each split sample. If the control limit of 3.0 is exceeded, the source of the problem is investigated and corrected (CES procedures, SOP-CES-P810, *Data Validation* and SOP-CES-P811, *Data Verification*).

5.3.4.1.2 Accuracy. The radiological laboratory runs blank and control samples traceable to standards of the National Institute of Standards and Technology (NIST). Currently, no field blanks are collected. The laboratory blank is obtained by bubbling argon gas through 250 mL of water known to be free of tritium. The 250 mL of water is trapped on silica gel and extracted by freeze-drying (CES-EM-P542, *Low Level Tritium Analysis – Freeze Dry*). A laboratory standard of known tritium concentration is prepared similarly to assess percent recovery. The efficiency of recovery is reported for each sampling period and must fall within the CES' arbitrarily set internal acceptance criterion of 75% ≤ recovery ≤ 125%.

The radiological laboratory also participates twice yearly in the DOE Environmental Measurements Laboratory Quality Assurance Program (SOP-CES-P820, *CES Performance Evaluation Program*). For tritium, the DOE sends water samples containing known concentrations to the participating laboratories, compares the analytical results (thereby determining the accuracy of the various participating laboratories), and publishes reports so that analytical laboratory personnel and their customers can evaluate their analytical laboratory's relative performance. The results of the study are published on the EML web site (http://www.eml.doe.gov/QAP/).

Air-moisture silica-gel reference samples are not currently available through NIST or any of the intercomparison laboratory study programs.

5.3.4.2 Audits and Self-Assessments

Internal analytical laboratories that perform analyses for this network are subject to the Environmental Protection Department (EPD*) Quality Assurance Management Plan* (Merrigan 2001), under which EPD performs assessments of the quality-affecting activities for organizations contributing supportive work to EPD. Such assessments are performed sporadically as part of the EPD Quality Assurance Program. Triennial self-assessments of all monitoring networks are also performed (LLNL procedure ORAD-QA-SA, *Self Assessments*).

5.3.5 Program Implementation Procedures

The primary responsibility for activities related to the air tritium monitoring network is assigned to a TAMM environmental analyst in ORAD. The analyst is responsible for the network design, implementation, and correct operation of the network; the analysis and evaluation of all monitoring results; data trending; documentation; and results reporting.

The laboratory preparation of the silica gel flasks is carried out by TSG technologists following EMP-AT-S, *Air Tritium Sampling, Instruction #1, Pre-Sampling Activities*. Technologists follow *Instruction #2, Air Tritium Sampling Activities*, for the work in the field, when silica gel flasks are replaced. These instructions also cover final treatment of the samples before delivery to CES. Air tritium samples are submitted for analyses using sample control, chain-of-custody, and documentation procedures (EMP-QA-DM, *Sample and Data Management*). The written procedures include requirements for sample collection and submittal for chemical analysis, keeping a log, and filling out FTFs and chain-of-custody forms. The procedures also require the sampling technologist to alert the environmental analyst about difficulties encountered during any sampling event.

Because the DOE/EH-0173T (DOE 1991) states that the "air sampling rate *should* not vary by more than ±20 percent, and the total air flow or total running time *should* be indicated", LLNL in early 1999 incorporated flowmeters into each of the air tritium sampling locations. These flowmeters provide the instantaneous flow rate, and the minimum, maximum, and total flow during a sampling period. Electronic flowmeters are removed from the field and calibrated either biannually or when the percent difference between the flow off as measured by rotameter (see below) and the flow off measured by flowmeter is greater than 10% for two consecutive sampling periods. Flow calibrations of the electronic flowmeters are done according to EMP-AT-S, Instruction #4, *Air Tritium Electronic Flowmeter Calibration*.

Gilmont rotameters are still used to set the flow rate of the flowmeter at the start of the sampling period to 500 cc/min and to measure the instantaneous flow when the sample flask is changed compared with the indicated flow of the flowmeter. Rotameter readings are also still used to determine the total flow when a flowmeter has failed or the location does not have a flowmeter. The rotameters used for tritium air sampling flow adjustments are serviced and calibrated to NIST standards annually by the LLNL Hazards Control Industrial Hygiene Instrument Laboratory. Technologists visually inspect the rotameter for damage prior to use. Additionally, they ensure that the rotameter has been serviced within the past year. The TSG sampling technologist delivers the rotameter to Hazards Control and picks it up, along with a new calibration curve, when the instrument has been calibrated (EMP-AT-S Instruction #3, *Annual Rotameter Calibration Check*).

5.3.6 Action Levels

Sample results are compared to the 5-year historic geometric mean for each sampling group in the air tritium monitoring networks:

- Perimeter sampling locations on the Livermore site
- Offsite sampling locations in the Livermore Valley
- Site 300 perimeter sampling locations
- Diffuse sources on site
- POOL

Geometric means, geometric standard deviations and the upper warning limit (2σ) and upper action limit (3σ) are shown for 1997–2001 in **Table 5-2** for concentrations expressed as Bq/m^3 and Bq/L. Each sampling period, the air tritium sample results for each location are checked to see if they fall within the warning limit. Any data results that are beyond the warning limit must be investigated. The investigation involves checking sampling operations by contacting the technologist who performed the sampling and by reviewing the appropriate FTFs. If the sample results that exceeded warning limits are not the result of sampling or field activities, further investigation is required. The data are checked for transcription errors, and the analytical lab is contacted to determine if any problems occurred during analysis. In some case, re-analysis may be performed. Atmospheric dispersion modeling will be used to assess the possibility that the number is real. Any results outside three standard deviations (the action level) are also subject to the same investigation as warning levels, but the environmental analyst must notify EPD management. Further action will be taken with EPD management concurrence.

5.3.7 Preparation and Disposition of Reports

Data are analyzed based on ORAD-QA-D, *Data Analysis*. The air monitoring results and inhalation dose assessments based on these data are reported in the annual *Environmental Report* (e.g., Biermann et al. 2001).

Table 5.2. Geometric means, geometric standard deviations, warning limits, and action limits for air tritium sampling groups in Bq/m^3 and Bq/L (1997-2001).

Bq/m^3	Geometric Mean	Geometric Standard Deviation	Warning Limit (upper)	Action Limit (upper)
Livermore Perimeter	0.046	2.7	0.35	0.96
Livermore Offsite	0.012	2.9	0.11	0.31
Site 300	0.0055	2.2	0.029	0.066
POOL	0.15	2.4	0.92	2.3
B292	0.085	2.5	0.56	1.4
B331	1.4	5.2	43	240
B514	1.7	3.8	27	110
B624	2.7	2.3	15	36
Bq/L[(a)]	**Geometric Mean**	**Geometric Standard Deviation**	**Warning Limit (upper)**	**Action Limit (upper)**
Livermore Perimeter	5.9	2.9	51	150
Livermore Offsite	1.5	2.9	14	43
Site 300	0.77	2.3	4.1	9.5
POOL	16	2.6	120	320
B292	11	2.6	80	220
B331	180	5.4	5,700	32,000
B514	220	3.8	3,400	13,000
B624	340	2.4	2,000	4,900

a Bq/m^3 is derived from Bq/L based on the total flow that has passed through the silica gel. Bq/L is the fundamental measured value; Bq/ m^3 is the reporting unit.

5.3.8 Future Plans

Although the present locations of the air tritium sampling sites are expected to adequately monitor air concentrations around the Livermore site, another set of tritium concentration contours will be calculated using CAP88-PC. The last time this was done, there was a significant contribution from the Sandia Tritium Facility, which no longer exists. The relative importance of sources of tritium has changed in the past year and will continue to change with the start-up of the DWTF in the short-term and the National Ignition Facility in the longer-term.

The long-term plan is to keep up to date with changes in LLNL operations and to add and remove sampling locations as these operational activities change. For example, if open-air explosives experiments using tritium are conducted at Site 300, it is likely that current tritium monitoring in the vicinity will be expanded. In addition, efforts will continue to reduce the chance of errors caused by either human or equipment error.

As always, periodic technical assessments of the air tritium network will be performed.

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6 Sewer Monitoring

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6.1 Introduction

The Livermore site of Lawrence Livermore National Laboratory (LLNL) is the largest single source of the sanitary sewage processed by the Livermore Water Reclamation Plant (LWRP). LLNL and Sandia National Laboratories, California (Sandia/CA) together produce an average of 1-million liters of sewage each day, approximately 4 percent of the volume treated at the LWRP. The combined volume, consisting primarily of sanitary wastewater and cooling tower blowdown water, is discharged to the city of Livermore sewer system from the northwest corner of the Livermore site (**Figure 6-1**).

After treatment at the LWRP, the wastewater is pumped out of the Livermore valley through a pipeline shared with five other Publicly Owned Treatment Works (POTWs) and discharged into the San Francisco Bay. The sludge produced in the treatment process is disposed of in landfills.

The research-and-development activities at LLNL require the use of hazardous and radioactive materials; if significant concentrations of these materials were inadvertently discharged to the sanitary sewer, they could seriously impact LWRP operations and potentially degrade the quality of water resources. Programs to control these materials are mandated in federal and state law, U.S. Department of Energy (DOE) orders, and local regulations. In some cases, these requirements impose specific engineering standards for discharge control measures. Generally, though, they impose numerical limits on the presence of pollutants.

LLNL also conducts operations at the Experimental Test Facility (Site 300) located near Tracy, California. Sewage from this location is not handled at the Livermore site. The main complex of buildings at Site 300, the General Services Area, discharges to sewer evaporation and percolation ponds. At remote facilities, separate septic systems are installed. The site does not discharge to a POTW. However, routine monitoring of the sanitary sewage (excluding septic system sanitary sewage) is required by Waste Discharge Requirements (WDRs) issued by the Central Valley Regional Water Quality Control Board (CVRWQCB). EPD also monitors parameters in groundwater monitoring wells downgradient from the pond. The sewer evaporation and percolation ponds and groundwater monitoring are discussed in Chapter 8. The remainder of this chapter focuses on the Livermore site monitoring programs.

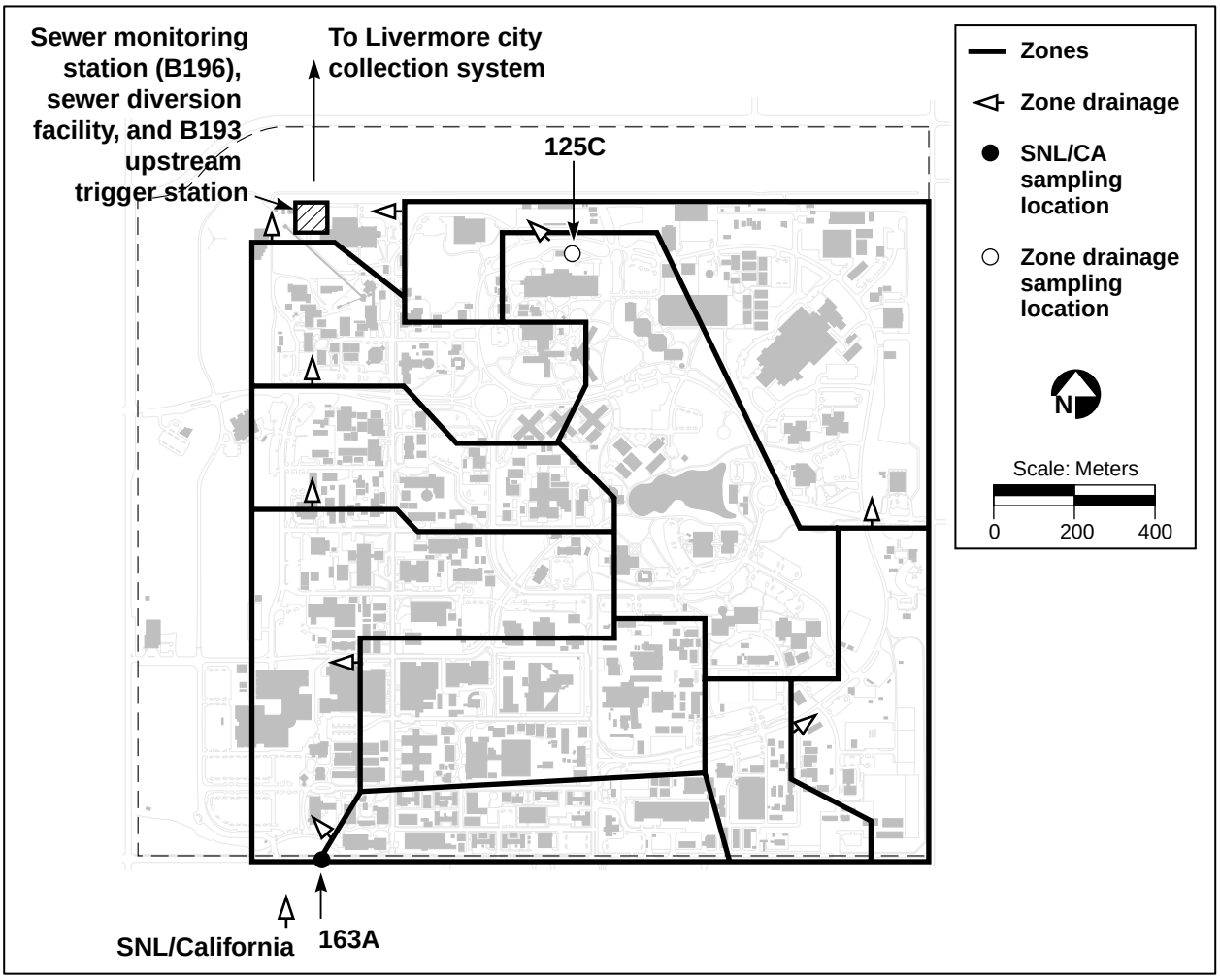

Figure 6-1. Livermore site sewer monitoring network

6.1.1 Pollutant Discharge Limits

Nonradiological pollutants generated at the Livermore site are covered under the wastewater discharge permit issued by the LWRP (City of Livermore 2002). The permit is issued following review of an application that provides a comprehensive overview of LLNL wastewater discharges (Grayson 2002). Documentation includes a complete listing of chemicals used at the site, process diagrams for specific waste treatment and materials processing operations, a description of retention tank systems, and an overview of the sewer monitoring program. The permit covers reporting and monitoring requirements, as well as specific outfall discharge limits (**Table 6-1**) and point-source discharge limits as prescribed by the federal Categorical Standards. These standards are discussed in **Section 6.5**.

Table 6-1. Nonradiological pollutant outfall limits specified in the LLNL wastewater discharge permit

Parameter	Limit (mg/L)
Arsenic	0.06
Cadmium	0.14
Chromium	0.62
Copper	1.0
Lead	0.2
Mercury	0.01
Nickel	0.61
Silver	0.20
Zinc	3.0
Cyanide	0.04
pH	5-10
Oil and grease	—[a]
Total toxic organics (TTO)	1.0

Source: City of Livermore 2002

a Analysis suspended

General discharge prohibitions are also stated for:

- Explosive or pyrophoric solids, gases, or liquids
- Solids or viscous substances
- Toxic pollutants
- Substances that would cause the LWRP to be in noncompliance with sludge use or disposal criteria
- Noxious or malodorous liquids, gases, or solids that would create a public nuisance or hazard to life
- Substances that would cause the LWRP to violate its National Pollutant Discharge Elimination System (NPDES) permit or receiving water quality standards
- Wastewater with objectionable color
- Heated waters that may inhibit biological activity
- Pollutants that may cause interference to the LWRP
- Wastewater that would cause hazard to human life or would create a public nuisance

- Radioactive wastes or isotopes that exceed limits established by a state or federal regulatory agency

The discharge criteria for radiological pollutants are covered under DOE Order 5400.5, Chg. 2, Chapter II, paragraph 1 (except 1.a.3.c. and 1.c.), *Requirements for Radiation Protection of the Public and the Environment* (see WSS B94 in Appendix B; Code of Federal Regulations (CFR), Title 10, Part 20.2003 (a)4, Subpart K, *Standards for Protection Against Radiation*; and, as summarized in the general discharge prohibitions, the wastewater discharge permit issued by the LWRP (City of Livermore 2002). Because DOE facilities are not licensed by the Nuclear Regulatory Commission, they are, in principle, exempt from the requirements of 10 CFR 20. However, LLNL has adopted parts of California Code of Regulations (CCR), Title 17, Section 30253, *Standards for Protecting Against Radiation* (CCR 1997), which incorporates by reference 10 CFR 20 requirements. Both DOE Order 5400.5 and 10 CFR 20 contain concentration-based discharge limits for specific radioisotopes. Also 10 CFR 20.2003 (a)4, Subpart K, contains total annual radioactivity discharge limits. The concentration-based discharge limits from DOE Order 5400.5 and the total annual radioactivity discharge limits from 10 CFR 20 are summarized in **Table 6-2**.

Table 6-2. Discharge limits applicable to LLNL for radionuclides in sewage

Source	Radionuclide	Limit
10 CFR 20.2003 (a)4, Subpart K,	Tritium	185 GBq/y
	Carbon-14	37 GBq/y
	All others	37 GBq total/y
DOE Order 5400.5, Chg. 2, Chapter II, Paragraph 1 (except 1.a.3.c, and 1.c)	Tritium	370 Bq/mL
	Potassium-40	1.3 Bq/mL
	Uranium-238	0.11 Bq/mL
	Plutonium-239	0.0056 Bq/mL
	Americium-241	0.0056 Bq/mL

After specifying the discharge limitations, the regulations generally leave to the discharger the development of administrative and engineering control systems that will ensure that the discharge meets established limits. At LLNL, administrative measures include implementation of internal discharge limits, training of materials handlers, control and tracking of certain materials, drain labeling, and inspection and review of facilities and operations. Engineering controls include isolating specific operations from sanitary connections and collecting industrial wastewater from entire facilities in retention tanks.

6.1.2 Discharge Controls

LLNL's upstream controls are supplemented by the Sewer Diversion Facility, an automatic sewer diversion and retention facility located adjacent to the sewer monitoring station (Building 196) in the northwest corner of the site (**Figure 6-1**). The facility consists of a below-grade diversion structure with pumps; 11 completely enclosed, onground holding tanks; one large, open-top optional treatment tank; one small, open-top chemical feed tank; and two large, concrete secondary containment structures. In addition, the facility has a paved staging area for vehicles or temporary tank placement. The total permanent capacity is 880,000 L of wastewater, or enough to contain roughly 6 hours of normal flow during peak operating hours. All tanks are equipped with provisions for aeration, pH adjustment, tank washdown, liquid chlorination, and odor control. When a potential release is detected, the facility is automatically activated by the Sewer Monitoring Station (SMS), mentioned below and described in **Section 6.4.1**. The facility is also automatically activated by the Upstream pH Trigger Station, as explained in **Section 6.4.1.3**.

6.1.3 Sewer Monitoring Program

The sewer monitoring program supports the discharge control effort in three ways. First, it defines criteria for the acquisition and analysis of retention tank samples. Occasionally, monitoring requirements for specific retention tank operations are specified in permits or regulations. More frequently, monitoring is based upon reviews of facility operations and chemical sources. In any case, the monitoring must be complete and representative to ensure that informed decisions are made regarding the disposal of collected wastewater.

Second, sampling and analysis of the sewage actually released to the LWRP enable EPD to assess the effectiveness of the control program in maintaining pollutant levels below discharge limits. These monitoring requirements are generally specified in detail by permit or DOE order. The effort covers a broad range of potential contaminants. Trending of the results identifies increases in pollutant levels that may require further investigation or potential revision of the control program (**Section 6.3.5**).

Third, LLNL continuously monitors in real time for those pollutants with the greatest potential to adversely impact the public welfare. The continuous monitoring effort seeks to detect any event in which failure of control measures results in a release that might adversely impact LWRP operations. The continuous monitoring system is designed to ensure that the bulk of any serious release is captured on site by the Sewer Diversion Facility.

The three elements of the sewage monitoring program (retention tank, sewer compliance, and sewer spill monitoring programs) are interrelated, but separate, efforts. Each is discussed in

turn below, starting with the retention tank monitoring program in **Section 6.2**. The chapter concludes with a discussion of the categorical pretreatment monitoring program in **Section 6.5**.

6.2 Retention Tank Monitoring Program

6.2.1 Rationale and Design Criteria

LLNL's wastewater retention systems consist of onground tanks, underground tanks, aboveground tanks, piping, pumps, and ancillary equipment for collecting dilute rinse water and wastewater generated by research activities. These wastewaters can be hazardous, nonhazardous, radioactive, or mixed (i.e., hazardous and radioactive) wastes. Most systems collect and temporarily store dilute, nonhazardous rinse water from materials fabrication or finishing operations. The systems ensure that discharges to the LLNL sanitary sewer system are within permit limits and that nonsewerable wastewater is properly stored until appropriate disposal can take place.

By LLNL policy, all wastewater retention tank systems are required to have secondary containment capacity. This capacity is usually provided by a berm around the retention tank and all aboveground piping. During the rainy season, storm water that falls into the berm presents maintenance and operational problems. Most serious is the reduction of the available secondary containment capacity. Consequently, LLNL's tank engineering guidelines (Graser 1993) suggest covering bermed areas or providing separate retention capacity for collected water.

Many systems in place do not have features to control berm water and so must be drained rapidly following any significant rainfall. By agreement with the Central Valley (Letter of April 18th, CV Regional Water Quality Board) and San Francisco Bay (Waste Discharge Requirements 95-174) Regional Water Quality Control Boards, and the LWRP (City of Livermore 2001, DOE Order 5400.5 Chg. 2, Chapter I, Paragraph 7, Discharges to Sanitary Sewer), as stated in LLNL's permit application to the LWRP (Grayson 2002), LLNL discharges uncontaminated berm water to the storm drain system or slightly contaminated berm water to the sanitary sewer provided that administrative controls are met. These controls include screening the wastewater to determine whether the pH is within an acceptable range and a visual inspection of the maintenance records, tank system, and the liquid.

When a retention tank nears capacity, the tank is isolated from the waste stream to prevent further collection of wastewater. A representative sample is taken and analyzed to determine whether the contents meet discharge requirements specified in LLNL guidance documents, which are, in turn, based upon LWRP permit limitations and categorical pretreatment requirements in federal law (see **Section 6.5**). The evaluation of the analytical results is the

responsibility of EPD's Water Guidance and Monitoring Group (WGMG), which issues a Wastewater Discharge Authorization Record (WDAR) authorizing disposal of the tank contents (formerly the Retention System Disposition Record or RSDR).

6.2.1.1 Retention Tank Release Criteria

Installation of a retention tank system is based upon the potential for chemical and radiological inventories and operations at a facility to impact LWRP operations. During normal operation, a retention tank collects small-quantity discharges that, given measures implemented at the source, usually comply with internal discharge limits. When the tank becomes full, the contents are sampled and analyzed to validate their suitability for discharge, and then released to the sanitary sewer. When pollutant concentrations are above internal discharge limits, the collected wastewater is transferred to the on-site Department of Toxic Substances Control (DTSC)-approved Radioactive and Hazardous Waste Management (RHWM) facility.

Except for waste streams that are federally regulated under the Categorical Pretreatment Standards (see **Section 6.5**), the criteria for discharge authorization into the LLNL sanitary sewer are established by internal policy; LLNL internal policy is designed to ensure that wastewater leaving the site meets the outfall limits. As enforced by the LWRP, the site outfall limits specified in LLNL's wastewater discharge permit (City of Livermore 2002) apply to the combined volume released to the city sewerage, rather than to individual processes. The outfall limits apply only to nonradiological contaminants. Discharge limits on radioactivity in sewage specified by Order 5400.5, Chg. 2, Chapter I, Paragraph 7 and Chapter III are also applied at the LLNL site outfall, rather than on wastewater released from individual processes. This allows LLNL some flexibility in developing criteria for releases from retention tanks that are upstream of the point of discharge to the city sewerage.

In principle, this flexibility could be implemented in a process whereby high-concentration, nonhazardous, noncategorical wastewater was slowly released to the sanitary sewer in such a way that the contaminant loading was not sufficient to result in a violation of outfall limits. Aside from the practical problems of managing simultaneous releases from many tanks, this approach violates the spirit of cooperation between LLNL and the LWRP. Though not required, as guidance LLNL follows DOE Order 5400.5, Chg 2, Chapter II, paragraph 3d(4), which states that all "discharges [of radioactivity] to the sewers shall be coordinated with the operators of the waste water treatment works" (DOE 1993). LLNL has also applied this principle to the development of nonradiological release criteria. Variable release criteria also present a problem in that they do not provide consistent guidance to programs designing wastewater control measures and so interfere with operational planning. For these reasons, LLNL developed uniform release criteria for most of its retention tanks and presented those

criteria for review by the LWRP (The one notable exception, the Sewer Diversion Facility, is discussed below.)

Although preferable in principle, uniform release criteria cannot completely encompass the complexity of actual operations and in-place facilities. Predicting the impact of a tank discharge on pollutant concentrations at the site outfall requires some assumptions concerning the rate of release from the tank and the flow rate at the outfall. To derive its internal discharge limits, a study was conducted using data from 1998–2000 tank releases coupled with time-proportional flow data. The internal limits were derived using conservative assumptions concerning release capabilities and discharge conditions.

For radioactivity, additional criteria follow from DOE Order 5400.5, Chg. 2, Chapter II, Paragraph 3d(2) and 10 CFR 20.2003 (a) 4, Subpart K limits the total activity released during any one year to 185 GBq. (For most radionuclides, this activity, divided by LLNL's average daily flow, is far less than the isotope-specific concentration limits.) Order 5400.5, Chg. 2, Chapter II, Paragraph 3d(2) contains narrative requirements limiting the total activity to levels that prevent "long-term buildup of radionuclides in solids" and exposures to members of the public (principally POTW operators) "exceeding a small fraction of the basic annual dose limit". Concentrations of radionuclides in wastewater shall be controlled so that long-term buildup of radionuclides in solids will not present a handling and disposal problem at the LWRP (DOE 1993). To address these requirements, as well as concentration limits, the release criteria constrain the total radioactivity that can be released from all retention tanks during a single day.

The criteria derived from these considerations are presented to the LLNL work force in the *ES&H Manual*, Document 32.4. The criteria, reproduced here in **Tables 6-3** and **6-4**, indicate the potential scope and sensitivity of LLNL's retention tank sampling program.

Absent in **Table 6-4** are release limits for specific radioisotopes other than tritium. Instead, limits are imposed on gross alpha and gross beta activities. This simplification reflects the practical aspect of managing a retention tank program: when retention tanks are at full capacity, the time between sampling and the return of analytical results imposes costs on the facility, either in the form of reduced storage capacity, the need to pay for additional storage capacity, or operational delays. Secondly, the cost of the analysis must be reasonable.

Table 6-3. LLNL's internal discharge limits for nonradioactive parameters in noncategorical wastewater

Parameter	Limit (mg/L)
Beryllium	0.20
Cadmium	0.9
Chromium	4.9
Copper	10
Mercury	0.05
Nickel	5
Lead	4.9
Silver	1
Zinc	15
Cyanide	5
Arsenic	0.06
pH	5-10
Oil and grease	500
Total toxic organics (TTO)	4.57

Source: *ES&H Manual*, Document 32.4

Table 6-4. LLNL's internal discharge limits for radioactive parameters in wastewater

Parameter	Individual discharges		Total daily limit for site	
Gross alpha	11.1 Bq/L	(0.3 µCi/1000 L)	185 kBq	(5.0 µCi)
Gross beta	111 Bq/L	(3.0 µCi/1000 L)	1.85 MBq	(50.0 µCi)
Tritium	185 kBq/L	(5 mCi/1000 L)	3.7 GBq	(100 mCi)
Gamma		—[a]		—[a]

Source: LLNL 2002

a There is no gross gamma limit; isotope-specific limits apply.

Radioisotopic analysis, unfortunately, is both time-consuming and expensive. As a practical compromise, retention tank samples are analyzed for gross alpha and gross beta activity, and the release criteria are based upon the permissible release concentrations of the commonly available alpha- or beta-emitting isotope with the lowest discharge limits. The values of **Table 6-4** assume uranium-238 as the alpha emitter and strontium-90 as the beta emitter.

6.2.1.2 Sampling Requirements

The retention tank sampling protocols must guarantee that a representative sample of the wastewater is collected for analysis. The analysis protocols must ensure that, without imposing needless cost, a meaningful assessment can be made of wastewater against the established

discharge criteria. Both protocols must be structured to minimize the time between when the tank has been filled and the final disposition of its contents.

The pollutants that can be found in a specific tank are dependent only on the types of processes that discharge to the tank. Operations in a specific LLNL facility may change routinely as research and development activities progress, and so the potential contaminants can change over time. As a result, the analysis list for each facility must be reviewed periodically.

Just as each retention tank has its own analytical requirements, the number and type of sample bottles and the preservation and holding time requirements for analysis also vary from location to location. A formal process should exist for communicating changing analytical requirements and training personnel to modify sampling procedures.

To obtain analytical results quickly, the tank should be sampled as soon as possible when it becomes full. Achieving this goal requires routine inspection of the tank, timely availability of sample bottles, and timely preparation of necessary paperwork.

Procedures for obtaining a representative sample from a retention tank vary from location to location, depending on the system design. For tank systems with recirculation capability, the waste should be recirculated for three tank volumes. For tank systems without this capability, a coliwasa or other appropriate sampling equipment should be used.

Turnaround times for analysis of tank samples are determined from the usage pattern of a particular tank system. Most tanks take three to six months to fill, and turnaround times of three weeks are acceptable. However, unusual or special circumstances can reduce fill times to a few days. For example, the Sewer Diversion Facility requires rapid turnaround to minimize the cost of operations while sewage is in the tanks. In addition, operations of the RHWM Division can be impacted when tardy analytical results delay discharge of wastewater from the treatment tanks. Ideally, turnaround times of five to seven days would be provided for these operations.

Given the relative infrequency and time constraints of the sampling activities, the individuality of the tank systems, and the variability of the sampling requirements, quality assurance (QA) and quality control (QC) sampling is an important consideration in this program. Field and trip blanks should be utilized, along with equipment blanks when samples are not transferred directly from the tank to the sample containers (i.e., coliwasas or pumps are used). Additionally, consideration should be given to a comprehensive analysis of a few samples each year to validate the process by which the analytical list is developed.

6.2.2 Extent and Frequency of Monitoring and Measurements

There are currently 45 in-service wastewater retention tank systems at LLNL, including those at Site 300. Sampling frequency for retention tanks is determined by operations:

- Nonhazardous waste tanks and radioactive waste tanks are sampled whenever the tank is full.
- Hazardous waste and mixed waste tanks are sampled and emptied within 90 days of the time they begin receiving waste.

Samples are collected by the RHWM Sampling Team, RHWM field technicians, technicians from the Technical Support Group (TSG) of the Operations and Regulatory Affairs Division (ORAD), or in isolated circumstances, LLNL program representatives. Sampling technicians use the Retention Tank Analysis List (RTAL) to determine which analyses are required and to sample accordingly.

The list of required analytes for an individual retention tank is based upon process knowledge. Considerations include any specific regulatory requirements for operations discharging to the tank, the type of operations generating the waste, and the contaminants that could potentially be present. For example, a retention tank that receives waste from a full-service analytical chemistry laboratory would need a full suite of analyses that includes pH, metals, total toxic organics, and possibly radiological analysis if the facility has a Radioactive Materials Management Area (RMMA). Other analyses such as cyanide or oil and grease can be added if those constituents are used in the facility or are required by specific regulation. However, a tank that receives only photoprocessing rinse water and is not connected to an RMMA may require only pH and metals analyses.

Special protocols are followed for sampling sewage diverted into the Sewer Diversion Facility. The tank contents are analyzed only for pH, normality, and the specific pollutant detected by the continuous monitoring system (see **Section 6.4.1**). Samples are taken by ORAD TSG technicians who follow procedure EMP-SW-DS, *Diversion Facility Tank Sampling*. Analysis is performed by LLNL's Hazards Control Analytical Laboratory (HCAL).

6.2.3 Laboratory Analysis Procedures

Most retention tank sample analyses are performed according to accepted EPA procedures. For screening purposes, a few analyses of nonregulated wastewater are done using noncertified methods, for example, field pH measurements. Except for the Sewer Diversion Facility samples handled by the HCAL, samples are analyzed by LLNL's Chemistry and Materials Science

Environmental Services Laboratory (CES), which may also contract samples to certified off-site analytical laboratories. (See **Section 6.6**.)

6.2.4 Quality Assurance Requirements

Although most sampling and analysis of retention tank volumes are not under the direct control or authority of ORAD personnel, protocols exist to ensure that quality objectives for these functions are met. Currently, the procedures and quality control manuals of the RHWM Sampling Team, the CES analytical laboratory, and subcontractor analytical laboratories are the controls that ORAD accepts to ensure the dependability of the results used in determining the deposition of the waste volumes from retention tanks.

QA/QC samples including field blanks, duplicate samples, and trip blanks are collected according to RHWM Procedure AP 158, *Waste Sampling Quality Assurance and Control Plan*. Only trained personnel who have completed the EP-5200 training course, "Waste Sampling," are allowed to submit samples for analysis. Sample collection follows RHWM Procedure 411, *Sampling Containerized Liquids*. CES laboratory chain-of-custody (CoC) forms and waste analysis request forms must accompany all samples submitted for analysis.

The RHWM Sampling Team or field technicians collect field, trip, and equipment blanks at the frequency prescribed in RHWM Procedure AP 158, *Waste Sampling Quality Assurance and Control Plan Overview*. According to this procedure, equipment blanks are collected for each decontamination event or for every 20 pieces of equipment decontaminated, whichever is lowest. One trip blank is collected for each day that volatile organics are sampled, and field blanks are collected if called for in the Sampling and Analysis Plan or by the Sampling Team Leader. Replicate samples are required 5 percent of the time, or every 20th time.

6.2.5 Program Implementation Procedures

Retention tank samples are collected by technicians following RHWM Procedure 411, *Sampling Containerized Liquids*. Sampling locations are at the point of discharge from the retention tank and are permanently marked with location and tank-specific identification. The written procedures include requirements for sample collection and submittal for chemical analysis, keeping a field log, and filling out the CES CoC form. The procedures also require the technicians to alert the Waste Generation Services Technical Lead if any difficulties or anomalies are encountered during the sampling event.

Although the facility users at LLNL are responsible for the operation and maintenance of the retention tank systems that service the facility, EPD is responsible for sampling, determination of appropriate analytes (with input from facility users and knowledge of operations that discharge

to the tank), collection methods, analytical methods, evaluation of the subsequent data and their quality, communication and coordination of network activities among sampling technicians and analytical personnel, and reporting of the results. Removal of the waste volume, followed by any required treatment and shipment, is managed by EPD's RHWM Division personnel. In a small number of cases, tank contents may be treated at the facility rather than removed, using a state-licensed transportable treatment unit (TTU). Following this treatment, the waste volume is sampled, analyzed, and reviewed following the same procedures as non-TTU treated volumes.

6.2.6 Action Levels

When the data package is received from the CES laboratory, the WGMG staff member responsible for discharge authorizations begins the processes of evaluation against the internal discharge criteria shown in **Tables 6-3** and **6-4**. Release authorization is granted as described in the WGMG procedure, WGMG-WD-AR, *Wastewater Discharge Authorization*. This procedure states that sample data are reviewed and, for the majority of tank systems, compared with the internal discharge limits. For the small number of tank systems dedicated to accepting waste streams from categorical processes, predetermined federal limits apply (for a more thorough discussion of categorical processes, see **Section 6.5**). Prior to completion of the WDAR, the data package sample numbers from the sample strategy form, the waste analysis request form, and the laboratory data report are reviewed to ensure that the results correspond to the waste volume intended. If the data indicate that contaminant loads are below numerical discharge limits, authorization for discharge to sewer is given via a WDAR. If they are above numerical limits, the waste volume is handled for treatment by the on-site RHWM facility or shipped to an off-site permitted treatment, storage, and disposal facility.

Sample results are also compared with historical data maintained on each retention tank system by WGMG staff. Unusual results are followed up by discussions with the analytical laboratory, sampling technician, responsible Environmental Operations Group (EOG) analyst, and/or the facility tank operator. If an error in sampling or analysis is determined, or an improper discharge to the retention system occurred, a Nonconformance Report (NCR) is filed with the ORAD QA coordinator. The NCR is processed according to the ORAD procedure, ORAD-QA-NCR, *Nonconformance Reporting and Tracking*, to determine whether further action is necessary.

6.2.7 Preparation and Disposition of Reports

A WDAR is generated for each tank sampling event and is kept on file for a minimum of five years. The form includes the final disposition alternative determined by ORAD discharge control personnel (following procedure WGMG-WD-AR, *Wastewater Discharge Authorization*) and records the date, time, and circumstances under which the tank was drained.

A Retention Tank Analysis List is generated at least annually to keep sampling technicians apprised of any changes in retention tank analytical requirements.

General engineering information about retention tanks and the Sewer Diversion Facility is included in LLNL's annual wastewater discharge permit application (Grayson 2002), which is submitted to the LWRP.

6.2.8 Future Plans

Because the retention tank monitoring program is a mature program that functions well, no significant changes are anticipated. The program does change as needed, to adapt to process changes, and to ensure compliance with any changes to regulatory requirements. Efforts to improve the efficiency of the retention tank analysis program and the associated data management are continual.

6.3 Sewer Compliance Monitoring Program

6.3.1 Rationale and Design Criteria

The primary goal of the sewer compliance monitoring program is to evaluate LLNL's compliance with regulatory requirements. This is performed under the regulatory framework described in **Section 6.1.1**. The program also seeks to aid in evaluating the control program that prevents violation of sewer discharge requirements imposed by local, state, and federal regulations, and by DOE Order 5400.1, Chapter IV, Paragraph 1.a. LLNL's compliance in the monitoring of nonradioactive contaminants is defined by the terms of the discharge permit granted by the LWRP (City of Livermore 200). Components of the radiation monitoring program also are keyed to demonstrating compliance with regulatory requirements (CFR, Title 10, Part 20, Subpart 2003(a)4, Subpart K, and DOE Order 5400.5, Chg. 2, Chapter I, Paragraph 7). However, demonstrating the effectiveness of a control program also requires measures that track certain contaminants at levels far below regulatory limits. An example of these measures is tracking plutonium at levels 1 million times lower than the most restrictive discharge standard.

6.3.1.1 General Considerations

Once contaminants are introduced to the sewer system, they travel along a well-defined route until they arrive at the LWRP for treatment. The primary monitoring location, as required by logic and regulation, is located at LLNL's point of discharge to the city collection system. Sampling at this location allows assessment of LLNL's compliance with discharge requirements. A complete analysis of the monitoring data also requires knowledge of any contaminants introduced by upstream dischargers (such as Sandia/CA whose sanitary sewer

effluent discharges to the LLNL sewer system in the southwest corner of the LLNL site). Assessment of the impacts of LLNL discharges requires sampling of process waste streams at the LWRP. On-site sampling requirements are discussed below.

The constituents in sewage are constantly varying. The most representative characterization of the overall quality of wastewater is, therefore, obtained by compositing: small aliquots of the discharge are combined into a large container, which at the end of the sampling period is mixed and decanted into sample bottles. There are two methods of compositing:

- For waste streams with fairly constant flow, aliquots may be taken at fixed time intervals. This time-proportional method is not applicable at LLNL because flow rates vary from 200 to 2400 L/min during the course of a normal day.
- In the flow-proportional method, integrating flow meter monitors the total volume of wastewater discharged and activates a sampler once for every fixed volume of wastewater (e.g., every 3785 L) discharged. This method provides an accurate daily average pollutant concentration when the flow rate varies widely.

The frequency of composite sampling should correspond with what is known about facility discharges and the hydrodynamics of the sewer flow. LLNL facility discharges generally are of two classes: brief releases of small (approximately 4-L) quantities through sinks or other plumbing fixtures, occurring at almost any hour of the day; and discharges on the 4,000-L scale, lasting from 10 to 30 minutes (as constrained by the capacity of most facility connections), and occurring mostly during normal working hours. The primary sources in the latter case are planned discharges from boilers, cooling towers, and retention tanks. Of the first class of discharges, pH fluctuations are most frequently observed. Monitoring data show that these releases usually last 2 to 10 minutes. From these considerations, flow-proportional compositing with an aliquot acquired every 2 to 5 minutes should be adequate for the types of releases observed at LLNL. In other words, with the flow-proportional method, the fixed volume of wastewater that activates the sampler should be adjusted (as determined by LLNL's flow-rate profile) such that the sampler acquires an aliquot every 2 to 5 minutes. At this frequency, the second class of discharges (larger volume, longer duration) will also be adequately sampled.

Compositing is not applicable to all analytes. Volatile organics may dissipate prior to analysis of the composite. Certain wastewater-quality parameters may be affected by the biological activity of the sewage. Compositing is most applicable for analysis of pollutants, such as heavy metals or minerals that are stable over time. This "rule" is evident in the monitoring requirements specified by DOE and the LWRP.

6.3.1.2 Specific Monitoring Requirements

The wastewater discharge permit issued to LLNL by the LWRP requires continuous outfall pH and flow monitoring and analysis of weekly flow-proportional composite samples for nine specific metals (**Table 6-1**). Once each month, the permit also requires analysis of 24-hour flow-proportional composite sample and grab samples. The composite sample must be analyzed for water quality parameters (biochemical oxygen demand, total dissolved solids, and total suspended solids) and toxic substances (tributyltin in January and July). The grab samples must be analyzed for an additional suite of toxic substances (cyanide in January and July, and volatile and semivolatile organic compounds monthly), and oil and grease (currently suspended pending ordinance revision allowing new freon extraction method). The regulatory requirements for the radiation monitoring program are less prescriptive. Gross alpha and gross beta analyses of daily flow-proportional composite samples are good screening measures for the presence of radioactivity, but do not give the specific radioisotopic concentrations necessary for comparison with limits contained in 10 CFR 20.2003(a)4, Subpart K, Total quantity of radioactive material released into the sanitary sewer in a year, and Order 5400.5, Chg. 2, Chapter III. Gross radiation screening is also not sensitive to very low-energy beta radiation, such as that produced by tritium. For these reasons, the general screening program must include some isotope-specific analysis.

Large quantities of predominantly gamma-emitting isotopes are not produced on site. At one time, LLNL operated a research fission reactor, and strontium-90 (a beta emitter) was monitored to track the discharge of fission products. Since the addition of a high-sensitivity gamma monitoring system to the continuous monitoring system (described in **Section 6.4**), it is clear that the gamma-emitting isotopes discharged with LLNL effluent are predominantly natural (radon and its daughters) and medical (e.g., iodine, gallium, thallium, and technetium) in origin; and the total activities are typically in millicuries per month.

As discussed in **Section 6.3.1.1**, to control daily discharges from the site, LLNL has developed internal retention tank discharge guidelines. The internal guidelines assume that the gross alpha activity detected in retention tanks is caused primarily by depleted uranium and conservatively apply the monthly discharge standards of DOE Order 5400.5 to the daily effluent concentration. The actual daily discharge guideline developed is 0.185 MBq (5.0 μCi) of alpha radiation, while the analytical limit of sensitivity corresponds to 0.1 MBq (2.7 μCi), following multiplication by the average daily flow.

6.3.2 Extent and Frequency of Monitoring and Measurements

6.3.2.1 Sampling Locations and Methodology

6.3.2.1.1 On-Site. On-site sampling locations are shown in **Figure 6-1**. The sewer monitoring station (Building 196) at the northwest corner of the site is the location for outfall compliance monitoring. Location 163A, on the south edge of the LLNL site, is the sampling point for Sandia/CA effluent. The remaining locations are sampling points that may be used to determine which drainage zone is the source of an unplanned release or is contributing to elevated pollutant concentrations, as measured at location Building 196 (see **Section 6.4**).

The outfall compliance sampling location is chosen to track the pathway of contaminants released from LLNL and Sandia/CA to the LWRP treatment process. As required by the terms of the sanitary sewer permit, the LLNL outfall compliance sampling point is located at the northwest corner of the site, where LLNL sewage is discharged to the city collection system. The flow-proportional composite and grab samples acquired here are used to determine the combined contribution of LLNL and Sandia/CA discharges to the LWRP. The acquired samples that are described here are all collected at the LLNL outfall. Three distinct sampling locations are used at the outfall:

- The Sewer Monitoring Station, or Building 196, which serves as the main monitoring station.
- C196, a composite sampling system located in a shelter to the east of Building 196.
- The flume, located in the vault to the east of Building 196. (The vault contains the flow-monitoring equipment used to trigger the composite sampling systems.)

The Building 196 sampler is activated once every 3785 L of flow (approximately every 2 minutes at normal on-shift flow rates, and about every 10 minutes off shift). The C196 sampler is activated once every 30,000 L of flow.

Sampling of Sandia/CA's effluent occurs at the point where it enters the LLNL sewer system. This sampling location in manhole number 163A allows the impacts of the two facilities to be separated and, as necessary, provides confirmation of Sandia/CA monitoring results. Because flow-measuring equipment has not been installed at this site, the Sandia/CA sampling equipment located next to the manhole is of the time-proportional type. This sampler is activated approximately every 15 minutes, and a 500-mL aliquot of the time-proportional composite sample is collected and archived daily.

6.3.2.1.2 Off Site. As described in procedure EMP-SW-LWRP, Sewage Sampling at LWRP, sampling at the LWRP occurs at two locations. Samples of the LWRP effluent are acquired to monitor the release of soluble contaminants to the San Francisco Bay, while samples of the liquid in the aerated digesters track levels of heavy metals and radionuclides that concentrate in the dried sludge. Conditions at the LWRP plant are characterized by the collection of composite samples for soluble contaminants, and, because of extensive mixing and long retention times of liquids in process tanks, grab samples from aerated digesters. LWRP personnel following LWRP procedures for sampling locations, methodology, and frequency collect samples. LLNL procedure EMP-SW-LWRP describes these LWRP procedures.

6.3.2.2 Sampling Frequency and Analytes Measured

Compliance sampling and analysis follow regular schedules and are subdivided into two types of programs: radiation and nonradiation monitoring.

6.3.2.2.1 Radiation Monitoring. Each day, a flow-proportional composite of LLNL effluent is acquired, as described in sampling procedure EMP-SW-B196, Sewage Sampling at Building 196. Each daily sample is analyzed for alpha, beta, and tritium activity. Monthly composites of the LLNL daily samples are analyzed for plutonium and cesium-137. In addition to analyzing the daily samples for alpha, beta, and tritium activity, a monthly composite of LLNL effluent from the C196 sampling location is also analyzed for tritium and gross alpha and beta activities (see procedure EMP-SW-C196, *Sewage Sampling at C196*). The results of this radiation monitoring program are used to assess compliance with gross radiation and isotope-specific discharge limitations imposed by 10 CFR 20.2003(a)4, Subpart K, and with the isotope-specific limitations of Order 5400.5, Chg. 2, Chapter III.

As described in procedure EMP-SW-LWRP, Sewage Sampling at LWRP, the composites of LWRP effluent collected each day are combined to create a monthly sample; these monthly samples are analyzed for alpha, beta, and tritium activity. Monthly composites of LWRP daily samples are analyzed for plutonium and cesium-137. Lastly, LWRP's microbially activated liquid sludge is analyzed monthly for gross alpha and beta activity, and quarterly composites are analyzed for plutonium and gamma activity.

6.3.2.2.2 Nonradiation Monitoring. The wastewater discharge permit issued to LLNL by the LWRP prescribes the requirements for the nonradiological monitoring program. As described in sampling procedure EMP-SW-C196, *Sewage Sampling at C196,* a weekly composite of LLNL effluent is acquired from the C196 sampling location and analyzed for metals content. In addition, once a month, 24-hour composite samples and grab samples of LLNL effluent are collected from the flume. These samples are submitted for analysis of water-quality parameters and concentrations of toxic chemicals. **Table 6-10** shows the complete list of parameters that are

analyzed under procedure EMP-SW-C196. Rationale, scheduling, and sampling protocols for this work are also detailed in EMP-SW-C196. Finally, inside the Building 196 Sewer Monitoring Station, a pH probe and circular chart recorder operate continuously to record the pH levels of the effluent. The rationale and scheduling of routine operations for this equipment are discussed in two procedures: EMP-SW-M, *Sewer Equipment Maintenance*, and EMP-SW-CA, *Sewer Equipment Calibrations*.

The nonradiological monitoring program also conducts additional sampling and analysis not required by the discharge permit. Portions of the LLNL daily samples from the Building 196 sampling location are combined and analyzed weekly for metals content, and LWRP microbially activated sludge samples are analyzed monthly for metals concentrations.

6.3.2.3 Quality Assurance/Quality Control Sampling

To verify the quality of the compliance monitoring program's analytical results, QC samples are systematically collected and analyzed. The QC samples are obtained by splitting the routine samples and are analyzed by either the primary laboratory or the QA backup laboratory.

The laboratories routinely performing the radiological analyses analyze all QC samples taken for the radiation monitoring program. Once a week, a split of the Building 196 daily composite sample is analyzed for gross alpha, gross beta, and tritium. Twelve percent of all Building 196 samples analyzed for gross alpha, gross beta, and tritium are QC samples. Once a year, a random month's archived splits of the monthly composites of the LLNL daily samples and the monthly composites of the LWRP effluent are submitted for plutonium and cesium-137 analysis; these QC samples account for 8 percent of the samples submitted.

All the QC samples collected for the nonradiation monitoring program are submitted to LLNL's outside, contract QA/backup analytical laboratory. Every month, as determined by rotating through a list of all the analyses routinely requested each month, two split samples are collected from the monthly 24-hour composite and its associated monthly grab samples. With a total of 12 different analyses requested on a monthly basis, submittal of two samples for QA purposes equates to approximately a 17 percent QC sample rate. During the second week of each month, a split of the weekly composite sample is collected, approximately a 24 percent QC sample rate.

6.3.2.4 Preparation and Transfer of Sample Aliquots

TSG technicians prepare sample aliquots and transfer the LLNL daily composite samples (procedure EMP-SW-B196, *Sewage Sampling at B196*), monthly composite and grab samples (procedure EMP-SW-C196, *Sewage Sampling at C196*), and Sandia/CA daily composite to the

analytical laboratories. LWRP personnel perform sampling of LWRP sewage, and TSG technicians transfer these samples to the LLNL analytical laboratories.

6.3.3 Laboratory Analysis Procedures

LLNL personnel perform radiological analyses (off-site checks for one day a month). The daily radiation analyses are provided by LLNL's HCAL; the CES laboratory performs high-sensitivity radiation analyses. Using these arrangements, turnaround times of 10 working days are typical for the analytes of most concern (gross alpha and beta radiation and tritium activity).

Nonradiological analyses are performed by LLNL personnel and by two outside contract laboratories. The portions of the LLNL daily samples that are combined weekly and LWRP monthly sludge samples are analyzed by LLNL HCAL for metals content using EPA methods. Off-site contract analytical laboratories perform all other nonradiological analyses. Specifically, one laboratory analyzes the weekly composite of LLNL effluent for metals content, and the monthly samples for water quality and toxic substances; the other laboratory is the QA/QC laboratory for weekly and monthly sample analyses performed by the first. The standard analytical methods used by both of these outside contract analytical laboratories are listed in **Table 6-5**. See **Section 6.6** for further details. Either HCAL personnel or TSG technicians perform sample preservation. (For a discussion of sample preservation and handling by the TSG technicians, see **Section 6.3.5.3**.) As prescribed in procedure EMP-SW-B196, *Sewage Sampling at B196*, HCAL personnel preserve Building 196 daily samples using nitric acid (HNO_3). HCAL personnel also preserve with HNO_3 sample aliquots of the C196 and LWRP weekly composite samples used for gross alpha and gross beta analysis and archival purposes.

6.3.4 Quality Assurance Requirements

The quality of the analytical results is ensured by two distinct methods. First, as discussed in **Section 6.3.2.3**; second, the analytical laboratories run laboratory QC checks. Depending on the analysis requested, the laboratory QC samples may include a method blank, laboratory control standard, laboratory control standard duplicate, matrix spike, and matrix spike duplicate. All QA data are received with the analytic results and are subsequently reviewed and evaluated by a WGMG analyst or the analyst assistant assigned to sewer monitoring.

6.3.5 Program Implementation Procedures

Accurate analytical results are important. The data are used to show LLNL's compliance with the discharge requirements and are trended by a WGMG analyst or the analyst assistant assigned to sewer monitoring to assess the effectiveness of the discharge control program; on a formal basis, data are trended annually (**Section 6.3.7**) and, informally, as needed. Important

factors in achieving accurate analytical results include sample identification systems, cross-contamination prevention measures, sample preservation and handling practices, and sample collection and equipment calibration procedures. These factors are discussed below.

Table 6-5. Analytical methods used by off-site contract analytical laboratories

Analyte	Method
Total settleable solids	EPA Method 160.5
Total suspended solids	EPA Method 160.2
Total dissolved solids	EPA Method 160.1
Alkalinity	EPA Method 310.1
Total phosphorus	EPA Method 365.4
Anion analysis	EPA Method 300.0
Chemical oxygen demand	EPA Method 410.4
Total organic carbon	EPA Method 415.1
Nutrients	EPA Methods 353.2, 351.2 and 350.1
Volatile solids	EPA Method 160.4
Aluminum, cadmium, calcium, chromium, copper, iron, magnesium, potassium, silver, sodium, and zinc	EPA Method 200.7
Beryllium	EPA Method 210.2
Nickel	EPA Method 249.2
Arsenic	EPA Method 206.2
Lead	EPA Method 239.2
Mercury	EPA Method 245.1
Selenium	EPA Method 270.2
Tributyltin	Gas Chromatography/Flame Photometric Detector
Total cyanide	EPA Method 335.3
Volatile organics	EPA Method 624
Semivolatile organic compounds	EPA Method 625
Total oil and grease[(a)]	EPA Method 1664
Biochemical oxygen demand	SM17-5210B

Source: Blanket service agreements between the Regents of the University of California and off-site contract analytical laboratories.

a The requirement to sample for oil & grease has been suspended until the Livermore Municipal Code can be modified to remove references to “freon-extractable” oil and grease (LWRP letter dated 4/1/99).

6.3.5.1 Sample Identification Systems

To ensure that requested analyses are performed for specific samples, the compliance monitoring program follows sample identification systems delineated in the *Analyte Request Sheets* maintained by TSG. The details of sample identification vary, but nominally TSG technicians apply sample bottle labels to all sample bottles, and both TSG technicians and LWRP personnel fill out these labels. A CoC form completed by LLNL personnel accompanies all sample bottles; the form reiterates the information contained on the bottle label and specifies the analyses to be performed.

6.3.5.2 Cross-Contamination Prevention Measures

The most likely source of cross-contamination for the compliance monitoring program consists of same-type sampling events, such as samples taken day to day, week to week, and month to month. This cross-contamination is minimized in several ways:

- The permanently installed samplers at the Building 196, C196, and Sandia/CA sampling locations are flow-through systems, which limits cross-contamination from the sampling equipment itself.
- The tubing of the portable samplers is cleaned between sampling events.
- The carboys and stainless-steel beakers used for sample collection are cleaned between sampling events.
- The disposable gloves worn by TSG technicians are discarded after each sampling event.

6.3.5.3 Sample Preservation and Handling

EPA protocol requires preservation of some of the compliance monitoring samples. All sample preservation is performed by LLNL personnel; the samples shipped off site for analytical work are preserved by the TSG technicians (**Table 6-6**), and those remaining on site are preserved by HCAL personnel (see **Section 6.3.3** for samples preserved by HCAL personnel). TSG technicians change gloves for each different sample preservative.

Table 6-6. Analysis desired and required preservative

Analysis	Preservative
Chemical oxygen demand, total organic carbon, and oil and grease[(a)]	Sulfuric acid (H_2SO_4)
Metals	Nitric acid (HNO_3)
Cyanide	Sodium hydroxide (NaOH)

a The requirement to sample for oil and grease has been suspended until the Livermore Municipal Code can be modified to remove references to "freon-extractable" oil and grease (LWRP letter dated 4/1/99).

6.3.5.4 Sample Collection and Equipment Calibration Procedures

To maintain sampling consistency, TSG technicians follow specific procedures for collecting LLNL samples (EMP-SW-B196, *Sewage Sampling at B196*, and EMP-SW-C196, *Sewage Sampling at C196*). LWRP personnel follow LWRP procedures for collecting samples of the treatment plant effluent and digester liquid; splits of these samples are given to LLNL. TSG technicians follow procedure EMP-SW-LWRP, *Sewage Sampling at LWRP*, for transferring LWRP samples from the treatment plant to the custody of LLNL.

The integrity of the flow meter and pH probe readings is confirmed by calibrations performed quarterly on the flow meter and weekly on the pH probe by TSG technicians. LLNL personnel follow calibration procedures in procedure EMP-SW-CA, *Sewer Equipment Calibrations*.

6.3.6 Action Levels

A WGMG analyst or the analyst assistant assigned to sewer monitoring checks routinely received data against action levels. For gross alpha, gross beta, and tritium analytical results, the informal, internally developed action levels are 3.7×10^{-4} Bq/L (0.01 pCi/mL), 0.02 Bq/L (0.5 pCi/mL), and 0.19 Bq/L (5 pCi/mL), respectively. The concentration-based discharge limits of DOE Order 5400.5 (WSS B94 in Appendix B) and annual totals of 10 CFR 20 are considered formal action levels for the radiological analytes. See **Section 6.1.1** for more information. For nonradiological analytes regulated by LLNL's wastewater discharge permit, the action levels are the discharge limits in the permit for pH, cyanide, and TTO and 50 percent or 100 percent of the limits for regulated metals (arsenic, cadmium, copper, chromium, lead, mercury, nickel, silver, and zinc), depending on whether the data reviewed are for the analysis of a weekly or 24-hour composite sample, respectively. (The discharge limits specified in the permit are provided in **Table 6-1**.)

If an analyte concentration exceeds an action level and the QC data are acceptable, the WGMG analyst looks for a correlation between a retention tank discharge and the analyte concentration. Depending upon the outcome of the attempted correlation, further investigation may be initiated by the WGMG analyst. The investigation may include, but is not limited to, the analysis of archived samples and the collection of nonroutine samples using strategically located portable samplers. However, in those cases in which a regulated metal concentration exceeds the 50 percent action level, archived 24-hour composite samples (corresponding to the weekly sampling period) must be submitted for analysis to provide direct comparison with LLNL's 24-hour discharge limit. If, in any case, the wastewater discharge permit limit is

exceeded, the investigation must include a subsequent resampling for the analyte in order to establish a time that marks LLNL's return to a state of compliance with the permit; the event is reported to the LWRP and DOE, as discussed in **Section 6.3.7**.

6.3.7 Preparation and Disposition of Reports

LLNL's wastewater discharge permit requires that outfall data be reported monthly. The report includes both the radiological and the nonradiological monitoring data received by the WGMG analyst during the month. It discusses any unusual data or data that indicate exceedence of permitted levels, summarizes changes in the monitoring program, and reports on activity in the continuous monitoring program (see **Section 6.4**). Data tables present: (1) monthly radiation monitoring (tritium, cesium, and plutonium) results for the year to date, (2) monitoring results for tritium in LLNL daily sewage samples for the previous month, (3) the last three months of weekly LLNL effluent metals concentrations, and (4) results for water quality and toxic substances of regulatory concern for the year to date.

If any analytical results exceed the LWRP-issued outfall discharge limits, the wastewater discharge permit requires LLNL to issue a Five-Day Report that details the incident. A copy of this report is sent to DOE. If LLNL receives enforcement action for the event, specifically a Notice of Violation, from the LWRP, then LLNL prepares an Occurrence Report, as required by Order 232.1A (DOE 1997).

The annual *Environmental Report* (Gallegos et al 2001) includes a summary and analysis of the radiological and nonradiological monitoring results, as well as raw data received from analytical laboratories.

6.3.8 Future Plans

The sampling procedure EMP-SW-C196, *Sewage Sampling at C196*, will be updated and revised, and maintenance procedures for equipment used to collect weekly and monthly samples will be formalized and documented. Second, data quality trends associated with metals analyses results will be identified and evaluated. Finally, the previously existing procedure EMP-SW-SNLL, *Sewage Sampling at SNLL*, will be revised and reinstated for sampling of Sandia/CA effluent at location 163A (see **Figure 6-1**).

6.4 Sewer Spill Monitoring Program

6.4.1 Rationale and Design Criteria

As a research and development facility, LLNL's discharges of nondomestic wastewater are almost universally batch discharges, as opposed to the continuous discharges typical of many

industrial facilities. Sources at LLNL can be as small as liter-quantity discharges of dilute chemical solutions by individual experimenters, lasting a few seconds or minutes. At facilities with retention tanks, these small-quantity discharges are consolidated in 1000- to 20,000-L batches and released to the sanitary sewer following chemical and radiological analysis (**Section 6.2**). Emptying a retention tank typically requires 30 minutes. For batches of this size, an inadvertent release of contaminants can cause a violation of LLNL's discharge limitations (which are averaged over weekly flows of 7 million liters) only if the contaminant concentration in the batch is much higher than the permit limitation. Because LLNL has historically contributed only 10 percent and, more recently, 3.9 percent of the influent received at the LWRP, for a release to disrupt LWRP operations the contaminant concentration would need to be 10 to 20 times higher than if LLNL were the sole contributor to the LWRP. Although LLNL cannot monitor continuously for the presence of all contaminants at concentrations near LWRP permit levels, it is possible to monitor for contaminants at concentrations that could pose an immediate threat to LWRP operations. Should a release occur, LLNL could then notify LWRP personnel to initiate mitigating measures (i.e., diversion of the contaminated influent into a holding pond for special treatment) and provide timely feedback to LLNL personnel so that corrective action (either further training or modification of wastewater handling procedures) could be implemented.

In the late 1980s, it became apparent to LLNL that, in the context of rapidly tightening regulations and the operational flexibility required by its research and development missions, its wastewater infrastructure was insufficient to guarantee continuous compliance with sewer discharge requirements. LLNL then initiated a comprehensive upgrade of its infrastructure. As part of this program, the spill monitoring system was completely redesigned to maximize its sensitivity to the contaminants of most concern; an 880,000-L sewage diversion and retention facility was constructed at the point of discharge to the city sewerage; and sampling stations were installed at a number of locations around the LLNL site (see EMP 1999, Section 6.4.8.1, Satellite Station Network).

With the addition of these capabilities, the spill-monitoring system became an integral part of LLNL's environmental control program. However, there is little formal guidance and few formal requirements for the system. DOE/EH-0173T (DOE 1991) does suggest "continuous radionuclide monitoring [at] those release points that could exceed 1 DCG [derived concentration guide] equivalent averaged over 1 year." This criterion, however, is far weaker than LLNL's Best Management Practices (BMPs), which maintain radionuclide concentrations at levels thousands to millions of times lower than their DCGs. The remaining EH-0173T guidance applies only to the calibration of equipment, spill response, and spill notification. Specific capabilities of the system are not identified. The other relevant standard—the self-monitoring program defined in the permit awarded by the LWRP—specifies only that pH and flow must be recorded continuously.

Specific monitoring goals are, therefore, based principally upon an institutional evaluation of the probability and potential impact of releases of specific contaminants. Currently, those goals have emphasized the real-time continuous monitoring of pH and flow, metals, and radioactivity. An evaluation of the compliance monitoring data establishes that other parameters of potential concern, such as organic chemicals and cyanide, are generally well within discharge limits and so do not merit the expense and effort of installing and maintaining real-time continuous monitoring capabilities.

The design criteria for a continuous monitoring system are a complex balance between the desired capabilities and the limitations of the currently available technology. The following sections discuss the goals for radiation and metals monitoring and then explore the issues raised in implementing the available technology.

6.4.1.1 Radioactivity

The most important monitoring goal is the detection and containment of releases of radioactive materials that contravene discharge limitations or LLNL BMPs.

Most discharge limitations are specified as bounds on the average monthly concentration for a specific radionuclide. See **Section 6.1.1** for details about regulatory guidance for the average monthly concentration. Evidence that releases have exceeded the discharge concentration limits (the DCGs) of Order 5400.5 would require that LLNL implement best available technology (BAT) to reduce discharges (DOE 1993). LLNL policy is to detect, as soon as possible, any release above the DCGs so that control measures may be implemented prior to violation of the DCG for the month as a whole.

As a specific example of LLNL's BMPs for radioactivity, quantities of transuranic materials greater than 3.7×10^5 Bq (10 μCi) must be handled in fume hoods with containers designated for the collection of liquid waste; quantities greater than 3.7×10^6 Bq (100 μCi) must be handled in glove boxes. Sensitivity in the continuous monitoring system to such quantities would provide immediate feedback (in the form of alarms) to personnel, should a release of this magnitude occur.

Detailed internal discharge limits for various radionuclides are presented in **Table 6-4**.

6.4.1.2 Metals

The hazard posed by LLNL's inventory of radioactive materials is mitigated by administrative and engineering controls upstream of the monitoring system. Early in the life of the Laboratory,

LLNL invested in these controls, and they have been successful in preventing releases that posed a serious threat (as defined in EPA and DOE public-protection standards) to the public welfare.

In the case of nonradioactive industrial pollutants, the development of upstream controls was less methodical. Standards prior to the implementation of the Clean Water Act in 1972 allowed the proliferation of small metal-finishing operations. This trend was encouraged by the nature of Laboratory operations. For sensitive operations, access to materials and information is limited to those with a "need to know," which is best managed when each project controls all of the resources necessary to accomplish its work. Additionally, research at the forefront of technical development is fostered when there is close contact among scientists and technicians. In this context, no concerted effort was made to consolidate metal-finishing operations until after 1986, when tightening pretreatment standards brought direct regulatory attention to the problem of the occasional release of metal-finishing solutions.

In setting its metals discharge limits, the LWRP considers three issues. First, the LWRP has discharge limitations of its own, established in its National Pollutant Discharge Elimination System (NPDES) permit. Compliance with these limits is evaluated through analysis of 24-hour composite samples of treated water. After accounting for the efficiency of the treatment process in removing metals, the NPDES limits translate to maximum concentration values allowed for metals in the influent wastewater. Second, those metals that are removed from the sewage are concentrated in sludge that is shipped to a sanitary landfill. Each shipment is generally a consolidation of sludge accumulated over weeks or months. When metals concentrations in the sludge are too high, it must be shipped to a hazardous waste landfill at significantly greater cost. Finally, bacteria in the activated digesters (the holding time in the digesters is only 6 hours) are suppressed when the concentrations of certain heavy metals become too high.

As may be inferred from the above, the primary purpose of the discharge limitations is to prevent disruption of LWRP operations. That purpose is the appropriate context for establishing the goals of LLNL's metals monitoring program. From the details of the LWRP operations schedule, it appears that 6 hours is the shortest timeframe over which a violation might result in serious disruption of plant operations. If the typical release at LLNL leaves the site over a 30-minute period, the target sensitivity for the monitoring system would be 12 times the discharge limit for the specific metal (resulting in a violation in the average concentration for the entire 6 hours). If the reduction in potency is accounted for by the addition of household wastewater prior to arrival at the treatment plant, a target sensitivity of 100 to 200 times the discharge limit could be acceptable.

For metals that do not strongly suppress bacteria, 24 hours is the appropriate timeframe for comparison with the discharge limitation; and that is, in fact, generally the enforcement

standard that has been applied by the LWRP in the recent past. Target monitoring sensitivities for these metals might be as much as 50 times the discharge limit. In this case, because the limit has been enforced at LLNL's outfall, any additional adjustments to account for reduction in potency are not appropriate for calculating target sensitivities.

The metals concentration limits imposed in the permit issued by the LWRP are presented in **Table 6-1**.

6.4.1.3 System Response Time

Having established the general goals for monitoring sensitivity, the next step is to determine acceptable bounds for the system response time. For the technologies chosen for metals and radioactivity monitoring in the current system (discussed below), rapid response and high sensitivity are actually competing criteria. Maximizing sensitivity would be unacceptable if response times were so long that a spill would arrive at the LWRP prior to annunciation of an alarm. Even with the Sewer Diversion Facility fully functional, it may be desirable for an alarm to annunciate well before the bulk of a release leaves the LLNL site.

Response time criteria can be developed in several ways. If analysis could establish a maximum credible concentration of a contaminant, the response time could be calculated as some fraction of the length of time necessary for the discharged mass to disrupt LWRP operations. A survey of historical retention tank records might provide a suitable basis for such an analysis. In general, though, contaminant discharges disperse and spread as they flow through the plumbing and pipes connecting the point of discharge to the monitoring station. Rather than a sharp increase, the concentration of the pollutant generally rises smoothly before the arrival of the main slug and falls slowly afterwards. The front-loading of the slug provides the possibility of detecting and containing a release when contaminants are still at moderate concentrations. An analysis of the dynamics of contaminant transport through the sewer system might show that more time was available to detect the leading edge of the spill than to contain the spill itself. As a benchmark, the shortest pH excursions observed are a full 2 minutes in duration, with rise-times of approximately 30 seconds.

Finally, the system responsiveness is limited by the mechanical characteristics of the monitoring and sampling equipment itself. Pumping a sample from the pipe to the monitoring station requires roughly 75 seconds (to ensure the representativeness of the sample, the delivery speed is constrained to the velocities typically observed in sewer systems, or roughly 61 cm/s [2 ft/s]). Phase separation equipment retains the liquid for roughly 30 seconds. The pneumatic valves of the Sewer Diversion Facility close approximately 6 seconds following activation. From this information, it can be concluded that performing analyses more frequently than once every 30 seconds would have no practical impact on spill control at the Sewer Diversion Facility.

(Because of these mechanical limitations to system response time, LLNL installed an Upstream pH Trigger Station in 1998.)

The Upstream pH Trigger Station (Building 193) was completed in FY 1998. This work included design and installation (upstream of the SMS and the Sewer Diversion Facility [SDF] retention tanks) of pH monitoring equipment to trigger a diversion at the SDF should the pH of LLNL effluent drop below the permit limit of 5 or above 10. A sewer vault was installed 32 meters upstream of the diversion valve for the SDF retention tanks in the SDF yard (with pH monitoring and communications equipment to identify and signal the need for diversion). New grinder vaults were installed on each of the major sewer trunk lines approximately 30 meters upstream of the pH monitoring vault. Each grinder vault contains a grinder for sewage homogenization. The intent of this upstream trigger is to capture the entirety of a pH spill before it is released to the Livermore collection system. The leading edge of such a spill could not be contained using the Building 196 real-time continuous monitoring system in the SMS because of limitations in the system response time.

On the basis of this analysis, it appears that practical response times should be in the range between 30 seconds and 10 minutes. The upper range is simply a reasonable fraction of the 30-minute period expected for most retention-tank releases and guarantees that a substantial fraction of the volume is retained prior to discharge.

6.4.1.4 Technologies

The factor that most complicates the continuous monitoring of sewage is the medium itself. Sewage is a mixed-phase and highly variable mixture of biologically and chemically active waste. Most sensors, when directly exposed to such sewage, suffer either interference or destruction as a result of the contact. pH sensors are the only common tool that has been shown to withstand extended contact with sewage. Flow monitoring, metals monitoring, and radiation analysis have all been implemented using noncontact methods. Unfortunately, to provide reliable analytical results, noncontact methods generally require that the effluent be constrained to a stable geometry. The required mechanical preparation and channeling usually result in restricted orifices and flow volumes that collect gravel, silt, grease, and/or biological growth. To manage these problems, two stages of phase separation remove gravel and grit: chlorine is injected to control bacteria, and a macerator reduces impassable solids to a manageable size.

The technologies implemented for metals monitoring and radiation analysis—x-ray fluorescence spectroscopy (XRFS) and gamma spectroscopy, respectively—are discussed in detail in **Section 6.4.3**. The ultrasonic sensing technology implemented for flow rate measurement is typical for use in flow-through systems, but XRFS and gamma spectroscopy are

usually used in a laboratory setting. The tendency of sewage to foul and clog the monitoring equipment complicates their use in an unattended system. Successful operation requires the design of fouling-resistant flow cells and the implementation of comprehensive maintenance procedures. Furthermore, diagnostic sensors (pressure and voltage gauges, for example) can be used to test for anomalous conditions in the monitoring and flow systems. When equipment is not operating properly, sewage release alarms should be disabled and personnel notified so that normal operation can be restored.

Finally, wear and age can change the performance of the monitoring equipment. Calibration checks generally should be conducted once each month, except as existing engineering standards allow otherwise (DOE's *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* requires annual calibration and weekly checks [DOE 1991]). When a piece of equipment does fail completely, it should be possible to reconfigure the system rapidly for continued operation. For the mechanical equipment, duplication is appropriate, as is the case for the pH- and flow-monitoring equipment required by permit. For the rest of the monitoring equipment—which is susceptible to failure when not operated continuously, and, therefore, cannot be kept in duplicate—simple flow bypasses and flexibly configurable computer software allow normal operation of the unaffected sensors while the broken component is repaired or replaced.

The final issue to be considered concerns computer hardware and software. XRFS and gamma spectroscopy are complex techniques that require sophisticated signal analysis to generate reliable results. Acquisition of both the monitoring and status information requires complex data acquisition hardware and software. Much of this can be provided by third-party vendors, but LLNL-designed and -implemented software is necessary to control analysis of the data and annunciate alarms that initiate response activities. To ensure the reliability and accuracy of the software, a subset of the Institute of Electrical and Electronics Engineers (IEEE) software QA procedures must be met. These documents must also be approved under the EPD QA procedures.

6.4.1.5 Alarm Response

When a possible contaminant release or system malfunction is identified, sewer monitoring personnel must be notified to control and/or correct the condition. DOE's *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (DOE 1991) requires that the alarm be in a location that is continuously occupied by operations or security personnel.

The response process begins with annunciation of the condition (and automatic diversion in the case of a possible contaminant release), followed by evaluation, and concludes with corrective

action. All alarms and response activities must be documented. In the first stage, the system annunciates either a contaminant release or a system malfunction. In the second stage, the monitoring system must provide access to archive data to aid in the evaluation of the alarm. In the third stage, operators must be able to adjust monitoring parameters to correct any hardware conditions that may have occurred. Alternatively, if a spill actually appears to have occurred, alarm-response personnel must work closely with discharge-control specialists in WGMG to develop an action plan for identifying and correcting the cause of the release (pre-established action plans are required by DOE [1991]).

Because alarms occur infrequently and releases even more rarely, response activities must be thoroughly documented, so that response personnel can work efficiently to control and correct the cause of the alarm (whether a hardware failure or an actual release).

6.4.2 Extent and Frequency of Monitoring and Measurements

The Sewer Monitoring Facility (Building 196) is located at the northwest corner of the Livermore site, where the combined effluent from LLNL and Sandia/CA is discharged to the city of Livermore sewer system. The facility sits at the permit-mandated location of the compliance monitoring system.

As described in previous sections, the continuous monitoring methods that have been implemented focus on those analytes that are either permit-mandated or considered to be high-risk contaminants, because of the extreme consequences of a spill or an established history of control lapses. This section describes the specific methods and scope of the system.

6.4.2.1 Alarm Annunciation

Although sampling is performed continuously, actual alarm analysis is performed by a computer in discrete intervals. As implied in the previous section, the frequency of analysis and the duration of an excursion prior to annunciation of an alarm are not strictly based upon compliance requirements. The actual alarm algorithms are based upon four considerations:

- Potential severity of the impact on the LWRP
- Impact of alarm response activities on monitoring program resources
- Accuracy of the methods
- Susceptibility of the equipment to false positives caused by fouling or instability of the monitoring equipment

Because each sensor system has different design parameters, each contaminant has a different alarm algorithm.

The terms of LLNL's discharge permit require that the pH effluent at the LLNL sewer outfall is no less than 5 and no greater than 10. Between the bounds of 2 and 12.5 (nonhazardous waste lower and upper bounds), the primary goal of the permitted pH values is to minimize damage to the sewer infrastructure. Alarm response is instantaneous below 5 or above 10 pH units.

"Instantaneous," in this case, is as frequent as monitoring readings are taken. Although it is possible to monitor pH continuously, the shortest pH releases appear to be at least 2 minutes in length, with rise times on the order of 30 seconds. Once-a-minute readings are capable of detecting extreme pH excursions and guarantee that all but the first couple of minutes of a serious spill will be captured by the diversion facility. (Upstream pH monitoring equipment installed in 1998 captures the first few minutes of low- and high-pH spills. See **Section 6.4.1.3**.) This is, therefore, the measurement frequency used for pH monitoring.

As summarized in **Table 6-1**, the discharge limitations for metals are in the parts-per-million (ppm) or sub-ppm range. LLNL's goals for metals spill monitoring sensitivity are roughly 50 times the values shown, with measurements made no less than once every 10 minutes. In the current system, analysis is performed once every 5 minutes, with alarm levels set in the 5- to 12-ppm range (see **Table 6-7**, where the discharge limits are reproduced to facilitate comparison). To justify this choice, **Figure 6-2** and **Figure 6-3** show typical metals monitoring results over the course of a 7-day period. The cadmium concentration plot of **Figure 6-2** shows primarily the effect of the fundamental uncertainty in the measurement method. The measurement results fall in a gaussian distribution, and the alarm levels are set at some multiple of the width of the distribution.

In **Figure 6-3**, the statistical distribution of the zinc measurements is systematically skewed by an upward trend. Such trends result from two effects: the accumulation of grit and the deformation of the flow cell itself. (The flow cells are thin, pancake-shaped volumes, one side of which is defined by 0.1-mm-plastic films. These films stretch over time, resulting in the flow-cell deformation.) The conclusion that must be drawn from the data is that increasing the analysis time to improve sensitivity will not lead to a corresponding reduction in alarm settings, which are driven by systemic effects. Decreasing the analysis time to 1 minute, however, more than doubles the alarm level for metals (the alarm level is inversely proportional to the square root of the analysis time). The 5-minute analysis time and individual alarm levels are reasonable compromises among response time, sensitivity, and resources expended on management of spurious alarms.

Table 6-7. Metals alarm levels

Metal	Permit limit (mg/L)	Alarm level (mg/L)
Arsenic	0.06	5
Cadmium	0.2	5
Chromium	0.62	10
Copper	1.0	11
Lead	0.2	7
Mercury	0.01	7
Nickel	0.62	12
Silver	0.2	5
Zinc	3.0	10

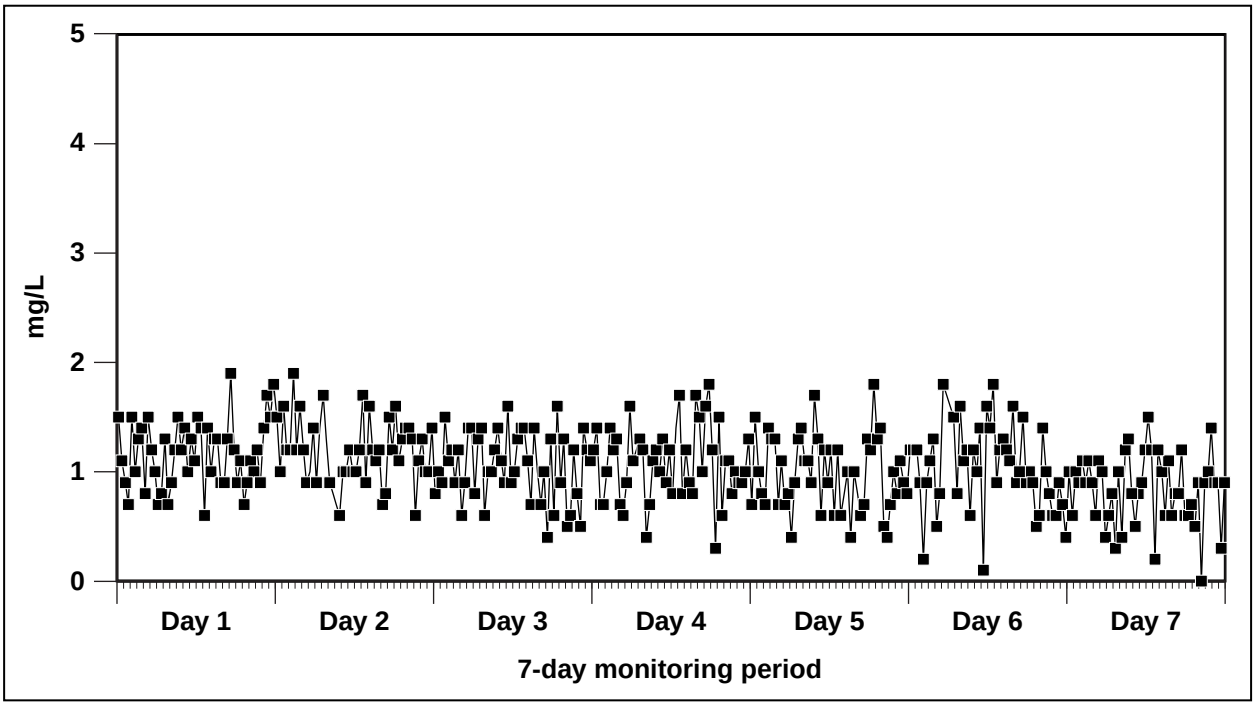

Figure 6-2. Cadmium concentration in LLNL sewage over 7-day period as measured by the continuous monitoring system

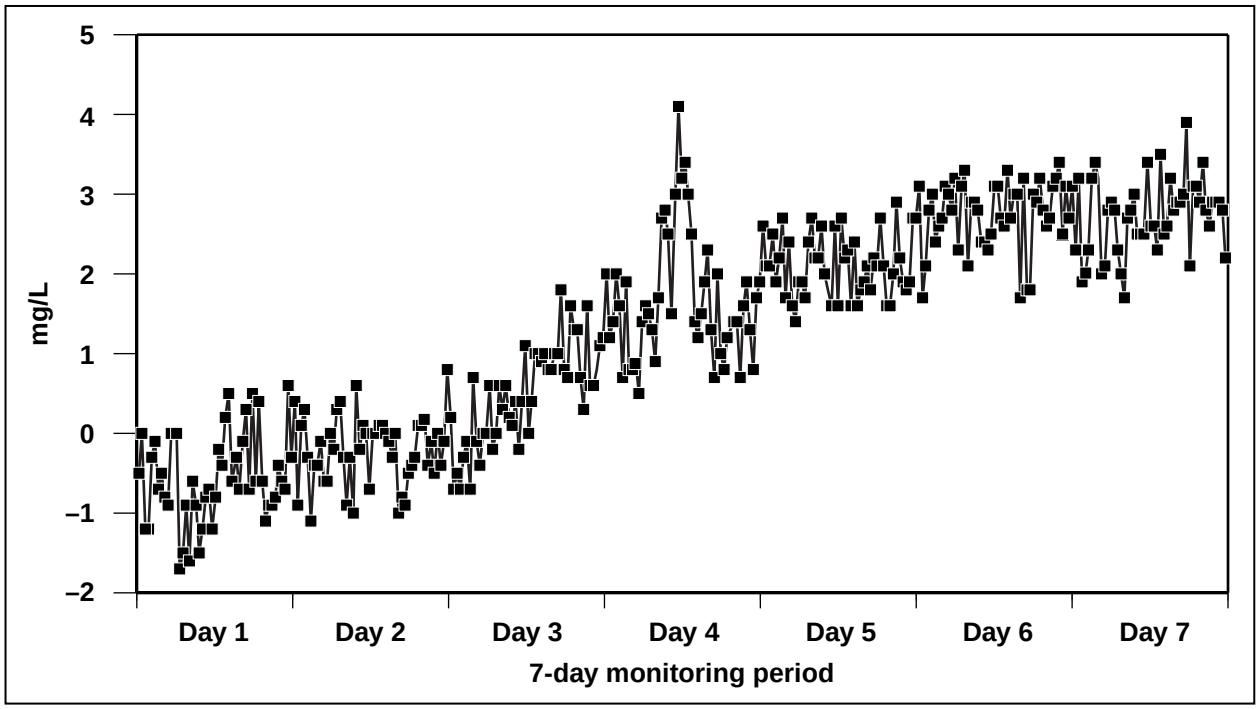

Figure 6-3. Zinc concentration in LLNL sewage over 7-day period

As well as flow-cell fouling, the alarm conditions for radiation monitoring are further complicated by interference among the various decay signals. Radiation monitoring is actually the analysis of three distinct phenomena: gamma emission, beta decay, and alpha decay. Noncontact analyzers are rarely capable of analyzing beta and alpha emission directly, and certainly cannot do so in the case of sewage. The system installed at LLNL instead detects the emission of gamma radiation emitted as an after-effect of alpha and beta decay. Unfortunately, these "follow-on" signals (x-ray emission and bremsstrahlung radiation, respectively) are not as distinctive as the monoenergetic lines from direct gamma decay. In fact, direct gamma decay generally masks both beta and alpha decay, while beta decay masks alpha decay. For this reason, radiation alarms for beta decay are only enabled when no gamma lines are identified in the spectrum, and alpha-decay alarms are only enabled when neither gamma lines nor bremsstrahlung are evident.

While the alpha- and beta-radiation algorithms (described in the next section) are fairly straightforward, the gamma emission algorithm is complex. The algorithm begins with a search for any peaks in the analyzer energy spectrum. Often this analysis is performed against a low-statistics background, and occasionally the algorithm identifies random fluctuations in the background as a peak. When peaks are found, they are typically from medical radio-isotopes such as technetium-99, thallium-201, iodine-131, or natural radioisotopes such as

bismuth-214 and lead-214. The identified peaks are scanned against a peak library to identify radioisotopes that emit at a given energy. To make this algorithm feasible on a workstation computer, this library contains only those radioisotopes most commonly used at LLNL. If an emitted isotope is not in the library, the algorithm attempts to assign its peak lines to other radioisotopes in the library, potentially causing a false alarm. Finally, Compton scattering of gamma radiation can obscure decay lines at lower energies or generate small peaks when fluctuations in the Compton signal occur.

In the alpha and beta analysis, as well as interference from gamma decay, it has been observed that numerous transient phenomena give rise to spurious signals. These transient phenomena include intense sound and poor electrical connections.

To suppress false positives and interferences, the alarm algorithm requires that the signal be reproduced over two-count intervals. For convenience, the interval is chosen to be the same as the metals analysis interval. This provides a 10-minute alarm cycle, compatible with the requirements outlined in the previous section.

6.4.2.2 Off-Line Sample Analysis

Given the incidence of false alarms caused by flow-cell fouling and signal interferences, the evaluation of an alarm cannot rest solely on the results of the real-time analysis. To support the evaluation, a grab sample is automatically collected each time an alarm is annunciated. For immediate substantiation of a release, a desktop radiation counter (swipe counter) and pH probe are kept in the sewer monitoring station. Use of these instruments by alarm responders is documented in procedure EMP-SW-HCAR, *Hazards Control Off-Shift Sewer Alarm Response*. For metals alarms, no immediate means of independently validating the alarm are available.

Even if an alarm can be initially substantiated, the interference and fouling problems described above make it impossible to evaluate the compliance implications of a release on the basis of the data provided by the continuous monitoring system. For that purpose, portions of the grab sample are submitted for analysis by analytical chemistry laboratories. The preparation and submission of the grab sample are described in monitoring procedures EMP-SW-HCAR, *Hazards Control Off-Shift Sewer Alarm Response,* and EMP-SW-B196, *Sewage Sampling at B196*, respectively. This off-line analysis is also performed for alarms that cannot, on the basis of the information preserved in the monitoring records, be definitively determined to have been false.

Finally, if a release is confirmed, the daily composite sample acquired by the compliance monitoring program is analyzed to assess the impact of the release on LLNL's compliance with the discharge limits for the day as a whole. Because these results are reported to the LWRP, EPA-approved methods must be used.

Analysis and disposition of material held in the Sewer Diversion Facility are discussed in **Sections 6.2.2** and **6.2.5**.

6.4.3 Laboratory Analysis Procedures

Although x-ray fluorescence and gamma spectroscopy are standard analytical methods, their application to continuous sewage monitoring is unique to LLNL. Equipment has to be designed to prepare and position sewage for analysis, and new spectral-analysis algorithms are required to correct for interference and fouling problems not commonly encountered in benchtop analysis. The monitoring program is actively developing solutions to these problems discussed below.

The monitoring program uses standard, EPA-approved analytical methods for the analysis of grab samples. For these samples, analysis performed under extreme urgency (2 to 3 days) is required to support the timely confirmation of a spill. See **Section 6.6** for further details.

6.4.3.1 Radiation Monitoring

Only minor mechanical modifications were necessary to modify a commercial radiation monitoring system for flow-through sewage analysis (**Figure 6-4**). The sewage is injected into the bottom of a 1-L Marinelli beaker, which surrounds the detector vacuum shield. The analysis flow rate, roughly 4 L/min, is sufficient to prevent stagnation of the liquid at the bottom of the

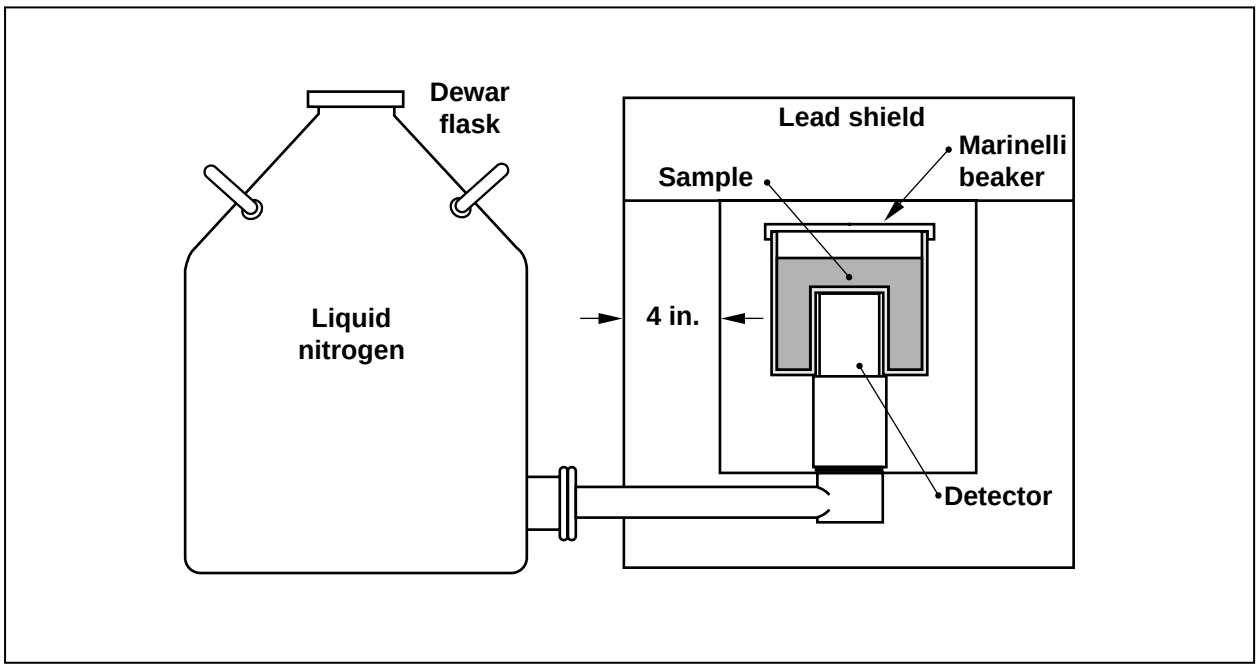

Figure 6-4. Flow-through monitoring system for radioactivity in sewage

beaker but does not prevent sediment settling on horizontal surfaces. The detector itself is a high-purity, liquid-nitrogen-cooled germanium crystal, 5.5 cm in diameter and 6.2 cm high. To maximize acceptance for low-energy photons (down to 12 keV), magnesium is used for the vacuum shield wall, while the top is 0.5-mm-thick beryllium. To shield the detector from external radiation, it is seated in a cylindrical container lined with 10 cm of pre-World War II lead (such lead has low lead-210 activity).

A typical 5-minute radiation analysis spectrum is shown in **Figure 6-5**. The region from 40 keV to 2.4 MeV is scanned for gamma peaks, which are then matched against a library of peaks from radioisotopes commonly used at LLNL. The detector efficiency is calibrated annually using a mixed fission product source, and the isotopic activity is determined from the results of the calibration and the total count rate in the highest branching ratio decay line. This industry standard algorithm has two significant deficiencies: it does not use multiline analysis to properly resolve interferences between isotopes with shared lines, and it does not use the activity information available in the side peaks and the Compton scattering edge (from partial conversion of gammas in the germanium detector). The most commonly detected gamma-emitting isotopes are medical isotopes and the radon daughters, bismuth-214 and lead-214.

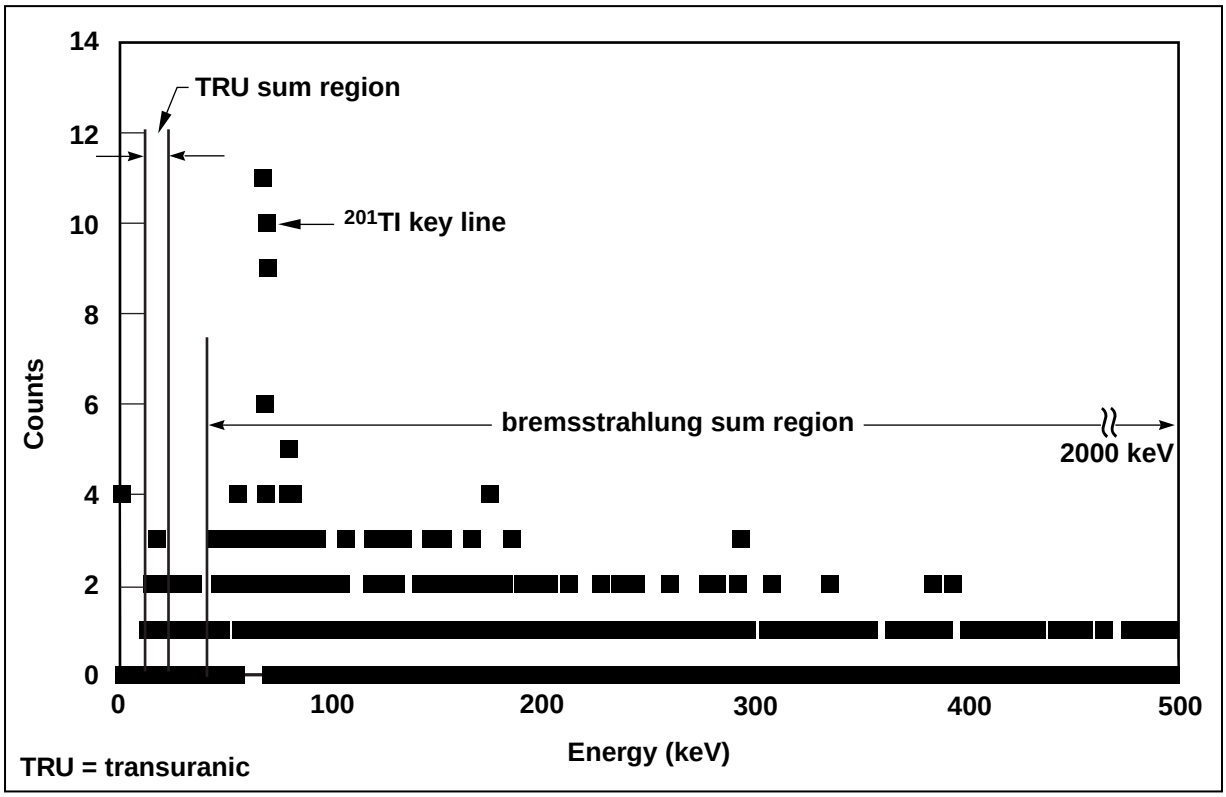

Figure 6-5. Typical gamma spectroscopy data

Pure beta-emitting radioisotopes can be detected through the bremsstrahlung photons emitted by the high-energy electrons as they thermalize through collisions with the sewage itself. Neither the decay electrons nor the bremsstrahlung photons are monoenergetic. The observable impact on the gamma spectrum is an elevated count rate at all gamma energies below the maximum decay energy of the electron, with the greatest relative effect appearing at the lowest energies. The most sensitive measure for beta activity is the total count rate in the spectrum, which shows a significant deviation from background readings well before an alteration to the spectral shape can be discerned.

Analytical deficiencies with this algorithm are a susceptibility to electronic noise with a characteristic shape, and interference from the Compton photons generated by gamma-emitting radioisotopes. In principle, spectral analysis could help to eliminate the electronics background, while an accurate determination of spectral peak heights should allow an accurate subtraction of the Compton background. This has not been attempted. The primary failing of this method is a lack of specificity and, therefore, an inability to perform a meaningful calibration of the detector; true quantification of detector readings must occur through off-line analysis.

Analysis for alpha-emitting radioisotopes is very similar to the x-ray fluorescence technique used for metals monitoring. Alpha emitters are generally heavy atoms, and the departing helium nucleus usually ejects several inner-shell electrons. As the inner-shell electronic states of the daughter atom are filled, x rays are emitted in the 12- to 20-keV energy range. Although these should in principle be resolvable as pure spectral lines, in the normal operating configuration the low-energy resolution and efficiency of the detector do not allow elemental identification. Thus, the analysis algorithm is again a simple comparison of the total count rate with the normal background, although this analysis is limited to the 12- to 20-keV range. The lack of spectral information makes the analysis susceptible to interference from electronics noise, bremsstrahlung, and partial conversion (Compton scattering in the detector). Calibration is also problematic, although a check source of dilute plutonium solution has been used to establish the sensitivity of the method to alpha activities near the DCGs of Order 5400.5 (DOE 1993).

6.4.3.2 Metals Monitoring

Adaptation of the x-ray fluorescence technique for flow-through analysis required significant technical innovation. A cross-section of the flow cell, with the attached x-ray generator and the detector, is shown in **Figure 6-6.** The base geometry is standard for x-ray fluorescence (XRF) analysis, with the generator positioned at right angles to the detector to minimize backgrounds from elastic scattering of the exciting x rays. The detector is an Si(Li) crystal,

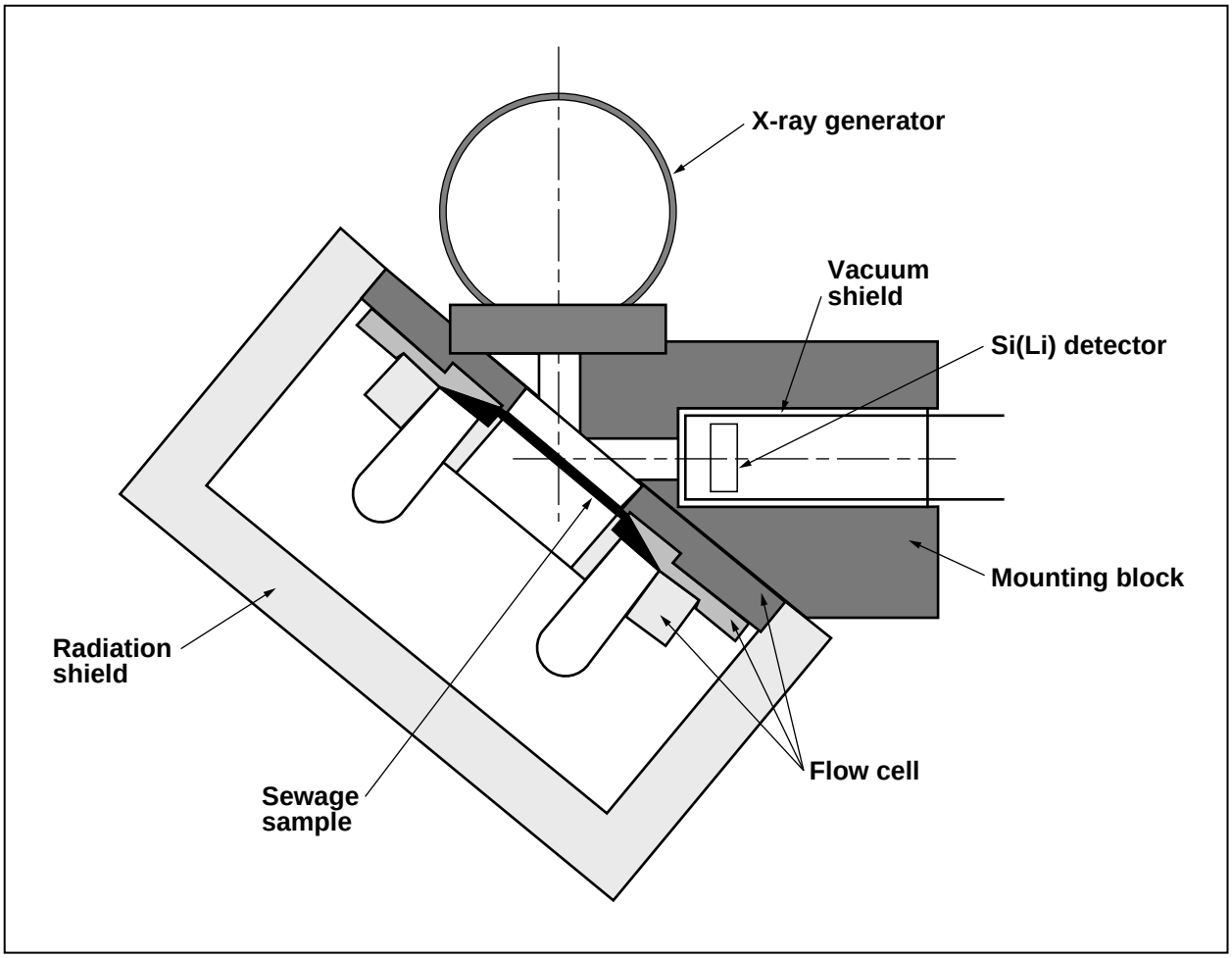

Figure 6-6. X-ray fluorescence analysis configuration for flow-through monitoring of metals in sewage

with a 30-mm^2 active area and 3-mm thickness. The flow cell is a three-piece construction with an aluminum base plate, an aluminum body plate, and a plastic cover. The x-ray generator illuminates a 4-cm hole in the center of the flow cell. A heavy Kapton sheet, glued to the cover, defines the rear of the analysis volume, while the front surface is bounded by spectroscopy-quality plastic films: a 0.04-cm Mylar film on the sample side provides water resistance, and a 0.04-cm Kapton film provides tensile strength. The thickness of the analysis volume is considerably less than that of the body plate itself. Finally, a 1-cm, leaded plastic shield provides radiation shielding in the forward beam direction. Shielding in the reverse direction is provided by the material of the x-ray tube, the flow cell, the detector, and the mounting block that orients the system components.

Sewage is injected perpendicular to the plate. The body plate serves to blunt the force of the flow, which develops into a laminar stream prior to entering the restricted area of the analysis volume. In the system as currently configured, sewage flows from the bottom to top of the cell; in the reverse configuration, a large air pocket remains trapped in the cell when flow is introduced. Unfortunately, the current configuration encourages the accumulation of heavy phases, including silt and sand, in the flow cell (see **Sections 6.4.1.4** and **6.4.2.1**).

Designing an analysis system for a specific metal begins with selection of a target fluorescence line. **Table 6-8** lists the target lines for the metals regulated by LLNL's discharge permit. Given a target line, then the x-ray tube voltage and target material are chosen, and a metal filter is selected to remove source x rays that could interfere with the fluorescence line. The tube current is based upon the maximum throughput of the acquisition electronics; higher currents imply higher count rates in the detector, which eventually saturate the electronics.

Given the tube voltage and target-line energy, the thickness of the flow-cell volume is determined through an optimization analysis of the signal-to-noise ratio in the detector. The higher energy source x rays penetrate to a greater depth than the fluorescence lines. Therefore, at any given depth the intensity of elastically scattered source x rays is greater than the intensity of the fluorescence lines, which undergo stronger attenuation. The ideal thickness is one that maximizes the intensity of the fluorescence lines relative to the background curve. The thicknesses of the three flow cells are shown in **Table 6-9**.

Table 6-8. Metals fluorescence line

Metal	Fluorescence line			XRF unit
	Transition	Energy (keV)	Attenuation length (mm)	
Silver	K_α	22.1	19	3
Arsenic	K_α	10.5	2	2
Cadmium	K_α	23.1	23	3
Chromium	K_α	5.4	0.3	1
Copper	K_α	8.0	0.9	2
Mercury	L_α	10.0	1.8	2
Nickel	K_α	7.5	0.7	2
Lead	L_α	10.5	2	2
Zinc	K_α	8.6	1	2

Table 6-9. X-ray fluorescence-unit design parameters

XRF unit	Generator		Target	Filters	Thickness (mm)
	Voltage (kV)	Current (µA)			
1	25	75	Nickel	Nickel	3
2	45	90	Rhodium	Molybdenum	5
3	50	67	Tungsten	Tantalum, copper	21

In a perfectly stable system, the concentration of a particular metal is proportional simply to the excess counts (over background) in the energy range of the fluorescence x rays (**Figure 6-7**). In practice, the intensity of the excitation beam, the electronics dead-time, and the volume of the flow cell are not perfectly stable. To account for these effects, the counts in the fluorescence range are normalized by the counts in the energy range populated by elastically scattered excitation photons. This algorithm suffices for the first and third configuration of **Table 6-9**;

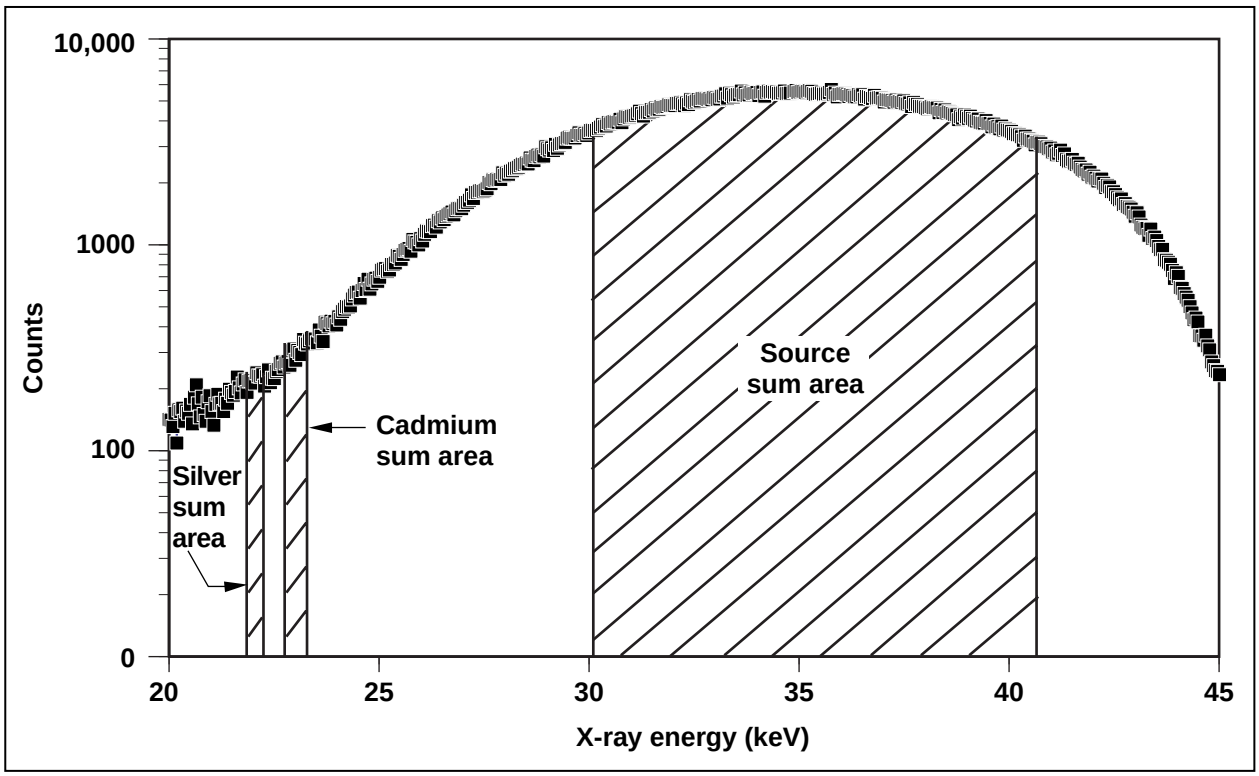

Figure 6-7. Typical x-ray fluorescence spectrum

XRF 1 is opaque to both the excitation and fluorescence x rays, and thus a change in analysis volume (caused by the stretching of the thin-film windows) does not result in a change in the volume that contributes to the signal in the detector. XRF 3 is thick compared with typical volume fluctuations and relatively transparent to the source and fluorescence x rays, so that a slight change in volume does not cause a large change in the relative count rate in the source and fluorescence energy ranges.

In the case of XRF 2, however, film stretching causes a change in the thickness of the flow cell, which is an appreciable fraction of the design thickness. Additionally, the x-ray attenuation lengths are comparable to the design thickness, with a strong increase in attenuation at lower energies. For these reasons, an increase in analysis volume thickness results in an appreciable change in the shape of the fluorescence spectrum, as the x rays scattered elastically from the additional volume at the back of the flow cell are more likely to be observed in the detector than fluorescence x rays from the same location. This effect can bias, by several milligrams per liter, the simple ratio analysis algorithm for the metals concentration.

This effect also complicates the metals calibration of the analysis systems. Calibration involves sequential loading of the flow cell with laboratory-standard metals solutions of known concentrations. Several spectra are acquired at each concentration. The ratio of the fluorescence counts to the elastic scattering counts is computed for each metal at each concentration; then the calibration constants (slope and background) are determined by a least squares fit of the ratio to the known metals concentrations. The background constants, however, are usually biased low because the static loading of the flow cell results in a different analysis volume, as compared with the normal operating state. Under the assumption (supported by the compliance monitoring data) that the actual metals concentrations in sewage are small compared with the alarm levels, the background constants are adjusted manually during routine system operation to achieve zero mean concentrations.

Currently, no routine check of the system calibration has been developed; the calibration procedure outlined above takes several days. Gross stability can be assessed by monitoring the total detector count rate, and the energy calibration is readily assessed by monitoring the position of fluorescence lines from common sewage constituents and the x-ray filters. The metals calibration coefficients are assumed to be stable on the basis of the stability of these other parameters.

Finally, because of the phase separation in the preparation of the sample stream for analysis, the metals monitoring results do not include a true proportional contribution from the heaviest solids, which encompass everything from gravel to bolts. Reviews of the summary of

operational impacts at the LWRP indicate that these settleable, nonleachable solids do not pose an operational concern.

6.4.4 Quality Assurance Requirements

6.4.4.1 Real-Time Continuous Monitoring System

Quality assurance in the context of a continuous monitoring system means not just achieving specific numerical goals for analytical sensitivity, but also ensuring reliability in system operation and alarm response activities. Target analytical sensitivities were discussed in detail in **Section 6.4.2.1**; this section focuses on the other measures of system performance that can be used to guide quality improvement activities.

The primary QA priority is the health and safety of the personnel in the monitoring program. Potential hazards include the medical hazards of handling sewage and equipment in contact with sewage, exposure to x rays, and the ergonomic hazards of working in crowded spaces and lifting heavy containers of sewage samples. These and other hazards are managed by developing and implementing a formal *Operational Safety Procedure L-92* (LLNL 2002), with full participation and review by the Hazards Control Department.

The sewer monitoring system was designed to activate control measures in the case of a materials release that could seriously impact the public welfare. Although the primary means of preventing these discharges are upstream controls, the monitoring station provides important back-up protection. Operability goals for the station are, therefore, 100 percent. Although there are certain unavoidable interruptions to monitoring (such as routine maintenance and calibration), other regular causes of interruption are analyzed and, where possible, reduced. Factors that have contributed to extended downtimes, including deficient plumbing, faulty hardware, electronics and computer equipment, and sampling pump failures, have been mitigated. As a result of these mitigation efforts, LLNL is significantly closer to achieving the 100 percent operability goal for the station.

The principal performance goal of the system is to provide stable and accurate measurements of the target contaminants. Specific QA targets in this area are difficult to formulate because the system is still under development to meet the two requirements stated above. However, broad goals for the ideal analysis system are outlined in the following discussion.

Systematic biases caused by flow-cell fouling or artifacts of the equipment design should be minimized. In the metals monitoring equipment, the metals readings should be stable to the statistical level (see **Section 6.4.2.1**). Over any 2-week period, they are stable only 25 percent of the time. In the radiation monitoring system, fouling of the flow cell by medical isotopes

effectively disables alpha and beta monitoring roughly 10 percent of the time. These percentages are larger than desired.

Another potential source of system failure or monitoring error is the software that controls the equipment, interprets the monitoring data, and annunciates alarms. Development and validation of the software is covered under the EPD *Quality Assurance Management Plan* (Merrigan 2001). The reference for this document is the IEEE Software Quality Assurance Standards. The documentation, validation, and verification requirements of these standards are quite extensive and beyond the resources of the monitoring program to implement. The elements that have been chosen for implementation are the *IEEE Standard for Software Verification and Validation Plans* (ANSI/IEEE Std 1012-1998 [ANSI 1998b]), the *IEEE Guide to Software Requirements Specifications* (ANSI/IEEE Std 830-1998 [ANSI 1998a]), and the *IEEE Standard for Software Test Documentation* (ANSI/IEEE Std 829-1983 [ANSI 1983]). Other software QA elements may be added following completion of the software development and documentation.

The final equipment performance measure is the frequency of false alarms. Since the system began operation in early 1990, the number of false alarms has fluctuated around four per month. Ideally, a combination of system sensors and software modifications could reduce the monthly number of false alarms to fewer than one.

Although the discussion to this point has focused heavily on the monitoring technology, the limitations of the technology require that personnel maintain a high level of competence in assessing system alarms and conducting source identification efforts in the event of a serious, ongoing release. The relative paucity of events (four false alarms per month, and less than an average of one release per month in the last two years) necessitates ongoing training and the completion of detailed alarm response procedures. Formal documentation of all alarm response activities is required to ensure analysis and correction of procedures, should a failure occur. Additionally, ongoing training is required for personnel from all organizations that may participate in an alarm response. EPD training programs will be developed as the Hazards Control and the EPD alarm response procedures are revised and completed, respectively. (See **Section 6.4.8**.)

The final measure of the monitoring system performance is the contribution made to the efforts of the discharge control program to prevent inappropriate upstream releases of regulated materials. In this regard, the immediate success of the system has been excellent. Detected releases were ten a year in 1990–1992, none in 1993, and one each in 1994 and 1995. The sharp decline in the number of releases in 1993 was primarily the result of the efforts by the discharge control program to identify sources of recurrent releases of zinc and silver.

There were 7 and 13 detected releases in 1996 and 1997, respectively. Three-quarters of these were related to pH. Between 1998 and November of 2001 there were ten detected releases; six of these releases were related to pH and four to metals. Five of the six pH events were completely captured by the SDF. The upstream triggers station was responsible for this accomplishment. The prospect of continued success of is excellent.

6.4.4.2 Post-Alarm Sample Analysis

The data quality objective requirements of the compliance monitoring program (**Section 6.3.4**) apply to the analysis of alarm grab samples and daily composite samples. However, the use of duplicate samples, field blanks, and trip blanks is not appropriate for these samples, which are acquired and analyzed under extremely rushed conditions. Quality control of the results is based primarily upon the analysis of control data gathered for the compliance monitoring program.

6.4.5 Program Implementation Procedures

Sewer spill monitoring team activities are divided between routine maintenance and calibration activities, and responding to sewer alarms.

6.4.5.1 Maintenance and Calibration

As discussed in earlier sections, the monitoring equipment is subject to the extremity of direct contact with a corrosive and biologically active mixed-phase medium. The plumbing and flow cells contain narrow conduits and stagnant volumes that can be fouled by silt, grease, hair, and bacterial growth. Continuity of operation requires frequent maintenance. These activities are described in LLNL procedure EMP-SW-M, *Sewer Equipment Maintenance*. The pH probe is cleaned daily. The x-ray flow cells, Marinelli beaker, phase separators, and plumbing are thoroughly cleaned twice a week. The flow monitoring stilling well is flushed every other week. Should any of the sophisticated electronics or computer equipment fail, the procedures provide telephone numbers of contract service personnel who can diagnose system failures and repair and/or replace components as necessary to restore operation. Procedure EMP-SW-M details the maintenance not only of the monitoring equipment itself, but also of ancillary systems, such as the uninterruptible power supply, chlorine pump, and composite sample refrigerator.

Calibration of the monitoring equipment is described in LLNL procedure EMP-SW-CA, *Sewer Equipment Calibrations*. As suggested in EH-0173T (DOE 1991), complete calibrations of the gamma and metals equipment are called for annually. The gamma system is calibrated for energy gain and conversion efficiency using a standard mixed fission product source, with

americium-241 added to provide a low-energy calibration endpoint at 60 keV. The metals energy calibration is achieved with a cobalt-57 source. The metals calibration coefficients (concentration versus the count rate ratio described in **Section 6.4.3.2**) are determined by a four-point calibration using metals concentrations of 10, 20, 50, and 100 mg/L. Although alarm levels are generally in the 10 mg/L range, this calibration scheme guarantees accuracy for the releases at higher concentrations that are of greatest concern.

The pH probe is calibrated weekly using standard buffer solutions. As well as the response of the recorder, the procedure verifies that the readings obtained by the computer acquisition system agree with the probe readings. At the same time, the computer and chart recorder flow readings are compared. Flow-meter calibration is checked once each quarter and is certified by a registered engineer, as required for equipment that is used to calculate City of Livermore sewer connection fees.

Procedure EMP-SW-CA includes worksheets and detailed computer operator instructions for execution of all of these calibration operations.

6.4.5.2 Alarm Response

When the computed pollutant concentrations surpass alarm levels or equipment parameters deviate from acceptable operating limits, the sewer monitoring computer annunciates an alarm. In the case of a hardware condition (system malfunction), the signal is sent to the LLNL Fire Dispatch control center, which is staffed at all times. When a spill alarm is annunciated, the signal is received by the Fire Dispatcher, the Building 511 Plant Engineering Main Control Center, and the Sewer Diversion Facility.

When an alarm is annunciated during normal work hours, the Fire Dispatcher notifies EPD response personnel. Off shift, the Hazards Control off-shift health and safety technician is notified.

6.4.5.2.1 Hardware Conditions. Correction of hardware failure conditions is dependent on the experience of the individual responder, who can also draw on standing relationships with support personnel in many situations. Mechanical utilities personnel and maintenance machinists typically respond to correct sampling pump failures. Canberra Industries is under contract to correct any failures of x-ray fluorescence or gamma spectroscopy equipment. Other systems, such as the pH and flow recorders and the macerators, exist in duplicate. Personnel who are not intimately familiar with the monitoring system are usually unable to diagnose and correct hardware failures. If monitoring program personnel are not available, the alarm is usually disabled or left active until such personnel can respond. Correction of hardware conditions is guided by reference to equipment manuals kept in the monitoring station.

6.4.5.2.2 Spill Response. If the condition is a spill alarm, the primary responder immediately notifies the LWRP that an alarm response has been initiated. During waking hours, sewage transit times from LLNL to the LWRP are roughly four hours; at night, transit times can be from four to six hours. This provides a buffer during which the alarm assessment can be completed. However, the LWRP expects verbal notification that an alarm response has begun within 20 minutes. Without this notification, preparations may be made to initiate a diversion of effluent entering the LWRP.

The primary role of the off-shift Hazards Control responder is to assess the facility condition and collect alarm data. Alarm data include off-line analysis of the grab sample for pH or radioactivity, as appropriate. These activities are guided by procedure EMP-SW-HCAR, *Hazards Control Off-Shift Alarm Response*, and documented on a sewer response report. Certain simple conditions, such as a false alarm caused by loss of flow from the sampling pump, may be corrected independently by the technician. Generally, however, an EPD responder is notified. The information collected by the technician is used by the EPD responder to determine the severity of the alarm condition. Occasionally, the condition can be assessed and/or corrected over the telephone. In all other cases, the EPD responder must report to the Sewer Monitoring Station to complete the alarm response.

Upon arrival at the facility, the EPD responder follows the procedures described in EMP-SW-SAR, *Sewer Alarm Response*. All activities are documented on a spill response report. A complete alarm response includes evaluation of off-line analysis data and examination of trend data and spectroscopy spectra. If the contaminant concentrations are unusually flat, flow-cell contamination may be assessed by running wash water through the analysis system. If the results of this investigation match any of the documented false-alarm criteria, the alarm response is terminated. If experienced personnel are available, they may attempt to correct the condition generating the false alarm, whether flow-cell fouling or an electronics failure. In any case, the LWRP, Fire Dispatch, and the Plant Operations first-line supervisor are notified of the conclusions of the investigation. If the alarm condition cannot be cleared, the alarm signal is disabled in the software until monitoring program personnel are available to correct the problem.

If the condition cannot be determined to be a false alarm, the EPD responder must assess the severity of the release and initiate further spill response activities as necessary. Criteria for deciding whether the release is minor or serious are provided in procedure EMP-SW-SAR. At this point, LLNL emergency response managers must be informed of the incident. This contact is managed by the Environmental Duty Officer (EDO), who also obtains authorization for the EPD responder to notify the LWRP that a release has possibly occurred.

For a minor release, the responder instructs sampling technicians to collect the alarm grab sample and the daily composite sample. The collection and handling of these samples are described in procedures EMP-SW-HCAR and EMP-SW-B196, *Sewage Sampling at B196*.

In the case of a serious ongoing release, the EPD responder may choose to activate the EPD Satellite Operations Center for assistance in managing the incident. The Sewer Monitoring Station becomes the site of a coordinated spill identification effort, involving sampling technicians and LLNL analytical chemists.

6.4.6 Action Levels

Action levels for the sewer spill monitoring program are described in **Section 6.4.2.1**. The associated actions are delineated in **Sections 6.4.2.2** and **6.4.5.2**.

6.4.7 Preparation and Disposition of Reports

The spill monitoring program generates documentation on all routine activities, as well as formal reports.

LLNL's wastewater discharge permit requires that outfall data be reported monthly. The report summarizes activity for both the compliance and spill monitoring programs. Five-Day Reports are also required under the terms of the permit (see **Section 6.3.7**).

The annual *Environmental Report* (Biermann et al. 2000) includes a summary and analysis of the spill monitoring results.

As maintenance activities occur, they are printed out by the computer and interleaved with the spill-monitoring status information generated by the software to aid in alarm analysis. These records are saved in both electronic and hardcopy format and can be analyzed to generate tracking information on the frequency of system failures.

Calibration records are defined and maintained by the WGMG analyst responsible for the real-time continuous monitoring system. Special report forms are used for the pH and flow-meter calibrations. Computer-generated printouts are retained for the metals and gamma calibrations.

Spill-response activities are documented on the report forms mentioned in the previous section. These reports are kept in the lead analyst's files. When a release is validated through analysis of the alarm grab sample, a formal report is written to the LWRP, as required in Section 8 of LLNL's *Wastewater Discharge Permit* (City of Livermore 2002). This permit requires a description of the incident, its duration, the extent of noncompliance, and a discussion of the steps taken to prevent future recurrence.

DOE Order 232.1A (DOE 1997) also requires reporting of sewer spills. LLNL's Implementing Procedures, Group 2, "Environmental," include the following off-normal categories:

- Any release of radioactive material to the environment that is not part of a normal monitored release or not federally permitted and exceeds 50 percent of a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Reportable Quantity specified for such material per Title 40 of the Code of Federal Regulations (CFR), Part 302, *Designation, Reportable Quantities, and Notification,* within a 24-hour period.
- Any detection of a radionuclide in a sanitary sewer system in which the amount exceeds a regulatory limit and triggers a Notice of Violation.
- Any controlled, uncontrolled, or accidental release that is not classified as an Unusual Occurrence but that will be reported in writing to state/local agencies in a format other than reports called for by permits or other compliance agreements.

Generation and filing of the reports required by DOE Order 232.1A (DOE 1997) follow the Implementing Procedures and EPD notification policy.

6.4.8 Future Plans

6.4.8.1 Satellite Station Network

Although the theoretical concept of the satellite station network as a discharge control aid is excellent, adequate resources for a complete reinvention of upstream monitoring are not available. Consequently, there are no future plans to reinstate a satellite station network. Individual locations may be considered for satellite sampling if a problem is identified. For more detail on the history of the satellite station network, see Tate et al. (1999). However, the problem of short-duration, low-pH excursions has been addressed, as discussed in the following section.

6.4.8.2 Real-Time Continuous Monitoring System

By the end of FY 2002, EPD anticipates reissuing existing procedures as well as completing the remaining sewer monitoring procedures, including the EPD alarm response procedure, EMP-SW-SAR, *Sewer Alarm Response*. An evaluation of alarm response training will be undertaken after procedure EMP-SW-SAR is issued.

Future improvements will focus on development of procedures to check the performance of the XRF metals monitoring equipment and the radiation monitoring equipment. Also an upgrade of the DEC computer in B-196 will be completed.

6.5 Categorical Pretreatment Monitoring Program

6.5.1 Rationale and Design Criteria

The Federal Water Pollution Control Act of 1972, as amended, grants authority to the U.S. Environmental Protection Agency (EPA) to establish and enforce National Pretreatment Standards for the indirect discharge of industrial wastewater. The intent of these regulations is to prohibit the discharge of wastes that are incompatible with wastewater treatment plant processes.

Categorical standards are a component of the National Pretreatment Standards. These are codified (40 CFR 405 through 471) standards specifying quantities or concentrations of pollutants that may be discharged to a sanitary sewer from specific industrial categories of wastewater-generating processes. Separate standards are established for specific industrial processes, in addition to the general prohibitions established in the National Pretreatment Standards. The intent of the requirements is to ensure that industrial wastewater effluent does not disrupt the ability of a treatment plant to treat wastewater. (Disrupting LWRP operations could cause contamination of the receiving waters of San Francisco Bay.) The LLNL categorical pretreatment, self-monitoring program accomplishes this intent by maintaining compliance with all applicable regulations (**Table 6-10**).

Because there are a number of these regulated processes in use at LLNL, LLNL is required by our Wastewater Discharge Permit (City of Livermore 2002) (Attachment A-2, 2001-2002 Permit) to maintain a categorical pretreatment program (Title 40 of the Code of Federal Regulations [CFR], Part 403, *General Pretreatment Regulations for Existing and New Sources of Pollution*). This program consists of administrative and engineering controls and procedures, coupled with process monitoring of nondomestic, industrial wastewater sources with specific discharge standards identified in Title 40 of the Code of Federal Regulations (CFR), Part 403, Subpart 5, *National Pretreatment Standards: Prohibited Discharges*.

The LLNL categorical, pretreatment, self-monitoring program is also mandated under the terms of the *Wastewater Discharge Permit/Chemical Storage Permit No. 1250* (2001-2002) (City of Livermore 2002), issued by the City of Livermore to LLNL governing the discharge of all wastewater from the Livermore site to the city's sewer system. Authority to enforce federal,

Table 6-10. LLNL's self-monitoring program for nonradioactive parameters in wastewaters from categorical processes

Parameter	Categorical Discharge Standards[a] (mg/L)	
	Metal finishing	Semiconductor
Metals		
Cadmium	0.26	—
Chromium (total)	1.71	—
Copper	2.07	—
Cyanide[b]	0.65	—
Lead	0.43	—
Nickel	2.38	—
Silver	0.24	—
Zinc	1.48	—
Organics		
Total toxic organics	2.13	1.37
Physical		
pH (units)	5–10	5–10

a These standards are specified in Title 40 of the Code of Federal Regulations (CFR), Part 433, Subpart 13, *Effluent Limitations Representing the Degree of Effluent Reduction Attainable by Applying the Best Practicable Control Technology Currently Available (BPT)*, and Title 40 of the Code of Federal Regulations (CFR), Part 469, Subpart 17, *New Source Performance Standards (NSPS).* Noncategorical discharge limits apply when no other standard is specified.

b Limits apply to CN discharges other than CN salts. CN salts are classified by the state of California as "extremely hazardous waste" and cannot be discharged to the sewer.

state, and local limits on waste streams discharged to the City of Livermore sanitary sewer system lies with the LWRP under the authority of the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB).

LLNL processes regulated under the categorical standards of the National Pretreatment Standards include metal finishing processes (Title 40 of the Code of Federal Regulations, Part 433, *Metal Finishing Point Source Category*, Subpart A, *Metal Finishing Subcategory)*, such as metal-plating and bright dipping located in the Building 322 Plating Shop, and certain semiconductor (Title 40 of the Code of Federal Regulations [CFR], Part 469, Subpart A, *Semiconductor Subcategory*) processes, such as the microfabrication for developing semiconductor and micromechanical devices that occurs in Building 153. Some categorical processes discharge directly to the sanitary sewer and are sampled at the point of discharge; other categorical processes discharge to dedicated retention tank systems, which are sampled and

characterized prior to each discharge. Some processes do not discharge to the sanitary sewer; they are contained and sent to LLNL's RHWM Division for treatment and/or shipment off site. Processes that do not discharge to sanitary sewer do not require sampling under this regulatory program.

Grab samples are collected for categorical process monitoring. A grab sample is collected over a period of time not exceeding 15 minutes (Title 40 of the Code of Federal Regulations [CFR], Part 403, Subpart 7, *Removal Credits*; and Title 40 of the Code of Federal Regulations [CFR], Part 136, *Guidelines Establishing Test Procedures for the Analysis of Pollutants*). Composite sampling is not appropriate because volumes from these processes are extremely small and flows are not continuous. Also, samples containing some constituents, such as cyanide, cannot be held for an extended period of time because of biological, chemical, or physical interactions after sampling that affect the results.

6.5.2 Extent and Frequency of Monitoring and Measurements

In its December 1996 written Inspection Summary of the June 1995 EPA/LWRP Facility Audit of LLNL, the EPA determined that LLNL wastewater generating processes that meet the defining criteria must comply with the applicable Categorical Standards. The defining criteria include:

- The process must discharge to the sanitary sewer, either directly or indirectly. (Processes that have their waste removed by means other than discharge to the sanitary sewer are not regulated under the Categorical Standards.)
- The process must not use radioactive materials. (Those processes are regulated under separate LWRP Permit conditions and DOE orders.)
- The process must generate sufficient volumes of wastewater to potentially impact the environment, currently considered to be 100 gallons per day or per batch discharge.
- The process must support other programmatic or institutional needs. If the process under evaluation exists solely for an R&D project, that process is not defined as a regulated categorical process. However, if that process discharges to sewer and supports widespread programmatic work or has other institutional customers, then that process is considered regulated under the applicable categorical standard.

As a result of this EPA decision, in July 1997, LLNL renews its compliance with all of the administrative and monitoring requirements for the Categorical Standards contained in Title 40 of the Code of Federal Regulations (CFR), Part 403, Subpart 6, *National Pretreatment Standards: Categorical Standards*; Title 40 of the Code of Federal Regulations [CFR], Part 433, Subpart A, *Metal Finishing Subcategory*; and 40 CFR 469, Subpart A, *Semiconductor Subcategory,* for those processes identified by the newly implemented defining criteria. These administrative and monitoring requirements are specified in LLNL's 2002-2003 *Wastewater Discharge Permit, #1250*, issued by the LWRP (City of Livermore 2002). LLNL samples, reports, and inspects three discharging processes: the Building 321 water-jet, the Building 153 wafer saw-cut, and the Building 153 microfabrication shop.

All LLNL wastewater-generating processes are evaluated to determine if they meet the definitions of specific industrial categories as set forth in the federal regulations. Currently, processes at LLNL fall into two such categories:

- Metal-finishing as defined in 40 CFR 433 A, Subpart A
- Semiconductor processes as defined under 40 CFR 469, Subpart A

Routine process review and evaluation occurs at least semiannually.

Monitoring for all categorical processes occurs at the point of discharge to the sanitary sewer. For instance, if the identified process discharges to a sink connected to the sewer, compliance samples are taken at the sink. If the process discharges to a retention tank dedicated to that process waste, the tank is sampled prior to discharge. The number of sampling locations is determined by the number of categorical processes that discharge to the sanitary sewer. Currently 15 metal finishing and 2 semiconductor processes are identified at LLNL. Of those, only three discharge to the sanitary sewer. These three, the Building 321 abrasive jet machining, Building 153 wafer saw-cut, and Building 153 microfabrication unit, are the only three that are inspected and sampled, with results reported to the LWRP in semiannual wastewater reports. The number of categorical processes at LLNL can change as existing processes are dismantled or new ones are installed.

The LWRP permit requires that both metal-finishing and semiconductor processes be sampled semiannually. Specific analysis requirements are mandated in the LWRP permit and federal regulations. Each Categorical Standard has its own defined sampling requirement. For instance, metal-finishing processes are sampled for pH, metals, total toxic organics (TTO), and cyanide. Semiconductor processes are sampled for pH, arsenic, and TTO.

6.5.3 Procedures for Laboratory Analysis

All categorical pretreatment sample analyses are performed by an off-site, state-certified analytical laboratory. For details on analytical laboratory procedures, see **Section 6.6**.

6.5.4 Quality Assurance Requirements

Although the QA requirements for the categorical program (e.g., data quality objectives) have not been through a formal technical assessment, procedures and methods exist and are utilized to ensure sample integrity. For instance, calibration of the handheld pH meter is performed prior to each day's use, according to procedure EMP-GW-CA, *Sewer Equipment Calibrations*. All calibration information is recorded on field tracking forms (FTFs).

WGMG-PT-S, *Pretreatment Sampling,* prescribes collection of pretreatment samples. This procedure states that, in general, duplicates should be 10 percent of the cumulative total of samples collected during the monitoring period (quarterly or semiannually, depending on the requirements prescribed in the Code of Federal Regulations for that category of process). In practice, duplicate sampling is performed far more frequently. By regulation, LWRP inspectors are required to sample all discharging processes annually. By internal policy, LLNL is required to take a split sample at the same time. These split samples are considered part of the duplicate sample process and constitute close to 50% of the cumulative total.

6.5.5 Program Implementation Procedures

Following the procedure for collection of pretreatment samples, WGMG-PT-S, *Pretreatment Sampling*, a unique numbering system is used in the field at the time of sample collection. The number begins with the letters "PT" to identify it as a pretreatment sample, followed by a building number, a sample location number, the number of the sample taken at that location, and finally the calendar quarter in which the sampling occurred, e.g., PT-321-02-01-Q2 indicates a pretreatment sample taken at Building 321 at the second sampling location, that it is the first sample, and that it was taken during the second quarter of the monitoring period.

The sampler (a WGMG analyst or TSG technician) wears clean, disposable gloves and changes them between each sampling event. The lids of the sample bottles for organic analysis are taped shut, and each set of samples is bagged separately. The sampler immediately places the sample in an ice chest and subsequently preserves the sample as called for in the appropriate EPA-approved method. After all sampling is completed, samples are placed in a locked refrigerator until the courier for delivery to the analytical laboratory arrives for pick-up, at which time the samples are returned to the ice chest with new ice and placed in a locked pick-up box from which the courier retrieves them. A CoC form is completed and accompanies the sample(s). Required analyses and methods are requested as specified in the federal regulations

(40 CFR 136) and the LLNL Wastewater Discharge Permit. An off-site, state-certified analytical laboratory analyzes the sample(s).

The only monitoring equipment used in this field sampling is a handheld pH meter, which is calibrated prior to use following the method described in procedure EMP-W-S, *Water Sampling*.

6.5.6 Action Levels

Sample analyses results are checked against the federal Categorical Discharge Standards by a WGMG analyst or scientific associate. The concentration-based discharge limits in 40 CFR 433, Subpart A, and 40 CFR 469, Subpart A, are considered formal action levels for the regulated pollutants. The discharge limits specified in the federal standards and implemented via the permit are provided in **Table 6-10**.

If the concentration of any regulated pollutant exceeds a discharge limit and the QC data are acceptable, the WGMG analyst contacts the Program representative responsible for that specific wastewater generating process. This inquiry will determine if the process was operated in any unusual manner or used in a different configuration than normal. Depending upon the outcome of that inquiry, further investigation may be initiated by the WGMG analyst. The investigation may include, but is not limited to, inspection of the usage logs, base material used, and any chemicals or reagents used in the process. Additional samples will be taken to determine if the process is still out of compliance or to establish a time that marks the return to a state of compliance with the Categorical limit. After the issue of noncompliance is confirmed, it is reported to the LWRP and DOE within 24 hours. This verbal report is followed by a Five-Day Report to the LWRP and the information in the Five-Day Report is included in the applicable semiannual wastewater report (see **Section 6.5.7**).

6.5.7 Preparation and Disposition of Reports

All monitoring results, as well as the current status of the identified wastewater generating processes, are reported in Semiannual Wastewater Point-Source Monitoring Reports. These reports are submitted to the LWRP every January and July (Grayson and Brigdon 2002), as required in Attachment A-2 of the *LLNL Wastewater Discharge Permit #1250* (City of Livermore 2002). As indicated in the previous section, Five-Day Reports are also required as necessary.

6.5.8 Future Plans

The most important goal for the Categorical Pretreatment Monitoring Program is to maintain an effective level of effluent discharge control ensuring full compliance under the appropriate regulatory standards. As a result of the newly implemented criteria for defining regulated

processes (**Section 6.5.2**), future resources will be best focused on those wastewater-generating activities that have the greatest potential to adversely affect water quality and cause interference or pass-though to the LWRP.

6.6 Procedures for Laboratory Analysis

6.6.1 Sample Preservation and Handling

6.6.1.1 Offsite Analytical Laboratories

Sample preservation techniques generally follow those specified in the applicable U.S. Environmental Protection Agency (EPA) analytical methodology. LLNL procedure EMP-QA-BOT describes the bottles and preservatives to be used for each type of aqueous environmental monitoring sample. Preservation requirements for air, vegetation, and soil samples are documented in the sampling procedures for those media.

Samples are transported to offsite laboratories by using either a common carrier or couriers who pick up all samples at a pre-designated LLNL location according to a regular schedule. Offsite laboratories are required to follow all LLNL sample tracking procedures (contained in procedure EMP-QA-DM) when handling LLNL samples. LLNL must be notified of any problems immediately, including broken or damaged containers, discrepancies between sample bottles and/or labels and the CoC, improper preservation temperature, broken seals on sample coolers, or any other compromises to the integrity of a sample. Identified problems must also be described in the case narrative that accompanies the final data report. Offsite laboratories must hold samples for a minimum of 30 days after the final report is generated and verified by LLNL. The laboratory must dispose of all unused sample portions in accordance with written procedures.

Offsite analytical laboratories are required to segregate nonradioactive from radioactive samples at the time of receipt. Segregation must be maintained throughout sample receipt, storage, and analysis. All samples transferred to the laboratory's custody must be kept in an appropriate sample storage facility in accordance with EPA and California Department of Health Services (DHS) regulations for sample storage, preparation, and holding times. DHS-approved sample-handling and custodial procedures must be maintained and followed.

All environmental radiological analyses must be completed in a low-level radiological laboratory with appropriate spatial segregation of samples, equipment, laboratory space, and labware to ensure the integrity of analysis of samples with natural levels of radioactivity.

6.6.1.2 LLNL Onsite Laboratories

6.6.1.2.1 CES: Sample preparation and counting procedures are performed in a segregated, low-level area of the building that is under negative pressure. Only authorized personnel may enter the low-level area, and they must wear protective shoe covers. Luminous dial watches and all other radioactive materials are prohibited. Samples are handled and stored to minimize cross-contamination and contamination from environmental and outside sources. Samples that require refrigeration or freezing are stored in a holding refrigerator or freezer in this low-level area.

6.6.1.2.2 HCD Safety Laboratories: The HCD safety laboratory HCAL is locked at all times. Samples received by HCAL are stored in a specially designated area that includes separate storage for incompatible samples and for volatile or unstable compounds. All personnel delivering samples to HCAL are trained in contamination control and taught to segregate any samples with potentially unusual activity.

Samples submitted to HCAL are preserved according to specific procedures for each sample and analysis type. HCAL uses established preservation methods found in *Methods for Chemical Analysis of Water and Wastes* (EPA 1983) and *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association et al. 1992) for environmental and waste samples. Typical preservation techniques include acidification of samples and refrigerated storage (≤4°C). In general, standard analytical methods are followed; any exceptions have been made in collaboration with environmental monitoring analysts.

6.6.2 Analytical Methods and Calibration

6.6.2.1 Offsite Analytical Laboratories

Attachment 1 of LLNL's blanket service agreement (BSA) with each offsite contract analytical laboratory lists all analyses that the laboratory provides and specifies the type of sample (environmental, waste, radioactive, etc.), the analytical method to be used, any acceptable alternative method(s), the sample matrix (aqueous, soil, etc.), required reporting limits, preliminary turnaround times, official turnaround times, pricing information, and whether or not the analysis can be subcontracted. An offsite laboratory is allowed, under the terms of the BSA, to subcontract a limited number of analyses to laboratories that are approved by the EPD Assurance Manager. The offsite laboratory retains all responsibility and liability for subcontracted work and must review and verify all associated data and quality control information before submitting them to LLNL.

Table 6-11 through **Table 6-13** show the methods used by offsite laboratories for the analysis of environmental monitoring samples during 2001. Standard analytical methods defined by

EPA, DHS, American Society for Testing and Materials (ASTM), or a method compendium, such as the *Standard Methods* for *the Examination of Water and Wastewater* (American Public Health Association et al. 1992), must be used by offsite laboratories wherever possible. If a nonstandard methodology or a modified standard methodology must be used, LLNL must approve this use in advance. During 2002, the only analyses that did not use standard EPA methodology and protocols were tributyltin in sewage, certain high explosive (HE) compounds in aqueous and soil media, and alpha spectroscopy.

Table 6-11. Methods used for metals analysis (offsite laboratories)

Metal	Retention tanks	Sewer compliance	Categorical pretreatment
Aluminum		200.7	
Antimony	204.2 or 6010A		
Arsenic	206.2 or 6010A	206.2	206.2
Barium	200.7 or 6010A		
Beryllium	210.2 or 6010A	210.2	210.2
Cadmium	213.2 or 6010A	200.7	200.7
Calcium		200.7	200.7
Chromium	218.2 or 6010A	200.7	200.7
Cobalt	200.7 or 6010A		
Copper	200.7, 220.2 or 6010A	200.7	200.7
Iron		200.7	200.7
Lead	239.2 or 6010A	239.2	239.2
Magnesium		200.7	
Manganese	200.7 or 6010A		
Mercury	7470A	245.1	245.2
Molybdenum	200.7 or 6010A		
Nickel	200.7, 249.2 or 6010A	249.2	249.2
Potassium	200.7 or 6010A	200.7	
Selenium	6010A	270.2	
Silver	272.2 or 6010A	200.7	200.7
Sodium		200.7	
Strontium	6010A		
Thallium	279.2 or 6010		
Vanadium	200.7 or 6010		
Zinc	200.7 or 6010	200.7	200.7

Table 6-12. Organic analyses (offsite laboratories)

Analytical method(s)	Monitoring program[a]	Description of analysis[b]
EPA 624	RT, SC, CP	Volatile organic compounds by GC/MS
EPA 625	RT, SC, CP	Semivolatiles by GC/MS
EPA 625 + dimethyl sulfoxide (DMSO)	RT	(DMSO) by GC/MS
EPA 8021 or 8260B/5030A	RT	Purgeable hydrocarbons and Freon 113
EPA 8080	RT	PCBs and organochlorine pesticides
EPA 8270	RT	Semivolatile organic compounds by GC/MS

a RT = Retention tank monitoring
SC = Sewer compliance monitoring
CP = Categorical pretreatment monitoring

b GC = Gas chromatography
MS = Mass spectrometry

Table 6-13. Wet chemistry (offsite laboratories)

Analytical method(s)	Monitoring program[a]	Description of analysis
EPA 150.1	RT	pH
EPA 160.1	RT, SC	Total dissolved solids
EPA 160.1, 160.2, 160.4, 160.5	SC	Total dissolved solids, total suspended solids, volatile solids, total settleable solids
EPA 300.0	RT, SC	Anions
EPA 335.3, 335.3	RT, SC	Total cyanide
EPA 300.0, 345.1, 350.2, 350.1, 351.2, 351.3, 353.2	SC	Nutrients
EPA 310.1	SC	Bicarbonate, carbonate, hydroxide, and total alkalinity
EPA 365.4	SC	Total phosphorus
EPA 410.4	SC	Chemical oxygen demand
EPA 415.1	SC	Total organic carbon
EPA 1664	RT	Oil and grease
EPA 8330[b]	RT	High explosives
Standard Methods 5210B	SC	Biochemical oxygen demand
TBTIN[b]	SC	Tributyltin (TBT)

a RT = Retention tank monitoring
SC = Sewer compliance monitoring
CP = Categorical pretreatment monitoring

b Typically subcontracted.
TBTIN = tributyl tin

6.6.2.2 Calibration

Table 6-14 lists the minimum requirements for internal calibration when such controls are applicable to a particular analytical method. The table identifies the calibration activity, the applicable type of analysis, and the minimum frequency of calibration allowable under the BSA. For the purposes of this table, a batch is defined as less than, or equal to, 20 samples.

A summary of calibration sample results for each sample must be provided with the analytical data report. This summary must include continuing calibration batch number, date and time of analysis, instrument ID number, analyst ID number, method number, theoretical result, actual result, percent recovery, and acceptable range. In addition, the laboratory must maintain initial instrument calibration data and make the data available upon request. Copies of each laboratory's standard operating procedures for performing and tracking calibration activities are maintained on file by the EPD Assurance Manager. Each laboratory's calibration program and its implementation are verified at the annual facility audit.

Table 6-14. Minimum calibration requirements

Required QC activity	Applicable type of analysis	Frequency provided to LLNL
Ongoing calibration checks	Rad and nonrad	With each sample batch
Initial calibration	Rad and nonrad	Upon request

6.6.2.3 LLNL Onsite Laboratories

6.6.2.3.1 Chemistry and Materials Science Environmental Services (CES): CES follows verified analytical methods (listed in **Table 6-15**) in its radiological analyses. Standard methods used include EPA 900.0 (gross alpha/gross beta) and EPA 901.1 (gamma spectroscopy). Other CES methods are consistent with standard methods but are modified for greater sensitivity. Modifications are different for each medium and type of sample. These radiochemical methods and their associated calibration requirements are documented in CES standard operating procedures. All analytical methods except those for alpha nuclides have been reviewed and certified by California Laboratory accreditation program (CA ELAP) and have met CA ELAP requirements for environmental radiochemistry. The state of California is currently beginning the process of certifying laboratories for the analysis of alpha nuclides.

Table 6-15. CES-performed radiological analyses

Analytical method(s)	Monitoring program[a]	Description of analysis
Alpha spectroscopy or Lab specific	RT, SS	Plutonium, thorium, and uranium isotopes
EPA 901.1 or Lab specific	RT, SS	Gamma spectroscopy
Lab specific	RT	Gross alpha/gross beta
Lab specific	RT	Tritium

a RT = Retention tank monitoring
SS = Sewer spill monitoring

Water, Sewage, and Sludge (Plutonium). Plutonium is separated by coprecipitation with manganese dioxide (MnO_2). The MnO_2 then is ashed and dissolved in nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). Plutonium is purified by ion exchange, electroplated onto a stainless-steel disk, and submitted for alpha spectroscopy.

6.6.2.3.2 Hazards Control Department (HCD) Safety Laboratories Division: HCAL uses EPA- and California-approved procedures for processing waste water samples. **Table 6-16** lists the analytical methods used by HCAL for waste water samples from the sewer spill monitoring program. The only exception is the digestion of composite sewage samples prior to metals analysis; these samples are subjected to the standard digestion process, and are then filtered and subjected to another (stronger) digestion. Then they are analyzed for metals by inductively coupled plasma/optical emission spectroscopy (ICP/OES). HCAL performs a standard acid digestion, followed by plating on a stainless steel planchet to prepare samples for gross alpha and gross beta counting by the RML. Modifications are currently being made to the procedure for preparation of sewer samples for gross alpha/gross beta counting based on recommendations from the DHS.

Table 6-16. HCAL–performed analyses

Analytical method	Matrices[a]	Laboratory	Description of analysis
EPA 200.7	SW	HCAL	Sewer metals
Laboratory specific	SW	HCAL	Digester metals
40 CFR 61, Method 114	AF, SW	HCAL/RML	Gross alpha, gross beta
Laboratory specific	SW	HCAL/RML	Tritium by liquid scintillation

a SW = Sewer water
AF = Air filter

6.6.2.4 Calibration

CES uses a database to manage the life cycle of measuring and test equipment (M&TE) from initial calibration through continued use, to retirement or disposal. M&TE is identified and inspection requirements are defined in CES standard operating procedures. Calibration intervals are based on required accuracy, intended use, frequency of use, stability

characteristics, and other conditions that affect performance. Appropriate tests are conducted to demonstrate that the equipment will perform as intended. All testing is done using established test requirements and acceptance criteria. Any M&TE found to be out of calibration or tolerance is tagged, and it must be re-calibrated prior to use.

Equipment within the HCAL and the RML is calibrated with sources that are traceable to National Institute for Standards and Technology (NIST). Calibration follows a variety of methods from calibration by a certified third party (as is done for laboratory balances), to calibration with known standards that are made from traceable materials (as is done for metals and most radiological analyses). Calibration practices are in accordance with standard procedures and are evaluated during audits required for maintenance of certifications.

The HCD Safety Laboratory Division laboratories are part of LLNL's calibration program. Calibration records are maintained for each piece of calibrated equipment.

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7 Surface Water Monitoring

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7.1 Introduction

Lawrence Livermore National Laboratory (LLNL) monitors surface water at its Livermore site and surrounding regions of the Livermore Valley, as well as at Site 300 and areas of the nearby Altamont Hills. Within the Livermore Valley, LLNL monitors the Laboratory grounds, swimming pool, Drainage Retention Basin (DRB), local rainfall, the domestic water supply (tap water), reservoirs and ponds, other surface water bodies, and storm water runoff from large construction sites and the entire facility. At Site 300 and in its vicinity, LLNL monitors rainfall, drinking water releases on Site 300, as well as storm water runoff from construction sites and industrial activities.

Water samples are analyzed for radionuclides, explosive compounds, total organic carbon (TOC), total organic halides (TOX), total suspended solids (TSS), electrical conductivity, pH, chemical oxygen demand (COD), total dissolved solids (TDS), oil and grease, residual chlorine, metals, minerals, anions, nutrients, physical parameters, a wide range of organic compounds, and microbiological indicators. In addition, fish bioassays and other toxicity tests are performed on water contained in the DRB, discharges from the DRB, and storm water entering and leaving the Livermore site via Arroyo Las Positas.

7.2 Storm Water

7.2.1 Rationale and Design Criteria

7.2.1.1 Regulatory Drivers

The applicable portions of U.S. Department of Energy (DOE) Order 5400.1 (see WSS B93 in Appendix B) is the primary regulation driving the monitoring of storm water at LLNL. The order states, "Environmental surveillance shall be conducted to monitor the effects, if any, of DOE activities on on-site and off-site environmental and natural resources . . . ."

In addition, the Federal Water Pollution Control Act (Clean Water Act, 1972, 33 USC 1251) was enacted to restore and maintain the chemical, physical, and biological integrity of waters of the United States. To this end, Section 402 established the National Pollutant Discharge Elimination System (NPDES) to set the conditions under which pollutants could be discharged to navigable

waters. NPDES requires industries to obtain permits before discharging storm water associated with industrial activities from their facilities. Specific U.S. Environmental Protection Agency (EPA) requirements applicable to the Laboratory's NPDES permits are contained in Title 40 of the *Code of Federal Regulation*s (CFR), Part 122, *EPA Administered Permit Programs: The National Pollutant Discharge Elimination System* (CFR 1983). NPDES permits requiring storm water runoff monitoring at the Livermore site and Site 300 are issued in California as Waste Discharge Requirements (WDRs). These permits regulate storm water discharges associated with industrial activities and low-threat, non-storm water discharges, such as air-conditioner condensate. The following WDR permits are the regulatory drivers for LLNL's storm water runoff monitoring:

- Order No. 95-174, *Waste Discharge Requirements and National Pollutant Discharge Elimination System (NPDES) for U.S. Department of Energy and Lawrence Livermore National Laboratory*, issued by the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB 1995) for the Livermore site
- Order No. 97-03-DWQ, *Statewide General National Pollutant Discharge Elimination System (NPDES) Permit for Storm Water Discharges Associated with Industrial Activities*, issued to LLNL for Site 300 by the State Water Resources Control Board (SWRCB 1999) in August 2000

Waters of the state of California are also regulated by the California Porter-Cologne Water Quality Control Act (California Water Code 13000). Under this act, the jurisdictional Regional Water Quality Control Board (RWQCB) must evaluate waste discharges and issue a WDR if it determines that the waste could adversely affect water quality. This act also requires the state to develop several statewide water quality plans and individual regional water quality control plans. Any WDR must be consistent with these plans and must protect the beneficial uses and the water quality objectives these plans identify.

7.2.1.2 Monitoring Objectives for Storm Water

The California State Water Resources Control Board and its associated Regional Water Quality Control Boards administer LLNL's NPDES permits. The LLNL NPDES storm water monitoring programs meet permit requirements by

- Aiding in the implementation of storm water pollution prevention plans (SWPPPs)
- Measuring the effectiveness of best management practices (BMPs) in reducing or eliminating specific pollutants in storm water discharges

- Ensuring that storm water discharges comply with discharge prohibitions, effluent limitations, and receiving water limitations as specified in LLNL's storm water discharge permits
- Determining that facility practices to control storm water pollution are evaluated and modified to meet changing conditions

NPDES permits specifically require visual observations at storm water discharge points during the dry and wet seasons. In general, the wet season occurs between October 1 and April 1. However, this is a regulatory definition, and it is defined differently in different cases. NPDES permits for storm water require LLNL to visually inspect the storm drainage system monthly during the wet season (if significant storm events occur). The regulations require chemical analysis of storm water from two storm events during which runoff occurs. Additionally, LLNL must visually inspect the storm drainage system twice (once each quarter) during the dry season to detect dry weather flows.

In addition to the NPDES requirements already stated, DOE's *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (DOE 1991) describes the environmental monitoring objectives applicable to runoff:

- "The purpose of the surveillance program is to characterize the radiological conditions of the off-site environs and, if appropriate, estimate public doses related to these conditions, confirm predictions of public doses based on effluent monitoring data, and, where appropriate, to provide compliance data for all applicable regulations. The results of this evaluation *should** be documented in the site Environmental Monitoring Plan."
- "The environmental surveillance program for DOE-controlled sites *should** be conducted in accordance with the requirements of DOE 5400.1 and DOE 5400.5. . . ."

  [* The term *should** in this quotation identifies a DOE "high-priority element."]

DOE Order 5400.1 further states that:

- "Ambient water quality monitoring should be conducted through a network of fixed stations from which data will establish well-defined histories of the physical, biological, and chemical conditions of local bodies of water and sediments. . . ."

- "Analysis of data collected from a fixed station monitoring network should support:
  - Characterizing and defining trends in the physical, chemical, and biological conditions of surface waters;
  - Establishing baselines of water quality;
  - A continuing assessment of water pollution control programs;
  - Identifying new water quality problems; and
  - Detecting, characterizing, and reporting unplanned releases and their effects on water quality."

The regulations described above represent the primary DOE drivers and regulatory objectives for the monitoring of domestic water sources, rainfall, surface water bodies, and storm water runoff at LLNL's Livermore site and at Site 300.

7.2.1.3 Storm Water Sources and Analytes

The LLNL storm water program meets specific permit requirements, and, in support of the DOE Orders described above, exceeds permit requirements for both the number of samples collected and the analyses conducted on the samples. Required analyses and additional analyses conducted on Livermore site and Site 300 storm water are summarized in **Table 7-1**.

Analyses are conducted for constituents that may be present in storm water discharges in significant quantities. At the Livermore site, storm water samples may contain contaminants from a variety of sources including: neighboring agricultural land, adjacent roadways, parking lots, and landscaped areas. As a result of the potential off-site sources and the diverse activities conducted at the Livermore site, it is necessary to monitor a range of constituents in storm water runoff. In contrast, storm water at Site 300 is sampled at locations that target specific activities, so a smaller range of analyses is performed.

The Environmental Protection Department (EPD) at LLNL has monitored storm water runoff at the Livermore site since 1975 (Gallegos et al. 1993). The original monitoring network, designed to detect pesticides, was expanded in 1990 to cover new locations and additional water quality parameters (i.e., radioactivity, metals, and additional organic compounds). Additional changes during 1993 complied with the National Pollutant Discharge Elimination System General Permit for Storm Water Discharges Associated with Industrial Activities (NPDES General Permit). At that time, in support of the General Permit, a review of storm water runoff data collected from 1978 through 1991 was used to select the constituents and parameters for

Table 7-1. Summary of analyses conducted on storm water samples, analytical methods are in parentheses.

Livermore site	Site 300
Chemical oxygen demand (EPA 410.4)	Chemical oxygen demand (EPA 410.4)
Dissolved oxygen (EPA 360.1)	Cyanide (EPA 335.2)
Oil and grease (EPA 1664)	Oil and grease (EPA 1664)
pH (EPA 150.1)	pH (EPA 150.1)
Specific conductance (EPA 120.1)	Specific conductance (EPA 120.1)
Total dissolved solids (EPA 160.1)	Total dissolved solids (EPA 160.1)
Total suspended solids (EPA 160.2)	Total suspended solids (EPA 160.2)
Anions (EPA 300.0)	Ammonia (EPA 350.2)
General minerals (EPA 310.1, 340.2, 345.1, 353.2, 425.1, SM2330B, SM4500P)	Potassium (EPA 200.7:K)
Metals (EPA 200.7)	Metals (EPA 200.7, 210.2, 245.1)
Polychlorinated biphenyls (PCBs) (EPA 8082)	Polychlorinated biphenyls (PCBs) and dioxins (E8082 + E8290)
Total organic carbon (EPA 9060)	Total organic carbon (EPA 9060)
Fish bioassay (fathead minnow) (EPA 1000TOX)	Organic compounds (EPA 624/625)
Diuron (EPA Method 632)	Pesticides (EPA 608)
Glyphosphate (EPA 547)	Explosives (HE)
Herbicides (EPA 525)	Total organic halides (SW 9020B)
Gross alpha and gross beta activity (EPA 900)	Gross alpha and gross beta activity (EPA 900)
Tritium (EPA 906)	Tritium (EPA 906)
Plutonium (AS:PULSO)	Uranium (AS:ULSO)

ongoing monitoring. Constituents and parameters selected for the Livermore site at that time were chemical oxygen demand, gross alpha activity, gross beta activity, tritium, total alkalinity, bicarbonate alkalinity, carbonate alkalinity, hydroxide alkalinity, aluminum, calcium, chloride, copper, fluoride, hardness, iron, magnesium, manganese, nickel, nitrate, potassium, sodium, sulfate, surfactant, and zinc. Most of these constituents are naturally occurring and are usually found in LLNL runoff at or near background levels.

In October 1993, also in response to the NPDES General Permit, LLNL established a new storm water monitoring program at Site 300. In 1994, CVRWQCB issued LLNL an individual discharge permit for industrial storm water discharges (NPDES No. CA0081396, WDR 94-131) (CVRWQCB 1994a). In 2000, the Central Valley RWQCB rescinded WDR 94-131 and began regulation of Waste Discharge Requirements at Site 300 under the Statewide General Permit for Storm Water Discharges Associated with Industrial Activities (NPDES No. CAS000001, WDR 97-03-DWQ). In contrast, the Livermore site site-specific permit was issued in 1995 by the San Francisco Bay RWQCB (NPDES No. CA0030023, WDR 95-174). Constituents and parameters required by the San Francisco RWQCB in the Livermore site permit are: pH, total dissolved

solids, total suspended solids, chemical oxygen demand, dissolved oxygen, gross beta, tritium, nitrate, phosphates, and fish toxicity. Constituents and parameters required by the Statewide General Permit for Site 300 permit are: pH, total suspended solids, specific conductance, and total organic carbon (or oil and grease) along with specific requirements for landfills (Sector L) and hazardous waste (Section K) facilities. In addition, post closure monitoring at Pit 6 requires (Ferry et al. 1997) analyses for potassium, beryllium, mercury, total dissolved solids, and a wide range of organic constituents (EPA Methods 608, 624, and 625). Finally, in support of the DOE orders, Site 300 storm water is also analyzed for gross alpha activity, gross beta activity, tritium, and uranium.

Historically, LLNL has also analyzed Livermore site storm water for a wide range of organic chemicals. In 1996, a review of laboratory operations identified oil and grease, as well as specific pesticides, as the organic chemicals most likely to come into contact with storm water. Most of the pesticides were not included in the organic analyses conducted at that time. Furthermore, a review of recent data (1991–1996), showed that no specific organic chemical was detected in more than 25 percent of the samples. The organic chemicals most commonly detected were acetone in 6 out of 49 samples (12 percent); bis(2-ethylhexyl)phthalate, 4 detections (8 percent); and Freon 113, 3 detections (6 percent). All other organic chemicals specifically identified were detected only once or twice in 49 sampling events. Therefore, beginning in fall 1996, organic analyses were selected to target oil and grease, plus pesticides known to have been used at the Livermore site. As listed in **Table 7-1**, current organic analyses conducted on Livermore site storm water employ four methods: EPA Method 525 (herbicides), EPA Method 547 (glyphosphate), EPA Method 8082 (PCBs), and EPA Method 632 (diuron).

7.2.1.4 Collection Methods for Storm Water Samples

Samples are collected by grab sampling from the runoff flow at specified locations. Sample bottle requirements, special sampling techniques, and preservation requirements for each analyte are specified in procedures EMP-QA-BOT and EMP-W-S (Appendix B); they are summarized in the paragraphs below.

Samples are collected using either a triple-rinsed stainless steel bucket or an ISCO peristaltic pump with polyethylene tubing. Sampling is conducted away from the edge of the water to minimize the collection of sediment with the sample matrix.

Sample vials for volatile organics analyses are filled first, before sample vials for all other constituents and parameters. After the bottles are filled, they are dried, labeled, packaged, and placed in an ice chest. If the water to be sampled is accessible to the technologist, grab samples are collected by partially submerging sample bottles directly into the water and allowing them to fill with the sample water.

7.2.2 Extent and Frequency of Storm Water Monitoring and Measurements

7.2.2.1 Routine Monitoring Requirements for Livermore Site

Both NPDES permits WDR 98-03-DWQ and WDR 95-174 require monitoring at least two storm events each wet season. LLNL monitors two additional storm events (4 total) in support of DOE Order 5400.1 (DOE 1988).

The storm water monitoring network consists of ten sampling locations (**Figure 7-1**). Each location has a unique alpha-numeric code identifier. A complete description of the sampling locations is entered in the Locations Database maintained by the Technical Support Group (TSG) in LLNL's Operations and Regulatory Affairs Division (ORAD).

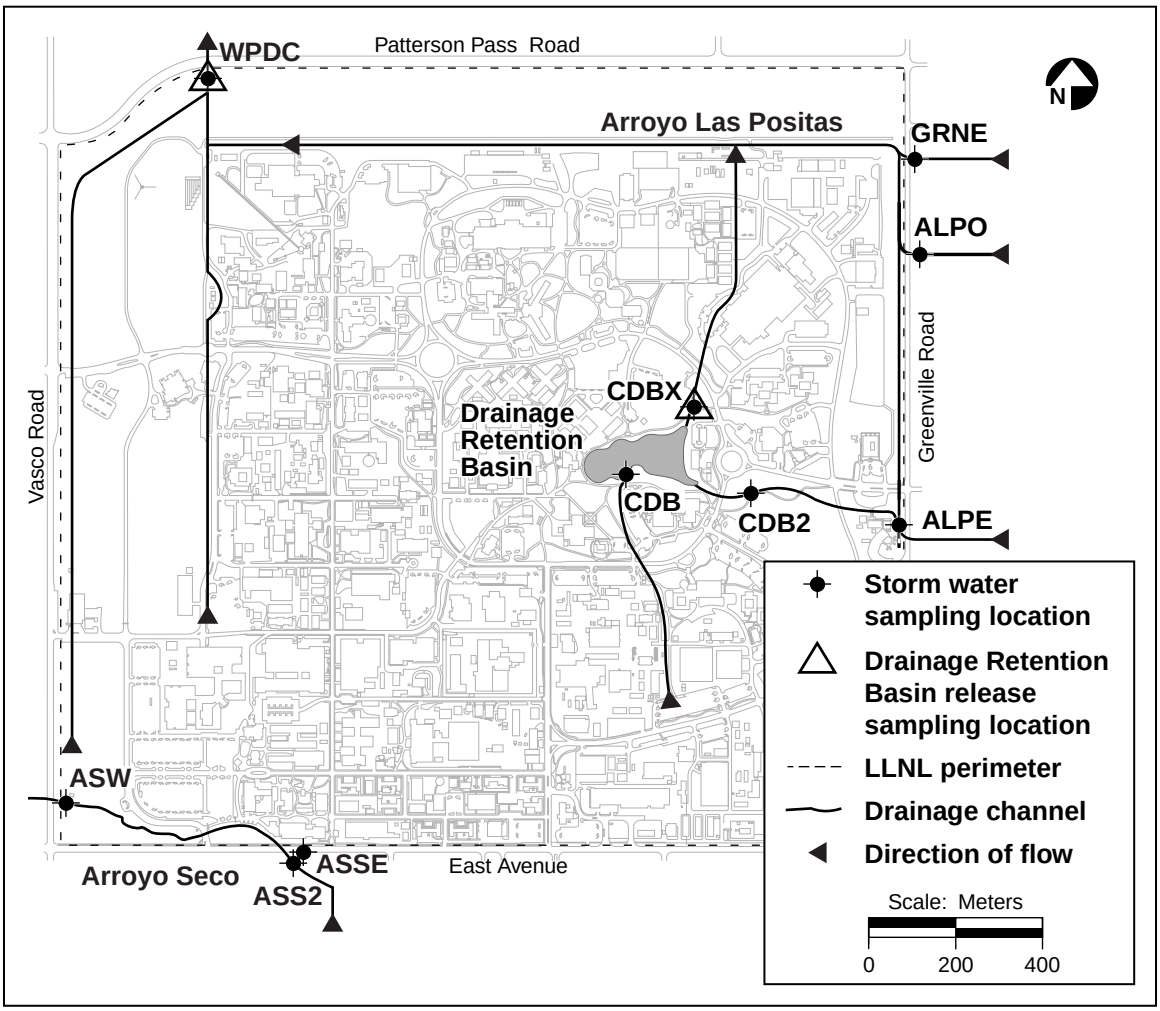

Figure 7-1. Storm water runoff sampling locations, Livermore site and vicinity

Two arroyos cross the Livermore site: Arroyo Las Positas and Arroyo Seco. NPDES monitoring points required by permit are ALPE, ALPO, ASW, ASS2, GRNE, and WPDC, a subset of the overall monitoring network. Of the ten locations in the Livermore site storm water sampling network (**Figure 7-1**), seven characterize storm water either entering (influent—ALPE, ALPO, GRNE, ASSE, and ASS2) or exiting (effluent—WPDC and ASW) the site, as required by the NPDES permit. Three additional locations (CDB, CDB2, and CDBX) serve the monitoring required for DRB discharges. Although the DRB locations are not required in the storm water NPDES permits, they are included in the storm water network in order to improve the efficiency of administration and sample collection.

Sampling location WPDC in the northwest corner of the site is used to monitor storm water discharges from LLNL into Arroyo Las Positas. Drainage channels converge at this point, collecting runoff from internal site channels and the DRB.

Three sampling locations characterize influent entering the site from the Arroyo Las Positas drainage. They are ALPE near the intersection of East Gate Drive and Greenville Road on the eastern edge of the Laboratory; GRNE in the northeast corner of the site; and ALPO, along Greenville Road between ALPE and GRNE.

In the southwest region of the site, ASSE and ASS2 characterize the influent of Arroyo Seco, while ASW characterizes its effluent.

Locations CDB and CDB2 characterize southeastern quadrant runoff entering the DRB, and location CDBX characterizes water leaving the DRB. The basin, located near the center of the Livermore site, collects storm water runoff from a large portion of the Laboratory. DRB monitoring is described in **Section 7.5**; a complete description of the design, operation, and maintenance of this basin can be found in the *Drainage Retention Basin Management Plan* (Limnion Corporation, 1991).

7.2.2.2 Livermore Site Metals and Suspended Sediment

A source evaluation for increasing metals concentrations in storm water on the Livermore site was performed beginning in 1999. The study deserves special attention as the results raise an important issue about the quality of historical metals data. This examination concluded that the high concentration values were the result of ambiguous laboratory analysis procedures that sometimes included suspended sediment in the analysis and sometimes did not. Many metals are closely associated with sediments, and the correlation has been specifically established in storm water samples for the Livermore site (Brandstetter 1998). Correcting this ambiguity, along with making additional requested analyses as a double check of the metal analysis procedures, has reduced this problem.

This source evaluation established that the increase of most metal concentrations was an artifact of the analysis. However, other metals (in particular zinc) that are not as closely related to sediment loading are still measured at values higher than LLNL's threshold criteria. Upon further investigation, however, it appears that zinc concentrations in LLNL storm water are consistent and show no increasing trend. Therefore, the LLNL site-specific target threshold for zinc has been increased to 0.35 mg/L, which is greater than EPA benchmark value (0.117 mg/L) (Marshack 2000).

7.2.2.3 Routine Monitoring Requirements for Site 300

Based on field examinations of Site 300 drainage (performed during storm events), communications with Central Valley RWQCB, and a review of the "industrial activity" criteria in the NPDES General Permit for discharges of storm water associated with industrial activities (SWRCB 1991), seven monitoring locations are used at Site 300 (shown in **Figure 7-2**). Five locations monitor runoff related to specific industrial activities, one location monitors water quality upstream of Site 300 in Corral Hollow Creek, and one location monitors water quality downstream of Site 300 in Corral Hollow Creek.

Monitoring location N829 is in Rifle Canyon in the southern portion of Site 300, a natural drainage for the Explosives Burn Pits at the Building 829 Complex. This area falls under the "K-classification" in the NPDES WDR 98-03-DWQ for hazardous waste treatment or disposal facilities that add additional chemical analytes to the monitoring list. Monitoring location N829 sits where Rifle Canyon exits the Site 300 perimeter, east of Pit 6. This sampling location is used to monitor surface water runoff from the Building 829 Complex since its closure.

Monitoring location N883 is in the Building 883 Facility (also a "K classification" facility), a hazardous waste container storage area (HWCSA); it is located in the General Services Area (GSA) in the southeast corner of Site 300. This RCRA-permitted facility stores containerized wastes awaiting off-site disposal by the Radioactive and Hazardous Waste Management (RHWM) Division of EPD. The facility design includes engineered controls that catch storm water in a sump, where it is pumped into barrels or drums, pending analysis and disposal. Roof runoff from this facility flows through storm drains in the GSA and exits Site 300 along Corral Hollow Road.

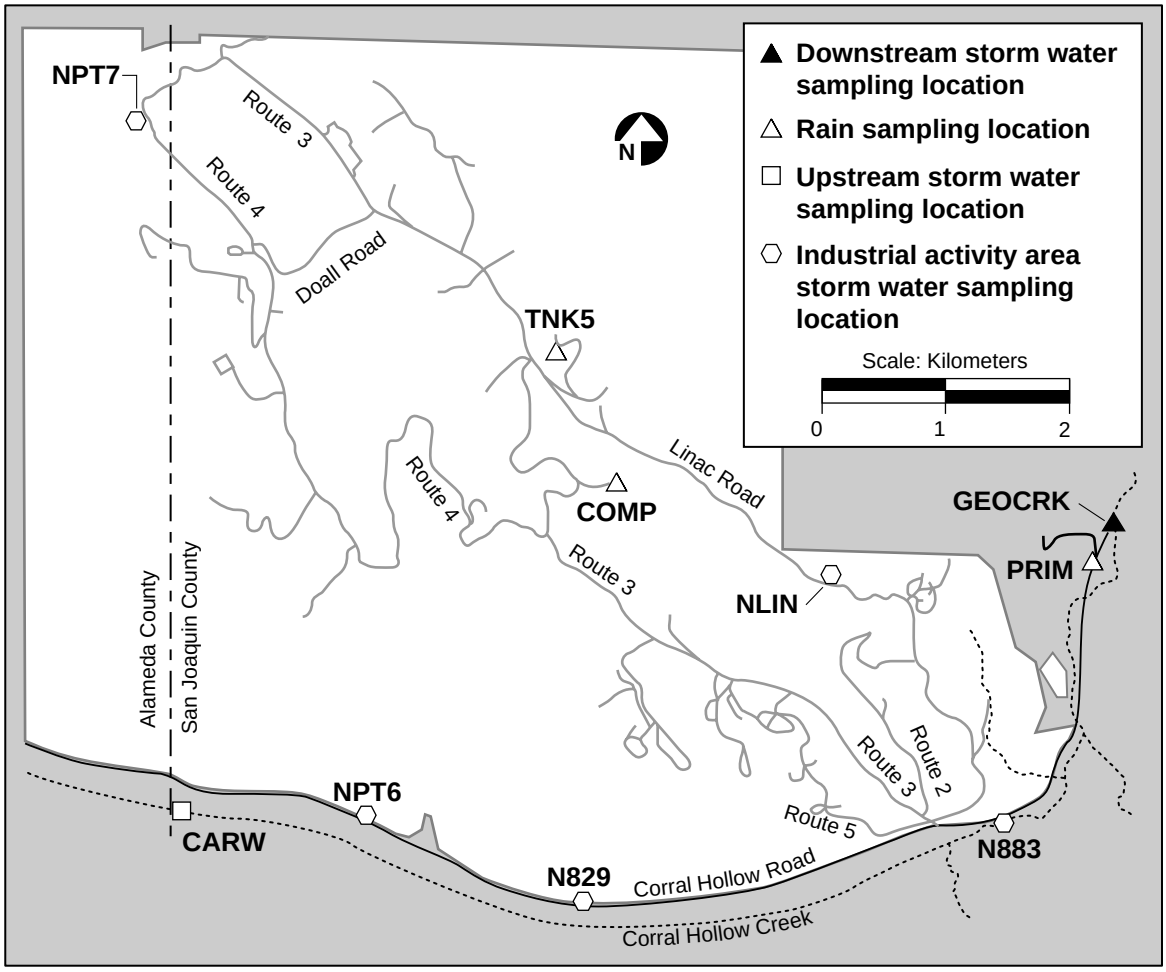

Figure 7-2. Storm water runoff and rainwater sampling locations at Site 300

Location NLIN is used to monitor runoff from several closed landfills at Site 300 that fall under both the "K-classification" and the "L-classification" for landfills. Pits 1 and 2 are landfills (L-classification) located south of the East Observation Post in the upper central portion of Site 300. Pits 3, 4, 5, and 7 lie directly above the West Observation Post in the northwest quadrant. Pit 8 is located in the northeastern portion of the site, just east of the 801 Facility, and Pit 9 is located near Building 845. These landfills hold debris from past experiments conducted at Site 300. A history of each pit's contents can be found in the *Final Site-Wide Remedial Investigation Report* (Webster-Scholten 1994). Although these landfills are capped so that the contents do not come in contact with storm water runoff, the RWQCB requires sampling of associated runoff.

NLIN is used to monitor drainage from the closed landfills (except Pit 6 and some drainage from Pit 7), which flows southeasterly until it passes through a culvert off Linac Road and then exits Site 300 via Elk Ravine to the east. Elk Ravine has no safe or accessible sampling point at the Site 300 boundary. No industrial activity occurs between the Linac Road culvert and the final Elk

Ravine exit point; therefore, LLNL collects samples at the Linac Road culvert (NLIN). This sampling point was approved in personal communication with Central Valley RWQCB staff on December 8, 1992 (and documented in a January 22, 1993, letter to Central Valley RWQCB [Isherwood 1993a]). Because of past activity at the Building 850 Area, storm water could become contaminated with polychlorinated biphenyls (PCBs) and dioxins. Therefore, samples collected at NLIN, which is downgradient from B850, are also analyzed for PCBs and dioxins.

NPT6 is used to monitor Pit 6 runoff. Drainage from the region surrounding the Pit 6 cap is diverted by a ditch and culvert north of the pit to prevent intermittent sheet flow over the landfill. Runoff is sampled at the culvert on the southern end of Pit 6 (NPT6). Post-closure monitoring at Pit 6 requires analysis for potassium, beryllium, iron, mercury, total dissolved solids, and a wide range of organic constituents (EPA Methods 608, 624, and 625) (Ferry 1997).

NPT7 is used to monitor Pit 7 runoff. The Pit 7 cap includes a graded concrete drainage system that directs flow away from the pit. Consequently, a portion of this storm water runoff now flows north and is monitored at location NPT7.

Location CARW is slightly south of Site 300 near its western border, where technical staff collect samples from Corral Hollow Creek. Because this location is upstream of any industrial discharge from Site 300 and the water contains constituents and parameters considered typical of the region, CARW samples aid LLNL in determining the water quality of storm water not impacted by Site 300 industrial operations. The location of CARW was moved slightly downstream to provide access on public rather than private land.

Sampling location GEOCRK lies downstream of Site 300 in Corral Hollow Creek. This location helps LLNL assess the potential influence of Site 300 on water quality in Corral Hollow Creek.

7.2.3 Procedures for Laboratory Analysis

All water quality chemical analysis is performed by certified off-site contract laboratories. A standard chain of custody form is used to track samples, double-check bottle labels, and exchange information with contract laboratories. Quality assurance and quality control procedures are implemented and checked by LLNL.

7.2.4 QA Requirements for Storm Water

To ensure that all quality assurance (QA)/quality control (QC) objectives are met, all storm water runoff water monitoring samples are collected and analyzed by trained personnel following written procedure EMP-W-S. Field duplicates are submitted for all analytes. The

field duplicates are collected from a randomly selected location at both the Livermore site and Site 300 for each storm event sampled. Currently, no field blanks or spikes are used.

7.2.5 Program Implementation Procedures

Storm water runoff sampling is conducted by LLNL technical staff according to procedure EMP-W-S. Samples are submitted for analyses using sample control and documentation procedures EMP-QA-SL and EMP-QA-DM. Sample bottle requirements and preservation requirements for each analyte are specified in procedure EMP-QA-BOT.

7.2.6 Action Levels

No numeric water quality criteria for storm water discharges from LLNL currently exist. In order to provide stringent criteria relevant to the environment around LLNL, site-specific comparison criteria have been calculated for a select group of parameters based on historical values in runoff samples. A value exceeds the threshold if it is greater than the 95 percent confidence limit computed for the historical mean value for a specific parameter (**Table 7-2**). The threshold criteria are used to identify out-of-the-ordinary data that should be investigated further to determine if concentrations of that parameter are increasing in the storm water runoff.

In addition, LLNL storm water analysis results are compared with other water quality criteria. The U.S. EPA established benchmark values for 41 parameters in the multisector permit (EPA 2000), but stressed that these concentrations should not be interpreted as effluent limitations. Rather, they are the levels that EPA uses to determine whether storm water discharges from specific categories of industrial facilities merit further monitoring. Storm water sample results are also compared with water quality criteria listed in *Water Quality Control Plan, San Francisco Bay Basin* (CRWQCB 1995) and *Central Valley Water Quality Control Plan: the Sacramento River Basin and the San Joaquin River Basin* (CVRWQCB 1994).

To evaluate LLNL storm water effluent, analysts carry out the following ordered sequence:

- Compare storm water effluent concentrations with the above LLNL site-specific threshold criteria.
- If effluent concentrations exceed any criterion, compare effluent values with corresponding influent concentrations.
- If effluent concentrations are lower than influent concentrations, assume that the sources are off site or naturally occurring and take no further action.

Table 7-2. LLNL site-specific threshold comparison criteria for storm water constituents of concern. Values were estimated based on historical runoff data.

Parameter	Livermore site	Site 300
Total suspended solids (TSS)	750 mg/L[a]	1700 mg/L[a]
Chemical oxygen demand (COD)	200 mg/L[a]	not monitored
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
Mercury	above RL[c]	above RL[c]
Beryllium	0.0016 mg/L[a]	0.0016 mg/L[a]
Chromium(VI)	0.015 mg/L[d]	not monitored
Copper	0.026 mg/L[d]	not monitored
Lead	0.015 mg/L[e]	0.015 mg/L[e]
Zinc	0.35 mg/L[a]	not monitored
Diuron	0.014 mg/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	0.34 Bq/L[a]	0.90 Bq/L[a]
Gross beta	0.48 Bq/L[a]	1.73 Bq/L[a]

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

b EPA benchmark

c RL = reporting limit, which is 0.0002 mg/L as of 2001

d Ambient water quality criteria (AWQC)

e EPA primary maximum contaminant level (PMCL)

- If data exceed the LLNL thresholds at the effluent locations (i.e., Arroyo Seco or Arroyo Las Positas), then construct a historical trend plot.
- If (a) a positive trend is observed or (b) data values exceed LLNL comparison criteria (**Table 7-2**) and are higher at the effluent than influent sampling locations, then a detailed investigation is initiated.
- A single, unusually high concentration (>2 orders of magnitude above background) may, by itself, trigger a detailed investigation (a toxicity evaluation).

Detailed investigations may include elements such as

- Management notification.
- Re-analysis of the samples.

- Analysis of archived samples. (Because it is not possible to resample a storm event, procedures dictate collecting archival samples.)
- Analysis of subsequent storm events. (Routinely, four storm events are sampled each year. During a detailed investigation, the storm event immediately following a finding may also be sampled for further evaluation.)
- Source investigation. (Results are compared with findings from other monitoring networks [e.g. air, rain, or sediments], and LLNL activities that may have contributed to the result are investigated.)
- Expanded monitoring (more locations).
- Increased monitoring frequency (i.e., more storm events sampled per wet season).
- Preparation of simple explanatory models for case study comparison and hypothesis testing.

7.2.7 Preparation and Disposition of Storm Water Reports

Storm water monitoring findings are presented in the surface water monitoring section of the annual LLNL *Environmental Report* (e.g., Biermann et al. 2001). In addition, storm water sampling results are transmitted annually in two reports to regulatory agencies. Livermore site findings are reported to the San Francisco RWQCB, and Site 300 results are reported to the Central Valley RWQCB (e.g., Campbell 2001a, 2001b). Both reports follow the *Storm Water Annual Report* format stipulated by the California State Water Resources Control Board (SWRCB) in the General Permit; they are due on July 1 (Site 300) and August 1 (Livermore site) of each year. All storm water data are reported and summarized, trends are discussed, and efforts to reduce constituent loading in storm water are evaluated.

7.2.8 Future Plans

In addition to the necessary continuous review and adaptation of the storm water monitoring networks at both sites, LLNL also plans to add regular monitoring of runoff volume at effluent locations (ASW and WPDC) at the Livermore site. As the network reviews usually result in only minor changes in a single sample or bottle requirements, only the addition of storm flow volume monitoring is discussed here.

7.2.8.1 Monitoring Runoff Volume from the Livermore Site

In order to estimate total mass loading of constituents in storm water runoff, an estimate of flow volume is needed. As concrete channelized areas exist near both effluent sampling locations at

the Livermore Site, ASW and WPDC, a simple regular stage (water depth) measurement at these locations can be calibrated to flow volume. The stage measurements, flow calibration, and mass estimation procedures are discussed in **Sections 7.2.8.1.**1, **7.2.8.1.2**, and **7.2.8.1.3**. Implementation of these components into the monitoring network has begun, but is not yet finished. Future plans are still in the formative stages. Preliminary details, as available, are provided in the sections below.

7.2.8.1.1 Regulatory Drivers: Under the NPDES permits for storm water discharges from industrial facilities, it is possible that mass discharges of a constituent could be regulated as a total maximum daily load (TMDL) assigned for a water body defined by the SWRCB as impaired. If LLNL were required to report the TMDL for a chemical moving off site, the total flow volume must be known.

7.2.8.1.2 *Stage Measurements*: Two water level loggers (item # WL15) have been purchased from Global Water Instrumentation (Gold River, CA). These loggers consist of a temperature-compensating pressure transducer attached to a data logger; all are placed as a unit in the field. As the depth of the water above the pressure transducer is directly related to the pressure measurement, the device can be calibrated to measure stage. The pressure transducer end of the device must be secured at the bottom of the storm drain channel in a manner that avoids fouling by debris and sediment mobilized during storms.

A portable computer is used to download the program that runs the water level loggers and also to collect stored data. This program can be used to set the sampling interval of 15 minutes. The stage data can be imported into Microsoft Excel or another spreadsheet program file for further analysis.

7.2.8.1.3 *Flow Calibrations*: Storm flow volume can be estimated from the stage measurements as long as the channel cross-section at the measurement point does not change. The channels at both measurement points ASW and WPDC are lined with concrete, ensuring that this assumption is correct. Therefore, the one-dimensional area (A) containing storm flow (in a plane perpendicular to the channel) is known using the water level loggers. In addition, as the channel slope is the gradient driving flow, there is a consistent relationship between the depth of water in the channel and its flow velocity. This stage-velocity relationship may either be estimated using Manning's equation for fluid velocity (v):

$$v = K/n\ R^{2/3} S^{1/2} \qquad [m/s]$$

Where:

v = velocity

K = 1.00 [SI]

n = Manning's roughness coefficient

R = hydraulic radius [m] = A/P_w

A = cross-sectional area of flow [m^2]

P_w = wetted perimeter [m]

S = channel slope (%)

or it may be empirically established with measurements during discharge events. Then total flow volume (Q) is simply Q = vA.

LLNL plans to empirically develop the stage-velocity relationship for the two storm drain effluents on the Livermore site. LLNL will then use this relationship to test the application of Manning's equation for future issues, such as estimating upstream flow on site.

7.2.8.1.4 *Mass Estimation*: Once the total volume of water flowing off site during each storm is known, then average mass loadings may be calculated. Assuming that the concentration of a water quality constituent measured during a storm represents an average value for that event, it may be used to calculate average mass. Mass (M) is the concentration (C_x) times the flow volume (V), or M= C_xV. This mass can be calculated for some given period of time (e.g., days, weeks, or months). This approach allows LLNL to estimate the total amount of a water quality constituent of concern that flows off site in storm water.

7.3 Construction Storm Water

7.3.1 Rationale and Design Criteria

7.3.1.1 Regulatory Drivers

The regulatory drivers for construction storm water monitoring are the same as those for storm water monitoring (see **Section 7.2.1.1**); however, a different permit regulates construction storm water monitoring. The California State Water Resources Control Board (SWRCB) issued *Waste Discharge Requirements (WDR) 99-08-DWQ for Discharges of Storm Water Associated with Construction Activities* (General NPDES Permit No. CAS000002) in 1999 (SWRCB 1999). Only construction projects that disturb an area of five acres or more are required to comply with Order 99-08-DWQ. The WDR satisfies both the federal NPDES regulations and the California Porter-Cologne Water Quality Control Act requirements.

In 2001, the SWRCB adopted Resolution 2001-046 (SWRCB 2001) amending WDR 99-08-DWQ to require storm water sampling and analysis when the conditions specified in Resolution 2001-046 are triggered. Prior to 2001, the monitoring requirements of WDR 99-08-DWQ were limited to inspections and visual observations performed by construction site personnel.

7.3.1.2 Construction Storm Water Monitoring Objectives

The objective of the construction storm water sampling and analysis program is to determine whether storm water runoff from a permitted construction site is being polluted by contact with construction materials. Resolution 2001-046 requires sampling and analysis of runoff in two instances:

- When construction site storm water is directly discharged into a water body that is on the 303d list (list of waters declared to be "impaired" under section 303d of the Clean Water Act) as being impaired for sediment, silt, or turbidity.
- When nonvisible pollutants might contaminate construction site runoff.

The first condition does not currently apply to LLNL construction projects because runoff from projects located at both Site 300 and the Livermore site is not directly discharged into a water body listed as impaired.

LLNL must evaluate each of its permitted construction projects to determine if sampling and analysis are required under the second condition. This evaluation is documented in each individual construction project's Storm Water Pollution Prevention Plan (SWPPP).

7.3.1.3 Sources and Analytes for Construction Storm Water

Nonvisible pollutants are materials that could contaminate storm water runoff that is discharged from the construction site, but are not visually detectable in the runoff. The source of these pollutants include

- Previously existing contaminants that may be mobilized by construction operations
- Construction phase materials including
  - Materials used on the construction site in manner that exposes them to storm water, e.g., soil amendments, such as gypsum, that are widely applied on the site
  - Materials stored on the construction site in a manner that exposes them to storm water

As required by WDR 99-08-DWQ (Sections A.5.b. and A.5.c), each individual construction SWPPP must identify known previously existing contamination and materials used and stored on a construction site that have the potential to pollute storm water. The SWPPPs are also required to identify the best management practices (BMPs) that will be employed on the project to prevent pollution of storm water. Potential sources of construction storm water pollution are those materials or previously existing contaminates that are not isolated from exposure to storm water runoff.

7.3.1.3.1 Evaluation of Previously Existing Contaminated Sources at LLNL Construction Projects: The United States Environmental Protection Agency (EPA) placed the two LLNL sites on the National Priorities List under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA). Because of this status as Superfund sites, there is a potential that construction activities may disturb contaminated soil. Therefore, preconstruction soil evaluations are conducted to provide advance information on whether or not soil from the project areas contains contaminants. These preconstruction soil evaluations form the basis of the determination of whether there are previously existing contaminants at permitted construction projects that will trigger storm water sampling and analysis.

Data from preconstruction soil sampling are compared with previously established background concentrations for both LLNL sites. Additionally, the soil reuse criteria for the Livermore site are also used. Soil reuse criteria were established for constituents that either do not occur naturally or are slightly elevated above the background concentrations. Reuse criteria currently in use at Livermore site were developed using the Designated Level Methodology (Marshack 2000) and were approved by the San Francisco Bay RWQCB (SFBRWQCB 1994). The Designated Level Methodology is implemented as follows:

- If evaluations determine that soil constituent concentrations on the construction site are consistent with background, then the soil constituents are not considered potential sources of storm water pollutants.
- If evaluations determine that soil constituent concentrations on the construction site are above background but below approved reuse concentrations or if there is no background value, then the soil will be further evaluated to determine whether the concentrations exceed established appropriate water quality objectives for aquatic life protection. If soil constituent concentrations exceed the appropriate water quality objectives for aquatic life protection, then the soil constituent(s) are considered potential sources of storm water pollutants. If soil constituent concentrations do not exceed the appropriate water quality objectives for aquatic life protection, then the soil constituent(s) are not considered potential sources of storm water pollutants.

- If evaluations determine that soil constituent concentrations on the construction site are above reuse concentrations, then the soil constituent(s) are considered potential sources of storm water pollutants.

This source evaluation takes into account the location of the potentially contaminated soil (e.g., depth), and its potential for exposure to storm water runoff by the construction activity.

The results of the evaluation to determine whether pre-existing contaminants are present on any specific LLNL construction project are documented in the project SWPPP.

7.3.1.3.2 *Evaluation of Construction Phase Contaminate Sources at LLNL Construction Projects:* Each specific construction SWPPP identifies the materials and activities planned, the potential pollutants (including whether this pollutant will be visually detectable), and the BMPs planned to prevent exposure of the potential pollutants to storm water runoff.

If evaluations determine that a material or activity has the potential to pollute storm water and cannot be isolated, then the contaminant(s) generated by that material or activity are considered potential sources of storm water pollutants.

In general, LLNL construction specifications and standards require that all materials that have the potential to pollute storm water be isolated from storm water either by BMPs that cover the storage or activity or by BMPs that contain the runoff from the storage or activity.

7.3.1.4 Collection Methods for Construction Storm Water Samples

Grab sampling or field measurements (e.g., pH with meters) are used for all construction storm water compliance monitoring. Sample handling and collection techniques used are similar to those for other environmental water sampling, as noted in procedure EMP-W-S. Standard chain of custody and field tracking form (FTF) procedures (EMP-QA-DM) are employed to track samples and to document field conditions that may affect the samples.

7.3.2 Extent and Frequency of Construction Storm Water Monitoring and Measurements

The frequency of sampling for nonvisible pollutants is determined based on the exposure of pollutant sources. Runoff needs to be sampled only when there is exposure of a pollutant source to storm water when the runoff enters a storm drain or surface water.

Sampling and analysis schedules for each construction project vary and are established in the individual project SWPPP. Factors that influence the collection of samples are rain events that produce runoff, exposure of materials that could result in the discharge of nonvisible pollutants to runoff, or the failure of a BMP designed to prevent exposure, such as the overflow of

secondary containment. Sampling for nonvisibly detectable pollutants is required under two conditions:

- Visual inspections, currently required before, during, and after storm events, indicate that there has been a breach, malfunction, leakage, or spill from a BMP that could result in the discharge of pollutants in storm water and the pollutants would not be visually detectable.
- Storm water comes into contact with soil amendments, or other exposed materials, or pre-existing contamination that is not visually detectable and is discharged off the construction site into the storm drainage system or surface waters.

Routine inspections of the construction site are required by WDR 99-08-DWQ before a predicted rain event, during rain events lasting more than 24 hours, and following rain events. Observations of failed BMPs during these inspections trigger the collection of storm water samples for analysis.

In cases where a known pre-existing contaminant is present in the construction site soil, or where a material, such as a soil amendment, will be used and exposure cannot be prevented, sampling frequencies can be established at the outset of a project to screen for the contaminant in runoff.

Sampling locations must be identified that provide information on both the runoff quality that is affected by material storage, pre-exisiting contamination, or other exposed potential pollutants, and the background runoff quality (i.e., an uncontaminated sample). Material storage may be confined to a small area of the project while pre-existing contamination or exposed materials, such as soil amendments, may be widely spread throughout the construction site. For this reason, the sampling locations identified for these two types of potential pollutants may be different.

Samples are collected at the locations identified in the specific project SWPPP or at the areas identified by visual inspections where there has been a BMP failure or breach.

A location that is not affected by material storage activities or by runoff from material storage areas should be selected as a background or reference sampling location for collecting the uncontaminated runoff sample. For a widely spread potential contaminant, sampling locations may need to be established at the perimeter of the construction site, where storm water enters (unaffected by the construction activities) and where storm water leaves (affected by construction activities) the site. The SWPPP must describe the sampling procedure, the location, and the rationale for selecting the sampling locations.

7.3.3 Procedures for Laboratory Analysis

Laboratory analyses are conducted by a laboratory currently under contract with LLNL that is accredited by the California Department of Health Services Environmental Laboratory Accreditation Program (ELAP). Analyses are conducted in accordance with 40 CFR Part 136 (CFR 1984).

Contract laboratories are required to follow all LLNL sample-tracking procedures (contained in procedure EMP-QA-DM) when handling LLNL samples. LLNL must be notified of any problems immediately, including broken or damaged containers, discrepancies between sample bottles and/or labels and the chain-of-custody (CoC) form, broken seals on sample coolers, or any other compromises to the integrity of a sample. Identified problems must also be described in the case narrative that accompanies the final data report. Contract laboratories must hold samples for a minimum of 30 days after the final report is generated and verified by LLNL. The contract laboratory must dispose of all unused sample portions in accordance with written procedures.

At a minimum, LLNL requires ongoing calibration checks from the contract laboratory for each batch. A batch is defined as less than or equal to 20 samples. Initial calibration is available upon request. A summary of calibration sample results for each sample must be provided with the analytical data report. This summary must include the continuing calibration batch number, date and time of analysis, instrument ID number, analyst ID number, method number, theoretical result, actual result, percent recovery, and acceptable range. In addition, the laboratory must maintain initial instrument calibration data and make the data available upon request. The EPD Assurance Manager maintains on file copies of each laboratory's standard operating procedures for performing and tracking calibration activities. Each laboratory's calibration program and its implementation are verified at the annual facility audit.

7.3.4 QA Requirements for Construction Storm Water

To ensure that all quality assurance (QA) and quality control (QC) objectives are met, all construction storm water runoff samples are collected in accordance with written procedures by trained sampling technicians. Field quality control samples are determined for each construction project, based upon the potential sources. Field duplicates are expected to be collected and submitted for analysis for all projects requiring sampling. Field blanks and spikes are not expected to be used.

7.3.5 Program Implementation Procedures

Each specific construction SWPPP identifies the sampling and analysis strategy for each construction project.

Standard field sampling protocols are followed and are contained in procedure EMP-W-S and the procedure supplement EMP-WSS-CR. Bottle requirements are contained in procedure EMP-QA-BOT. Hazards associated with this network are identified, along with their controls, in EMP-HAZ-SUP.

Sample locations are identified in accordance with procedure EMP-QA-DM. Sample locations are tracked in the TSG locations database.

Laboratory results are checked by the Data Management Team (DMT) staff, who ensure that the chain of custody is intact, all signatures are present, and the data results are complete. DMT staff then key all QA/QC samples with the original samples from the same locations.

All required permit documentation, such as calibration and monitoring records, is recorded on FTFs archived by DMT per procedure EMP-QA-DM.

7.3.6 Action Levels

There are no numeric effluent limitations for construction storm water runoff. However, the purpose of the sampling and analysis is to evaluate the BMPs and help determine if storm water runoff is being contaminated by construction activities. Therefore, when sample test results indicate that the construction site's storm water discharges significantly exceed the background concentrations, two actions are required:

- Report the results to the Regional Board in accordance with section B.3 (Receiving Water Limitations) of WDR 99-08-DWQ.
- Evaluate the BMPs to determine what is causing the difference between the runoff and background concentrations.

The evaluation needs to identify the source and possible solutions to correct the problem. These solutions may include repairing the existing BMPs, evaluating alternative BMPs that could be implemented, and/or implementing additional BMPs (cover and/or containment) that further limit or eliminate contact between storm water and nonvisible pollutant sources at the construction site. Where contact cannot be reduced or eliminated, storm water that has come in contact with the nonvisible pollutant source should be retained on the construction site and not allowed to be discharged to the storm drainage system or a water body.

Additional samples should be taken during the next runoff event after corrective actions are implemented to demonstrate and document that the problems have been corrected.

If sampling and analysis during subsequent storm events show that there is still a problem, then repeat the steps above until the analytical results of upstream and downstream samples are relatively comparable.

7.3.7 Preparation and Disposition of Construction Storm Water Reports

Results of field measurements and laboratory analyses must be filed in the SWPPP, which is required to be kept on the project site until the Notice of Termination is filed and approved by the appropriate RWQCB. Waste Discharge Requirement 99-08-DWQ requires that the records of all inspections, compliance certifications, and noncompliance reporting must be retained for a period of at least three years from the date generated or after project completion.

Each year LLNL prepares an annual certification of compliance for each permitted construction project. The sampling and analysis data are included in this report. The data are also included in the annual LLNL *Environmental Report*.

7.3.8 Future Plans

The 303d list of impaired water bodies is updated by the SWRCB every two years. These updates are monitored to determine if sediment monitoring described in **Section 7.3.1.2** is required in the future.

7.4 Rainwater

Rainwater is collected in stainless-steel buckets mounted at fixed locations within the Livermore site, in the Livermore Valley, and at Site 300. Tritium measurements of rainwater samples are used to measure the effects, if any, of LLNL operations on rainwater in the Livermore Valley.

7.4.1 Rationale and Design Criteria

7.4.1.1 Regulatory Drivers

The regulatory driver for rainwater monitoring is Order 5400.1 (DOE 1988). In addition to the monitoring requirements noted in **Section 7.2.1.1**, Order 5400.1 states, "Representative meteorological data are required at DOE facilities to support environmental monitoring activities. This information is essential to characterize atmospheric transport and diffusion conditions in the vicinity of the DOE facility and to represent other meteorological conditions (e.g., precipitation, temperature, and atmospheric moisture) that are important to environmental surveillance activities such as air quality and radiation monitoring" (DOE 1988).

7.4.1.2 Monitoring Objectives for Rain

Although no state or federal laws require rain monitoring, the same DOE Order-driven objectives (DOE 1988; DOE, 1991) for environmental monitoring apply to rainwater monitoring (see **Section 7.2.1.2**).

7.4.1.3 Collection Methods for Rainwater Samples

Samples for tritium analysis are collected directly from stainless steel buckets into 250-mL glass bottles with Teflon-lined lids. This collection method follows procedures EMP-W-S, EMP-QA-SL, and EMP-QA-DM.

7.4.2 Extent and Frequency of Rainwater Monitoring and Measurements

7.4.2.1 Routine Monitoring Requirements for Livermore Site

Rainfall samples are collected in the Livermore Valley whenever storm water runoff samples are collected, or at least four times a year. Rainwater from storms not needed for monitoring purposes is regularly discarded.

Livermore Site. Tritium activity in air-moisture and, thence, in rainwater in the Livermore Valley, results from atmospheric emissions of tritiated water vapor (HTO) from stacks at LLNL's Tritium Facility (Building 331) and, prior to 1996, the Sandia National Laboratory/ California's (Sandia/CA) former Tritium Research Laboratory, where experiments involving tritium are conducted. Historically, rainwater that could be impacted by these two facilities has been monitored. Rainwater sampling locations at the Livermore Site and in the surrounding Livermore Valley are shown in **Figure 7-3**.

Rainwater sampling is conducted adjacent to air-moisture sampling locations wherever possible. Air-moisture is rapidly entrained and precipitated locally during rain events. Co-location of rain water and air-moisture sampling allows for comparison of results for these media. Air-moisture sampling locations have been sited based on knowledge of HTO source locations and wind directions in the Livermore Valley (see Chapter 3). Winds measured during rain events prevail from the southwest but are occasionally recorded from the northeast. Winds from the northwest and southeast are rare during rain events. A typical annual wind rose for LLNL and vicinity is shown in **Figure 7-4.**

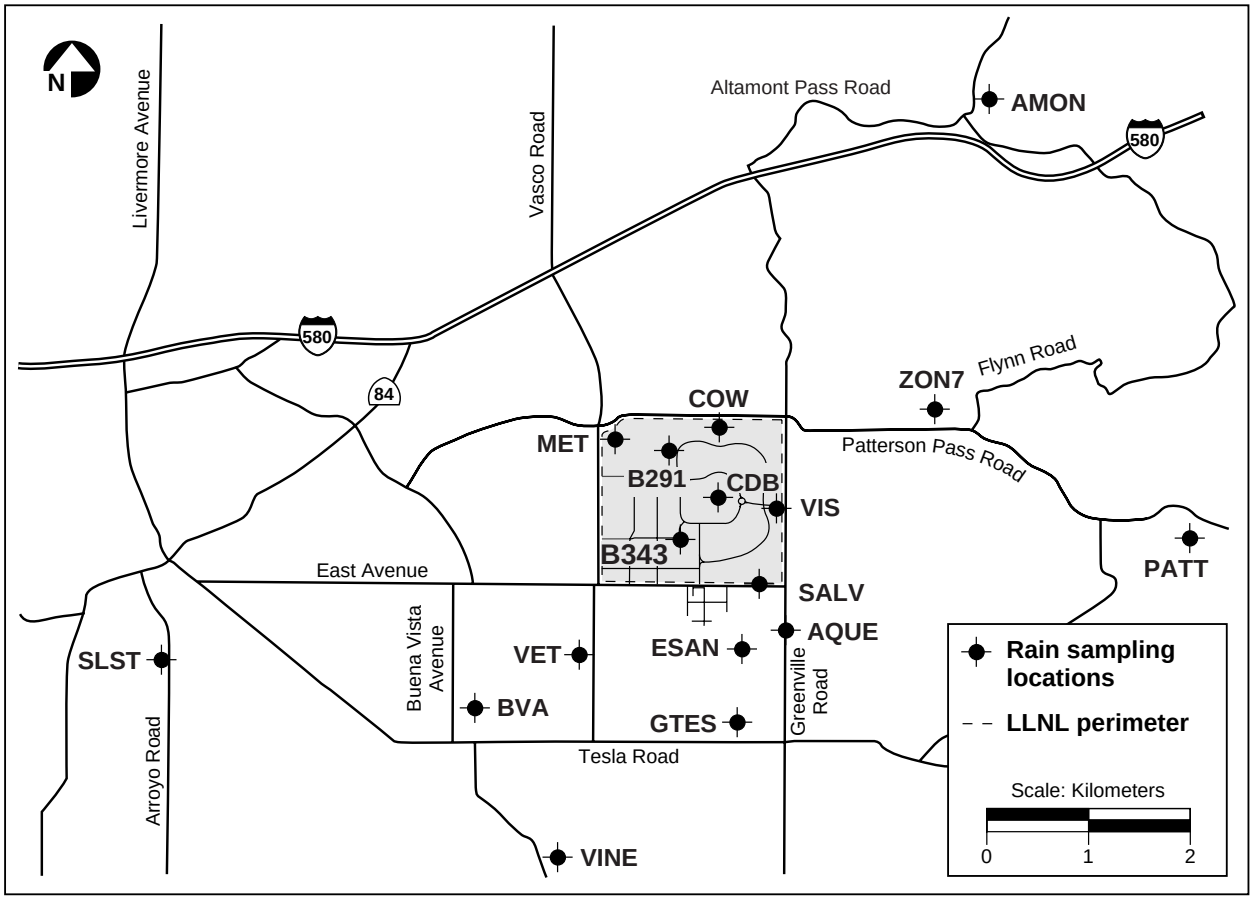

Figure 7-3. Rainwater sampling locations, Livermore site and Livermore Valley

Although total HTO emissions have declined significantly over the past decade, as shown in **Figure 7-5**, emissions continue from Building 331 from ongoing operations. Because Building 331 remains a source of HTO in local rainwater, and because new tritium experiments may be initiated there in the future, most of the original rainwater sampling locations continue in use (**Figure 7-3**). Several distant rainwater sampling locations, historically known as PARK and FCC, have been discontinued, because they are no longer needed to determine background tritium activity in Livermore Valley rainwater. Historical tritium activity measurements demonstrate that tritium activity in rainwater decreases exponentially with distance from Building 331, reaching background level at distances of 3 km or more from the Livermore site.

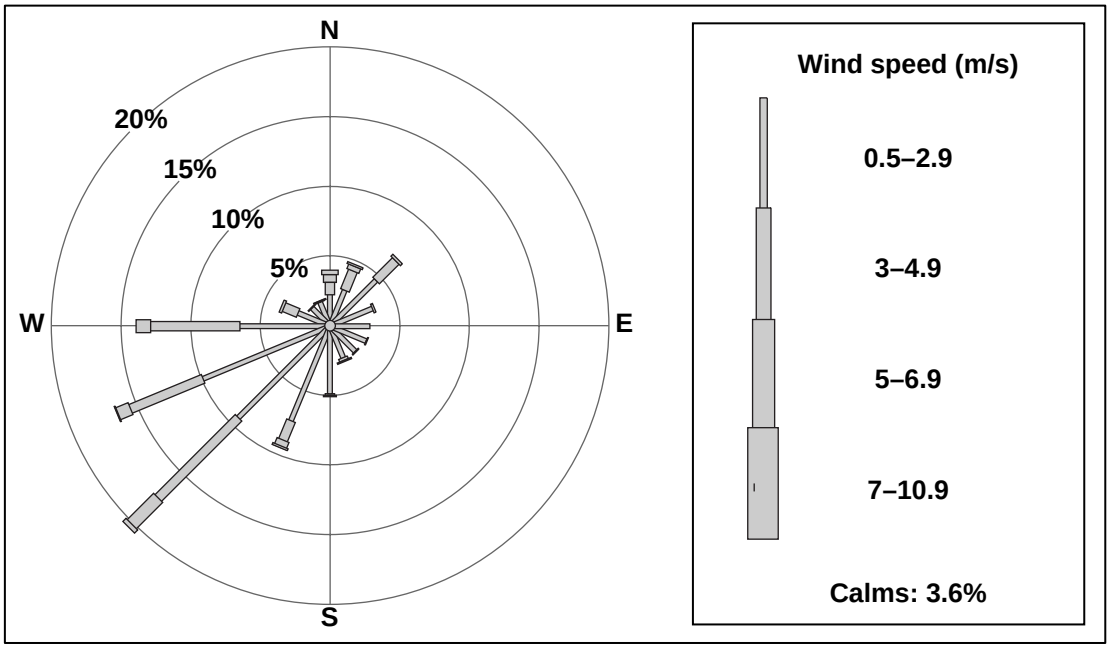

Figure 7-4. Typical LLNL and vicinity annual wind rose (year 2000)

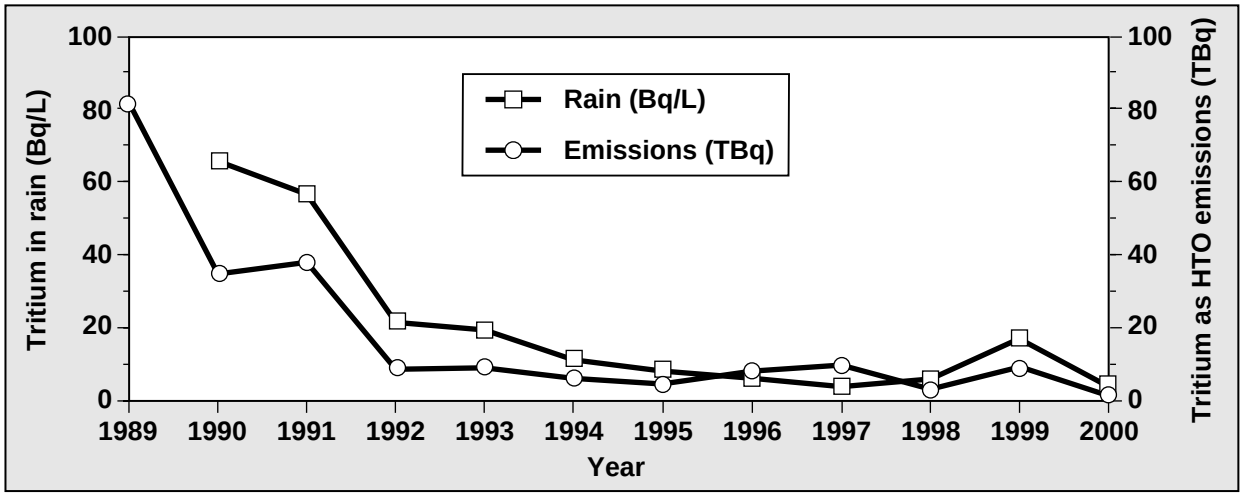

Figure 7-5. Annual HTO emissions and median tritium activity in LLNL rainwater

7.4.2.2 Routine Monitoring Requirements for Site 300

Minute quantities of tritium are occasionally used in open-air explosive experiments at Site 300. Up to 1988, HTO-contaminated firing table gravel was removed and placed in waste pits on site that are now covered landfills. Since 1988, firing table gravel has been containerized and

shipped off site to a disposal facility in Nevada. For the past 30 years, rainwater samples have been collected from a central location within the test site (COMP) near the meteorological tower. From the beginning of monitoring there, measurements of tritium activity in rainwater samples have shown only background levels, averaging about 4 Bq/L (100 pCi/L). However, to ensure that tritium activity in rainwater at Site 300 was being adequately monitored, two rainwater sampling locations were added in 1999; one onsite to the north (TNK5) and one offsite to the east (PRIM) of location COMP (**Figure 7-2**). Their placement was based on knowledge of potential HTO source locations and prevailing wind direction from the south-southwest, as shown in **Figure 7-6**. Since 1999, no tritium activity above background has been measured in any rainwater sample from any of the three monitoring locations at Site 300.

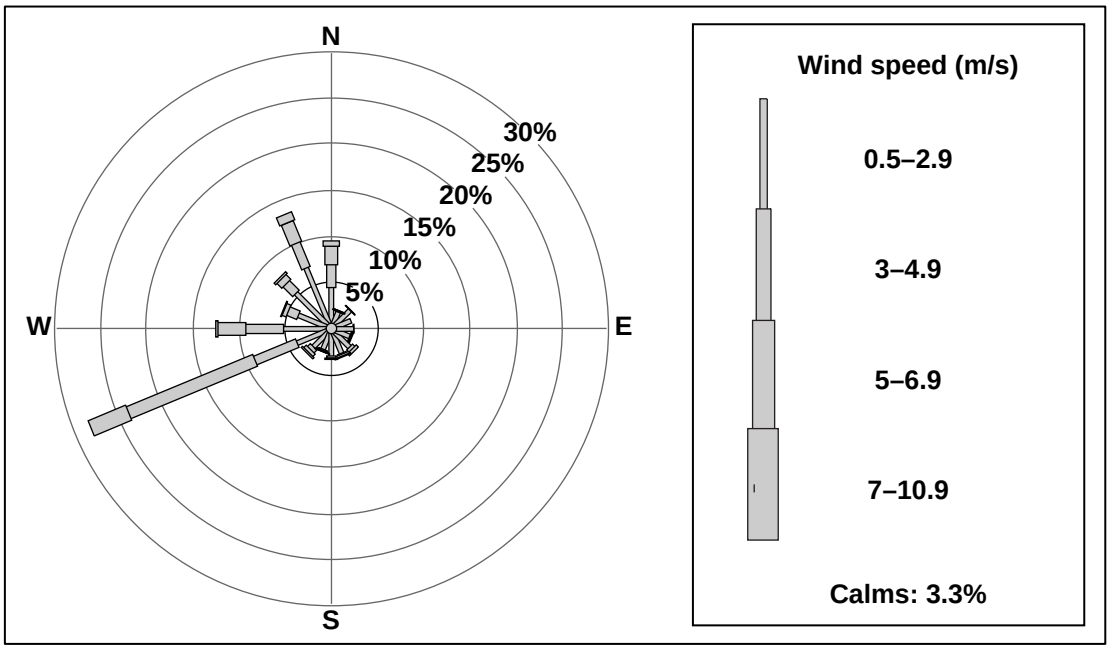

Figure 7-6. Typical Site 300 annual wind rose (year 2000)

7.4.3 Procedures for Laboratory Analysis

Tritium analyses are performed off site by contract analytical laboratories using a liquid scintillation counting method (EPA Method 906). Contracted data quality objectives (DQOs) specify a practical quantitation limit (PQL) of 100 pCi/L for aqueous tritium activity measurement.

7.4.4 QA Sampling and Requirements for Rainwater

For each rain event sampled, a field duplicate is collected from a randomly selected location at the Livermore site and at Site 300.

7.4.5 Program Implementation Procedures

All rainwater sampling is conducted by LLNL technical staff according to procedure EMP-W-S, and samples are submitted for analyses using sample control and documentation procedures (EMP-QA-SL and EMP-QA-SD). Sample bottle requirements for tritiated water analysis are specified in procedure EMP-QA-BOT.

7.4.6 Action Levels

There are no numeric criteria directly applicable to tritium concentrations in rainwater. Rainwater tritium concentrations are, however, routinely compared with the drinking water MCL for tritium (740 Bq/L), and are generally less than 10% of the MCL. If rainwater tritium concentrations were to approach the MCL or increase dramatically, a detailed investigation of the cause of the high result or results would ensue. A detailed investigation may include elements such as

- Management notification.
- Re-analysis of the samples.
- Analysis of subsequent storm events. (Routinely, four storm events are sampled each year. During a detailed investigation, the storm event immediately following a finding may also be sampled to confirm or negate the concentration being investigated.)
- Source investigation. (Results are compared with findings from other monitoring networks [e.g., air], and LLNL activities that may have contributed to the result are investigated.)
- Expanded monitoring (more locations).
- Increased monitoring frequency (i.e., more storm events are sampled per wet season).

7.4.7 Preparation and Disposition of Rainwater Reports

Rainwater monitoring results are summarized and discussed annually in the surface water monitoring chapter of the annual *Environmental Report* (e.g., Biermann et al. 2000). The *Environmental Report* summarizes the rainwater tritium activity data, discusses trends, and

includes a brief statement regarding the impact, if any, of LLNL operations on the local environment.

7.4.8 Future Plans

We anticipate adding one or more rainwater sampling locations along the northeastern perimeter of the Livermore site to monitor the Decontamination and Waste Treatment Facility (DWTF) and the National Ignition Facility (NIF), which are being constructed within the northeast quadrant of the Livermore site.

7.5 Drainage Retention Basin

7.5.1 Rationale and Design Criteria

The 53-megaliter (ML) Drainage Retention Basin (DRB), which covers 1.6 hectares (see **Figure 7-7**), was lined as part of Livermore site remediation activities. Remediation action studies indicated that infiltration of storm water from the basin caused increased dispersal of groundwater contaminants beneath the DRB. Basin lining to halt infiltration was completed in March 1992. LLNL adopted the *Drainage Retention Basin Management Plan* (Limnion Corporation 1991) as the protocol to maintain high water quality in the DRB, and monitoring began in 1992.

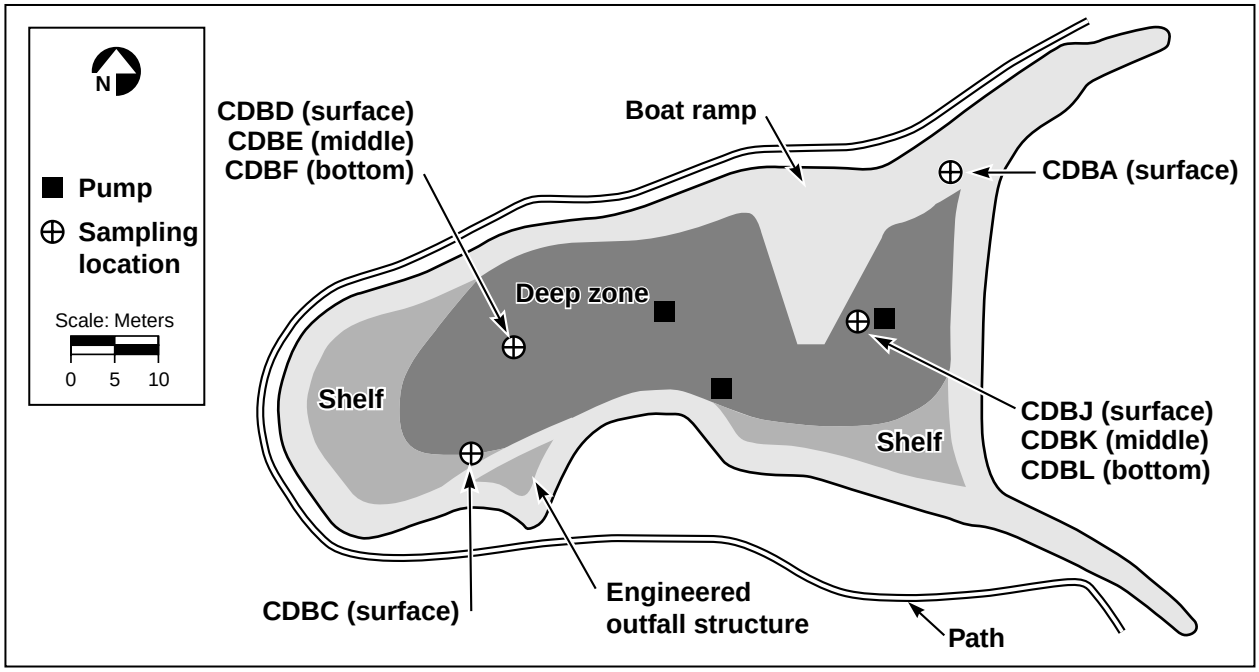

Figure 7-7. Sampling locations within the Drainage Retention Basin (DRB)

7.5.1.1 Regulatory Drivers

DRB Management Plan water quality recommendations drive the DRB monitoring program, and the San Francisco Bay RWQCB prescribes discharge monitoring requirements.

Water quality monitoring verifies compliance with the appropriate, relevant, and applicable requirements (ARARs) identified in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) *Record of Decision (ROD) of the Lawrence Livermore National Laboratory, Livermore Site* (LLNL 1992).

The DRB discharges into LLNL's storm drainage system and eventually to Arroyo Las Positas, a navigable water of the United States. Discharges are governed by ARARs derived from the Federal Clean Water Act, Federal and State Safe Drinking Water Acts, and the Porter-Cologne Water Quality Control Act.

Because the DRB was constructed as a CERCLA-directed remediation, its discharges are regulated like those of treated groundwater from other LLNL CERCLA cleanup activities. A Federal Facility Agreement (FFA) among the San Francisco Bay RWQCB, DTSC, EPA, and DOE is in place, requiring that all ARARs specified in the CERCLA ROD be observed. Limits for discharging treated groundwater into the storm drainage system, including the DRB, are established by the ROD (**Table 7-3**) as amended by the *Explanation of Significant Differences for Metals Discharge Limits at the Lawrence Livermore National Laboratory, Livermore Site* (Berg et al. 1997). Discharges from the DRB exceeding these limits constitute CERCLA noncompliance. The management objectives and management action levels (MALs) set forth in **Table 7-4** are identified in the *DRB Management Plan*.

7.5.1.2 Monitoring Objectives for the Drainage Retention Basin

The DRB monitoring program has two primary objectives:

- To ensure that concentrations of metals, organics, physical properties, and toxicity remain within the discharge limits identified in the amended CERCLA ROD
- To provide the data used in making management decisions regarding DRB operation

Comprehensive DRB management goals are listed below:

- Overall water quality in the basin and its outflow waters shall be maintained within the discharge limitations stipulated in LLNL's CERCLA ROD and all amendments.

Table 7-3. Treated groundwater and DRB discharge analytes for sampling locations CDBX and WPDC, and discharge limits in the amended CERCLA ROD applied at CDBX

Constituent	Location	Frequency[a]	Discharge limits	
			Dry season[b]	Wet season[c]
General minerals				
Total alkalinity	CDBX	A	Not applicable	Not applicable
Nitrate (as N)	CDBX	A	Not applicable	Not applicable
Nitrite (as N)	CDBX	A	Not applicable	Not applicable
Metals (µg/L)				
Antimony	CDBX, WPDC	A & B	6	Not applicable
Arsenic	CDBX, WPDC	A & B	50	10
Beryllium	CDBX, WPDC	A & B	4	Not applicable
Boron	CDBX, WPDC	A & B	Not applicable	Not applicable
Cadmium	CDBX, WPDC	A & B	5	2.2
Chromium (total)	CDBX, WPDC	A & B	50	Not applicable
Chromium (VI)	CDBX, WPDC	A & B	Not applicable	22
Copper	CDBX, WPDC	A & B	1300	23.6
Iron	CDBX, WPDC	A & B	Not applicable	Not applicable
Lead	CDBX, WPDC	A & B	15	6.4
Manganese	CDBX, WPDC	A & B	Not applicable	Not applicable
Mercury	CDBX, WPDC	A & B	2	2
Nickel	CDBX, WPDC	A & B	100	320
Selenium	CDBX, WPDC	A & B	50	10
Silver	CDBX, WPDC	A & B	100	8.2
Thallium	CDBX, WPDC	A & B	2	Not applicable
Zinc	CDBX, WPDC	A & B	Not applicable	220
Organics (µg/L)				
Herbicides (507, 547, 632)	CDBX	A	Not applicable	Not applicable
Volatile organic compounds (EPA Method 601 only)	CDBX	A	5	5
Tetrachloroethene	CDBX	A	4	4
Vinyl chloride	CDBX	A	2	2
Chemical oxygen demand	CDBX	A	Not applicable	Not applicable
Total organic carbon	CDBX	A	Not applicable	Not applicable
Polychlorinated biphenyls	CDBX, WPDC	A & B	Not applicable	Not applicable

(continued)

Table 7-3. Treated groundwater and DRB discharge analytes for sampling locations CDBX and WPDC, and discharge limits in the amended CERCLA ROD applied at CDBX (concluded)

Constituent	Location	Frequency[a]	Discharge limits	
			Dry season[b]	Wet season[c]
Physical				
Conductivity	CDBX, WPDC	A	Not applicable	Not applicable
pH (units)	CDBX, WPDC	A & B	6.5–8.5	6.5–8.5
Total suspended solids	CDBX, WPDC	A & B	Not applicable	Not applicable
Total dissolved solids	CDBX, WPDC	A	Not applicable	Not applicable
Turbidity (NTU)[d]	CDBX, WPDC	A & B	<0.914	<0.914
Toxicity				
Aquatic survival bioassay (96 hours)	CDBX, WPDC	A & B	90% survival median, 90 percentile value of not less than 70% survival	
Radiological (pCi/L)				
Alpha	CDBX	—	15	15
Beta	CDBX	—	50	50
Tritium	CDBX	—	20,000	20,000

Source: LLNL 1992

a A = Monitoring occurs at the first DRB discharge of the wet season and at one or more additional discharges associated with storm water runoff monitoring. Toxicity testing is required only on the first release.

B = Monitoring occurs at each dry season release. For purposes of discharge sampling, the dry season is defined to occur from June 1 through September 30.

b Dry season limits apply to CDBX from April 1 to November 30.

c Wet season limits apply to CDBX from December 1 to March 31.

d Nephelometric turbidity units

- Turbidity shall be maintained below a level that would limit growth of aquatic vegetation.
- The basin shall be maintained in an aesthetically pleasing condition (i.e., algae blooms and trash accumulations shall be avoided).
- Use by wildlife will be encouraged, consistent with the view that the basin serves as open space, wetland buffer, and open water habitat.
- Establishment of domesticated waterfowl populations will be discouraged as their presence can be detrimental to wild birds, and excessive resident duck and goose populations can significantly contribute to water quality degradation.

Table 7-4 DRB surface water quality constituents, management objectives, and management action levels.

Constituent	Location[a]	Frequency[b]	Management objectives		Management action levels	
			Dry season[c]	Wet season[d]	Dry season[c]	Wet season[d]
Field measurements						
Dissolved oxygen (mg/L)	CDBA, CDBC, CDBD, CDBE, CDBF, CDBJ, CDBK, CDBL	Weekly	Greater than or equal to 90% saturation		Not less than 5 or <80% saturation	
Temperature (°C)	CDBA, CDBC, CDBD, CDBE, CDBF, CDBJ, CDBK, CDBL	Weekly	Varies seasonally	Varies seasonally	<15 and >26	<15 and >26
Turbidity (ms)	CDBE	Weekly	>1.52	>1.52	<0.914	<0.914
General minerals and nutrients						
Total alkalinity (mg/L)	CDBE	Monthly	>75	>75	<50	<50
pH (units)	CDBE	Monthly	6.5 to 8.5	6.5 to 8.5	<6.0 and >9.0	<6.0 and >9.0
Total suspended solids (mg/L)	CDBE	Monthly	Not applicable	Not applicable	Not applicable	Not applicable
Total dissolved solids (mg/L)	CDBE	Monthly	<250	<250	>360	>360
Conductivity (µS/cm)	CDBE	Monthly	<900	<900	900	900
Nitrate (mg/L) as N	CDBE	Monthly	<0.2	<0.2	0.2	0.2
Nitrite (mg/L) as N	CDBE	Monthly	<0.2	<0.2	0.2	0.2
Ammonia nitrogen (mg/L)	CDBE	Monthly	<0.025	<0.025	0.1	0.1
Phosphate as P (mg/L)	CDBE	Monthly	<0.02	<0.02	0.02	0.02
Microbiological						
Total coliform (MPN/0.1L)	CDBE	Quarterly	<240	<240	>5000	>5000
Fecal coliform (MPN/0.1L)	CDBE	Quarterly	<200	<200	>400	>400
Metals (µg/L)						
Antimony	CDBE	Semiannual	<6	Not applicable	6	Not applicable
Arsenic	CDBE	Semiannual	<50	<10	50	10
Beryllium	CDBE	Semiannual	<4	Not applicable	4	Not applicable
Boron	CDBE	Semiannual	Not applicable	Not applicable	Not applicable	Not applicable
Chromium (total)	CDBE	Semiannual	<50	Not applicable	50	Not applicable
Chromium(VI)	CDBE	Semiannual	Not applicable	<22	Not applicable	22
Copper	CDBE	Semiannual	<1300	<23.6	1300	23.6
Iron	CDBE	Semiannual	Not applicable	Not applicable	Not applicable	Not applicable

(continued)

Table 7-4. DRB surface water quality constituents, management objectives, and management action levels (concluded)

Constituent	Location[a]	Frequency[b]	Management objectives		Management action levels	
			Dry season[c]	Wet season[d]	Dry season[c]	Wet season[d]
Lead	CDBE	Semiannual	<15	<6.4	15	6.4
Manganese	CDBE	Semiannual	Not applicable	Not applicable	Not applicable	Not applicable
Mercury	CDBE	Semiannual	<2	<2	2	2
Nickel	CDBE	Semiannual	<320	<100	320	100
Selenium	CDBE	Semiannual	<50	<10	50	10
Silver	CDBE	Semiannual	<100	<8.2	100	8.2
Thallium	CDBE	Semiannual	<2	Not applicable	2	Not applicable
Zinc	CDBE	Semiannual	Not applicable	<220	Not applicable	220
Organics (µg/L)						
Chlorophyll A (mg/L)	CDBE	Monthly	<10	<10	10	10
Chemical oxygen demand[e] (mg/L)	CDBE	Quarterly	<20	<20	20	20
Oil and grease (mg/L)	CDBE	Quarterly	<10	<10	15	15
Total organic carbon (mg/L)	CDBE	Semiannual	Not applicable	Not applicable	Not applicable	Not applicable
Total volatile organic compounds (EPA Method 601)	CDBE	Semiannual	>5	>5	5	5
Tetrachloroethene	CDBE	Semiannual	<4	<4	4	4
Vinyl chloride	CDBE	Semiannual	<2	<2	2	2
Herbicides (EPA Methods 507, 547, and 632)	CDBE	Semiannual	Not applicable	Not applicable	Not applicable	Not applicable
Polychlorinated biphenyls	CDBE	Semiannual	Not applicable	Not applicable	Not applicable	Not applicable
Radiological (pCi/L)						
Gross alpha	CDBE	Semiannual	<15	<15	15	15
Gross beta	CDBE	Semiannual	<50	<50	50	50
Tritium	CDBE	Semiannual	<20,000	<20,000	20,000	20,000
Toxicity						
Acute fish bioassay (96-hour survival)	CDBE	Annual	90% survival median; 90 percentile value of not less than 70% survival			
Chronic toxicity (3 species)	CDBE	Annual	Not applicable	Not applicable	Not applicable	Not applicable

a DRB sampling locations are shown on **Figure 7-7**.

b Frequencies shown are those required in the *DRB Management Plan* and Galles, December 9. 1997, letter to the SFBRWQCB (Galles 1997). These may be varied as required by special water quality studies.

c Dry season is from April 1 to November 30.

d Wet season is from December 1 to March 31.

e The *DRB Management Plan* calls for *biochemical oxygen demand*. *Chemical oxygen demand* is used here in place of *biochemical oxygen demand*.

- Appropriate mosquito abatement and other vector control measures will be instituted.
- Maintenance activities should be minimally intrusive.
- Maintenance activities should be minimally disruptive to fish and wildlife, in addition to being simple and economical.

The *DRB Management Plan* proposes a long-term biological monitoring and maintenance program to prevent water quality problems (such as sedimentation, algae blooms, anaerobic conditions, and objectionable odor). Proposed maintenance measures include bioremediation and reduction of nutrient loading. Water quality management objectives are maintained through:

- Removal of sediment in storm water influent by the use of sedimentation basins
- Management of upstream watershed activities
- Nutrient and pollutant removal and erosion control using plants
- Oxygen addition by means of recirculation pumps

7.5.1.3 Drainage Retention Basin Sources and Analytes and Indicators

The *DRB Management Plan* identifies two sources of water for filling and maintaining the DRB:

- Water generated from groundwater treatment units that discharge to the DRB through the existing storm water drainage system or pipelines (the primary source)
- Storm water runoff (drainage from approximately one-fourth of the Livermore site) (a secondary source)

From 1993 through 1997, storm water runoff was the primary source of water to the DRB, and the treated groundwater contribution was only minor. Dry season discharges to the DRB have become dominated by treated groundwater discharges as more treatment facilities began discharging to the DRB. Storm water will continue to be the major source water during the wet season.

Potential pollutant sources discharging to the DRB in addition to the two main water sources include

- Storm water runoff from parking lots
- Excess landscape irrigation (a potential source of nutrients and pesticides)

- Pesticides washed in from applications upstream of the DRB
- Sediments from multiple upstream sources
- Unplanned releases of materials to the ground

Groundwater discharges to the DRB have been a main source of phosphate introduction into the DRB.

7.5.1.4 Collection and Survey Methods for Drainage Retention Basin Monitoring

Water samples at depth are collected using a portable electric pump dedicated to the DRB sampling program. It collects samples at any discrete depth. Sample collection methods using the portable electric pump are outlined in procedure EMP-W-S.

Sampling in the DRB typically requires motorboat transport to the sampling location. (See **Section 7.5.4.3** for DRB sampling boat protocols.) Upon arriving at a sampling location, the operator shuts down the motor and secures the boat in position by placing the sampling buoy (a 20-gallon nalgene jug anchored to the bottom of the DRB) in the boat.

During release sampling at CDBX and WPDC (see **Figure 7-1**), grab samples are collected per procedure EMP-W-S. If water is flowing in Arroyo Las Positas, samples at WPDC must be collected following the release and after it is estimated that the release has reached monitoring location WPDC.

The biological monitoring program instructions are detailed below and follow standard characterization and survey protocols such as *Standard Methods for the Examination of Water and Wastewater* (Greenberg et al., 1992), *Raptor Management Techniques Manual* (Pendleton 1987), *Inventory and Monitoring of Wildlife Habitat* (Cooperrider 1986), *Wildlife Management Techniques Manual* (Schemnitz 1980), and *U. S. Army Corps of Engineers Wetlands Delineation Manual* (Environmental Laboratory 1987).

During amphibian monitoring, nocturnal spotlighting is used to locate adult amphibians and egg masses. A seine is used to identify larvae.

Bird populations are characterized through observation, by walking around the DRB, its tributaries, and Arroyo Las Positas before 7 a.m. All bird species in evidence on and around the area are identified and the number of individuals are recorded. This listing includes a notation of whether the species were actually observed or were identified by the presence of nests, tracks, pellets/droppings, or other evidence.

Fish are identified and characterized by using a seine. The DRB is seined with a vertical net with a mesh size not greater than 1.6 mm (1/16th inch) to sample water for aquatic organisms (fish) in several locations throughout the DRB. The intent is to identify all creatures that may be present, not merely to take a random population sample. Therefore, samples are not collected at pre-selected sites but rather from all points within the basin where fish appear to be present. Netted species are identified and recorded. Fish age classes are noted whenever possible. Where the water is not deep enough to allow seining in the Arroyo or in the DRB tributaries, a dip net is used at locations likely to harbor aquatic organisms.

Direct observations, tracking plates, or infrared-triggered cameras set up at four predetermined stations are used to document mammal species. Observations are recorded.

In addition to the species characterization, a basic water quality evaluation is conducted at the time of the biological surveys. This evaluation is made in addition to the routine monitoring when necessary. Water quality observations include depth, flow, temperature, and sedimentation of the DRB, its tributaries, and Arroyo Las Positas.

Wetland habitat is a unique habitat resource that is directly affected by DRB operations. To document the change in wetland habitats, an informal wetland characterization is made generally following the *U.S. Army Corps of Engineers Wetlands Delineation Manual* (Environmental Laboratory 1987) as a guideline. The wetland characterization primarily uses techniques based on observations of wetlands plant species. The location and extent of all wetland plant species distributions are recorded. Photographic records taken at specific locations identified in the DRB biological monitoring plan are used to further document the time succession of plant species.

7.5.2 Extent and Frequency of Monitoring and Measurements of the Drainage Retention Basin

Management monitoring sampling is conducted at the locations and frequencies identified in **Table 7-4.** Simultaneous field dissolved oxygen (DO) and temperature measurements are taken at all eight locations identified in **Figure 7-7** (i.e., CDBA, CDBC, CDBD, CDBE, CDBF, CDBJ, CDBK, and CDBL). These sites are also registered in the sampling locations database maintained by TSG personnel and are located by features within or around the DRB. The sample locations were chosen to provide two locations within the middle of the DRB where surface (CDBD and CDBJ), middle depth (CDBE and CDBK) and bottom (CDBF and CDBL) samples are collected. In addition, because the shallower water above the shelves located on the south, west, and northeast sides of the DRB has the potential to have different water quality, two shelf locations (CDBA and CDBC) are monitored.

During the 1992–93 wet season, sampling for all other constituents and parameters was conducted at the eight monitoring locations. However, beginning March 31, 1993, because of evidence of limited variability among sampling locations, only DO and temperature are routinely collected at all eight sampling locations. The remaining parameters listed in **Table 7-4** are sampled at CDBE, located at mid-depth in the DRB. This reduced sampling program will continue, provided that DO and temperature measurements continue to show that adequate mixing and minimal variability are maintained within the DRB.

DRB influent samples are collected at sample locations CDB and CDB2 (**Figure 7-1**), part of the storm water runoff network. Other influent samples are collected as part of routine groundwater treatment operations. Sampling is conducted in tandem with storm water sampling events.

The annual compliance sampling program analyzes discharges from the DRB at CDBX and at WPDC, the Livermore site storm water outfall. Samples are collected during the first wet season release from the DRB, and at least once during an additional storm (in conjunction with storm water runoff monitoring). Sampling frequencies of releases from the DRB were determined in agreement with the San Francisco Bay RWQCB (Isherwood 1993b, Galles 1997) and are listed in **Table 7-3**. Surveillance sampling frequencies for each parameter are specified in the *DRB Management Plan*, based on the water quality management objectives, and are listed in **Table 7-4**.

In September 1997, LLNL conducted the first dry-season release from the DRB. Sampling requirements and frequency were approved by the San Francisco Bay RWQCB. In a December 1997 letter to the San Francisco Bay RWQCB, LLNL established that each dry-season release from the DRB would be sampled as identified in **Table 7-3**. For the purpose of DRB releases, the dry season is defined for the DRB as occurring from June 1 through September 30.

Special studies are occasionally implemented to address specific issues that may arise in managing the DRB. They may include increased monitoring frequencies for specific analytes, additional toxicological testing, adding constituents or field measurements, and supplemental biological or microbiological monitoring.

7.5.3 Procedures for Laboratory Analysis

All radioactivity and radioisotope measurements are performed by an off-site laboratory. The laboratory may vary based on laboratories available through the analytical laboratory contract in effect at any given time.

Nonradioactive water analyses are also performed off site by facilities under the analytical laboratory contract. In addition to analytical methods listed for storm water monitoring for the Livermore Site (**Table 7-1**), the DRB analytical protocol includes toxicity assays for algae and water flea (methods E1003TOX and E1002TOX, respectively). Additionally, chlorophyll-a is analyzed using standard method 10200, and acute fish toxicity is performed using fathead minnows (EPA method 600).

7.5.4 QA Requirements for the Drainage Retention Basin

Each month one QA sample is collected at CDBE. The analytical suite used for the QA sample is randomly generated by the TSG Data Management Team (DMT) or by the TSG technician. The sample is submitted on rotating quarters as an intralaboratory and an interlaboratory duplicate. Analytical laboratory acceptance criteria determine the validity of the sample. Sampling of the DRB does not include the use of field blanks or QA spikes and blanks.

The DO/temperature meter is calibrated before each field sampling event, following instructions on the back of the meter. Between uses, it is stored in Trailer 5477. Calibration results are recorded on the FTF.

7.5.5 Program Implementation Procedures

To the extent possible, the network monitoring discharges from inflows to the DRB have been integrated with the storm water monitoring network. DRB inflows and all but the first wet season discharge are collected as part of the storm water monitoring network. Data from these events are evaluated independently for DRB compliance/management and for storm water quality evaluation.

Sampling is performed by TSG staff. Chain-of-custody and sample control procedures EMP-QA-DM and EMP-QA-SL apply when samples are delivered to laboratories for analysis. EMP-W-S and SOP Supplement EMP-WSS-DRB outline methods for sampling water within the DRB, discharges from the DRB at CDBX and WPDC, and storm water runoff into the DRB. Sampling follows ORAD IWS 2271, developed for this procedure. Sample bottle requirements and preservation requirements for each analyte are specified in procedure EMP-QA-BOT. Biological surveys are currently performed by the Environmental Operations Group (EOG) wildlife biologist following the DRB biological monitoring plan.

7.5.6 Action Levels

LLNL responses to DRB water quality may include some or all of the steps listed below as well as follow recommendations identified in the *DRB Management Plan*.

A single, unusually high concentration may, by itself, trigger a detailed investigation. Detailed investigations may include elements such as

- Management notification.
- Re-analysis of the samples.
- Additional sampling and analysis of water contained within the DRB or analysis of subsequent releases. During a detailed investigation, a release occurring immediately following a finding may be sampled to confirm or negate the concentration being investigated or to determine whether the finding was a single or chronic occurrence.
- Source investigation. (Results are compared with findings from other monitoring networks [e.g., air, rain, and storm water], and LLNL activities that may have contributed to the result are investigated.)
- Expanded monitoring (more locations).
- Increased monitoring frequency.

In addition, findings of concentration levels not meeting management action levels or release limits are reported in quarterly reports submitted to the San Francisco Bay RWQCB. The written report contains information on the nature, time, duration, cause of the finding, and a description of any measures taken to remedy it and to prevent its recurrence. The finding is also evaluated to determine compliance with occurrence reporting requirements in DOE Order 232.1A (DOE 1997).

7.5.7 Preparation and Disposition of Drainage Retention Basin Reports

Since September 1993, results of routine water quality monitoring for management parameters and discharge monitoring have been reported to regulatory agencies in quarterly and annual groundwater project reports submitted under the CERCLA ROD. Monitoring results are also reported in the annual *Environmental Report* (e.g., Biermann et al. 2001). LLNL reports to the San Francisco Bay RWQCB in quarterly and annual self-monitoring reports (e.g., Hoffman et al. 1998). These reports note any discharges exceeding limits, and any DRB conditions that exceed the MAL. The *DRB Management Plan* includes specific recommended solutions to conditions exceeding the MAL (e.g., DRB circulation pumps are operated to maintain dissolved oxygen levels within management parameters).

7.5.8 Future Plans

No changes in the monitoring strategy are anticipated until the *DRM Management Plan* is updated.

7.6 Site 300 Drinking Water System Discharges

7.6.1 Rationale and Design Criteria

LLNL Site 300 operates a nontransient, noncommunity water system. Water is pumped from the regional aquifer by two on-site supply wells (Wells W-18 and W-20) into the distribution and storage system. Groundwater is chlorinated at the well heads and may also be chlorinated, as needed, at the booster/transfer stations. Occasional discharges are necessary from the drinking water system that may enter waters of the United States. In 2001 there was a change in the way in which water discharges from this system at Site 300 were regulated.

7.6.1.1 Regulatory Drivers

The Federal Water Pollution Control Act (Clean Water Act, 1972, 33 USC 1251) was enacted to restore and maintain the chemical, physical, and biological integrity of waters of the United States. To this end, Section 402 established the National Pollutant Discharge Elimination System (NPDES) to set the conditions under which pollutants could be discharged to navigable waters. The Central Valley RWQCB chose to regulate low-threat discharges to surface waters under a general NPDES permit (CAG995001, WDR 5-00-175). These low-threat discharges are defined to include discharges of potable water from drinking water systems. Previously at Site 300, these discharges were regulated under WDR 94-131, a NPDES permit from storm water and low-threat nonstorm water discharges.

7.6.1.2 Drinking Water System Discharges Monitoring Objectives

The objective of the monitoring program is to demonstrate compliance with the effluent limitations of WDR 5-00-175 and to provide timely information to stop discharges if effluent limitations are not met.

WDR 5-00-175 establishes monitoring requirements to verify compliance with established effluent limitations and to test for adverse impacts to the receiving waters. Effluent limits are established by the Central Valley RWQCB for constituents of concern that could adversely affect waters of the state of California and of the United States.

7.6.1.3 Sources and Analytes for Drinking Water System Discharges

Anticipated pollutants from the drinking water system are residual chlorine and pH. The residual chlorine in the drinking water system is maintained between 0.2 and 3.0 parts per million (ppm). The pH of the drinking water is 7.84 to 8.4.

7.6.1.4 Collection Methods for Drinking Water System Discharges Samples

Compliance monitoring for this permit is done by field measurements on grab samples because immediate measurements provide more representative information than laboratory analysis for pH and residual chlorine. Sample handling and collection techniques used are similar to those for other environmental water sampling, as noted in procedure EMP-W-S. Standard FTF procedures (EMP-QA-DM) are employed to track samples and to document field conditions that may affect the samples.

7.6.2 Extent and Frequency of Drinking Water System Discharges Monitoring and Measurements

The *Pollution Prevention and Monitoring and Reporting Program* (PPMRP) (Mathews 2000) prepared by LLNL and approved by the CVRWQCB establishes the specific monitoring requirements for the following discharges at the specified frequencies.

- **Drinking water storage tanks**—monitor discharges that have the potential to reach surface waters.
- **System flushes**—monitor one flush per pressure zone per year.
- **Deadend flushes**—monitor flushes that have the potential to reach surface waters and, for any discharge that continues for more than four months, monitor semiannually.

Each release is monitored at up to three points, depending upon how far the water flows from the source of discharge. Residual chlorine and pH measurements are taken at the point of discharge, at the point the discharge enters the surface water, and, if it reaches the receiving water, at the established downstream monitoring location in Corral Hollow Creek (GEOCRK). When a discharge reaches Corral Hollow Creek, the established upstream monitoring location in Corral Hollow Creek (CARW) is also sampled in order to evaluate the impact of the discharge on the receiving water. See **Figure 7-8** for the locations of the drinking water tanks, surface waters, and receiving water monitoring locations.

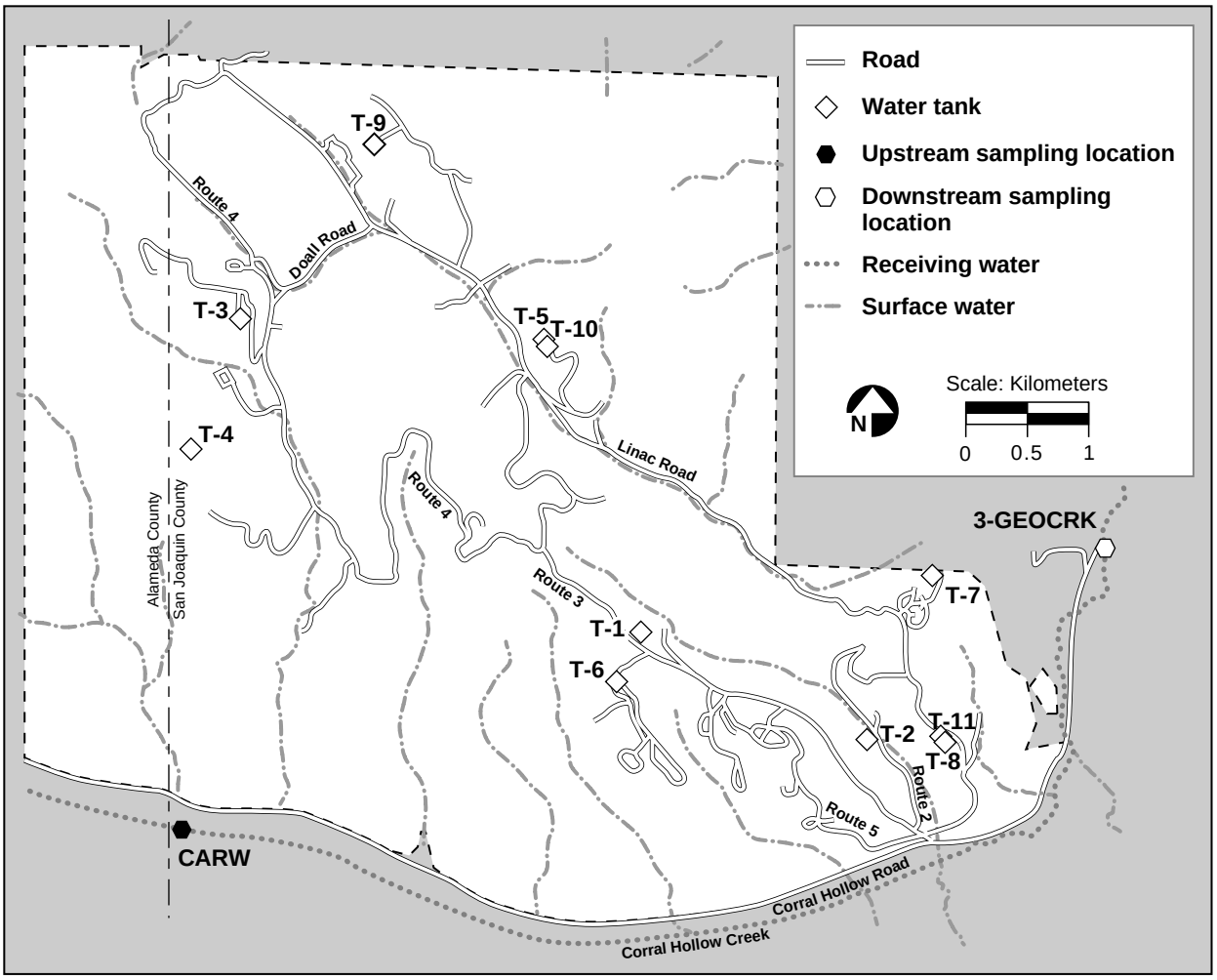

Figure 7-8. Locations of drinking water sources and monitoring locations at Site 300

Observations of the discharges are also made. At the discharge point, the effluent is observed for evidence of other pollutants being carried with the discharge (such as oil and sediment), discoloration of water, and estimate of flow rate from the source. At the point that the effluent discharges into surface waters, observations are made for the same parameters.

If the effluent reaches the receiving water, Corral Hollow Creek, observations are made at the upstream and downstream locations for evidence of

- Floating or suspended matter
- Discoloration
- Bottom deposits
- Aquatic life

- Visible films, sheens, or coatings
- Potential nuisance conditions
- Fungi, slimes, or objectionable growth

7.6.3 Procedures for Laboratory Analysis

All monitoring for this network is done in the field; no samples are submitted for laboratory analysis.

7.6.4 QA Requirements for Drinking Water System Discharges

To ensure that all quality assurance (QA) and quality control (QC) objectives are met, all samples are collected in accordance with written procedures by trained sampling technologists. All required permit documentation, such as calibration and monitoring records, is recorded on FTFs archived by DMT per procedure EMP-QA-DM.

7.6.5 Program Implementation Procedures

The PPMRP identifies the approved monitoring and reporting program for WDR 5-00-175. Standard field sampling protocols are also contained in procedure EMP-W-S, and specific network sampling requirements are identified in EMP-WSS-WSD. Sample locations are identified in accordance with procedure EMP-QA-DM. Sample locations are tracked in the TSG locations database.

7.6.6 Action Levels

Action levels for this permit are the permitted effluent limits for the two pollutants of concern: a residual chlorine concentration above 0.02 mg/L and a pH level outside the range 6.5–8.5.

If the field measurements indicate discharges above the allowed residual chlorine concentration or outside the allowed pH range, the measurement is immediately repeated in the field. Once the out-of-range measurement is confirmed, immediate corrective actions may include ceasing discharges or redirecting effluents away from the surface water. Afterward the procedures for discharges may be reviewed and modified, if necessary, to prevent future recurrences.

If observations indicate that other pollutants, such as eroded sediment, are carried in the effluent, immediate corrective actions may include

- Ceasing the discharge
- Reducing the flow rate of the discharge

- Redirecting the effluent away from the surface water
- Redirecting the effluent away from the area where the pollutants are being picked up by the effluent flow

If noncompliance with any prohibition, daily maximum effluent limit, or receiving water limitation contained in WDR 5-00-175 is identified, it must be reported by phone within 24 hours, followed by a written report within 5 days (unless this is waived by the Central Valley RWQCB). The written confirmation must include the nature, time, duration, cause of the noncompliance, and a description of measures taken to remedy it and to prevent its recurrence.

7.6.7 Preparation and Disposition of Drinking Water System Discharge Reports

Monitoring reports are prepared and submitted quarterly to the Central Valley Regional Board. These reports are due on the first day of the second month following the end of the calendar quarter. The data are also included in the annual LLNL *Environmental Report*.

7.6.8 Future Plans

In the future, LLNL anticipates the delivery of drinking water from the Hetch Hetchy system. Chlorine residual concentrations are not expected to change in the new water source. The pH of Hetch Hetchy water as reported by the San Francisco Public Utilities Commission in its 1999 Water Quality Report ranges from 7.8 to 9.6 with an average pH of 9.2. When Hetch Hetchy water is delivered, LLNL will begin pH adjustment of discharges from the water system if necessary. In 2003, the San Francisco Public Utilities Commission is expected to switch from chlorine to chloramine disinfection. This may require alteration of the monitoring protocols.

7.7 Other Waters

Surface drainage in the Livermore Valley is by westward-flowing arroyos that merge in the west end of the Livermore Valley. There they form the southward-flowing Arroyo de la Laguna, a tributary to the Alameda Creek drainage system, which eventually flows to San Francisco Bay. LLNL monitors other on-site and off-site waters, such as domestic water (also referred to as drinking water or tap water), surface water bodies (e.g., Lake Del Valle, the Laboratory swimming pool), and other nearby waters. Sample data from the off-site locations at both the Livermore site and Site 300 provide information on tritium, gross alpha, and gross beta levels in nearby surface water bodies. Data are used to characterize long-term trends relating to tritium, gross alpha, and gross beta in water resources.

7.7.1 Rationale and Design Criteria

7.7.1.1 Regulatory Drivers

The regulatory driver for monitoring other waters are the applicable portions of DOE Order 5400.1, as described in **Section 7.2.1.1**. Therefore, domestic water and surface water bodies are monitored to characterize off-site and on-site waters.

7.7.1.2 Monitoring Objectives for Other Waters

Although no state or federal laws require domestic water or surface water monitoring, the DOE order-driven objectives (DOE 1988; DOE 1991; **Section 7.2.1.2**) for environmental monitoring also apply to monitoring of other waters.

7.7.1.3 Other Water Sources and Analytes

Samples are analyzed for tritium, gross alpha, and gross beta radiation. Surface water locations are positioned to monitor either rainout or direct runoff of tritium from atmospheric discharges. In addition, three locations upwind and not directly connected to LLNL runoff are used to determine background concentrations.

7.7.1.4 Collection Methods for Other Water Samples

Surface water sampling is performed with a tethered stainless-steel pail. Domestic drinking water locations are sampled directly from the tap. Sample bottle requirements, special sampling techniques, and preservation requirements for each analyte are specified in procedures EMP-W-S and EMP-QA-BOT. Samples for tritium analysis are collected in 500-mL, argon-flushed glass containers; those for gross alpha and gross beta analyses are collected in acidified, 1000-mL polyethylene bottles.

7.7.2 Extent and Frequency of Other Waters Monitoring and Measurements

7.7.2.1 Livermore Site

Surface and domestic waters are sampled at two locations on the Livermore site and at ten locations in the Livermore Valley (**Figure 7-9**). On the Livermore site, POOL provides samples from the swimming pool, and TAP provides samples of on-site drinking water (LLNL's primary on-site drinking water is Hetch Hetchy Water; Zone 7 is the backup supplier.). Of the remaining ten sampling locations in the Livermore Valley, four (BELL, GAS, ORCH, and PALM) provide samples of domestic drinking water, and the other six provide samples from various surface water bodies. On-site samples provide information about potential radioactive constituents in the LLNL drinking water supply and in the pool. Off-site drinking water

samples provide information about potential radioactive constituents in the local supplies that could possibly be related to LLNL activities. A complete description of these sampling locations is in the TSG Locations database.

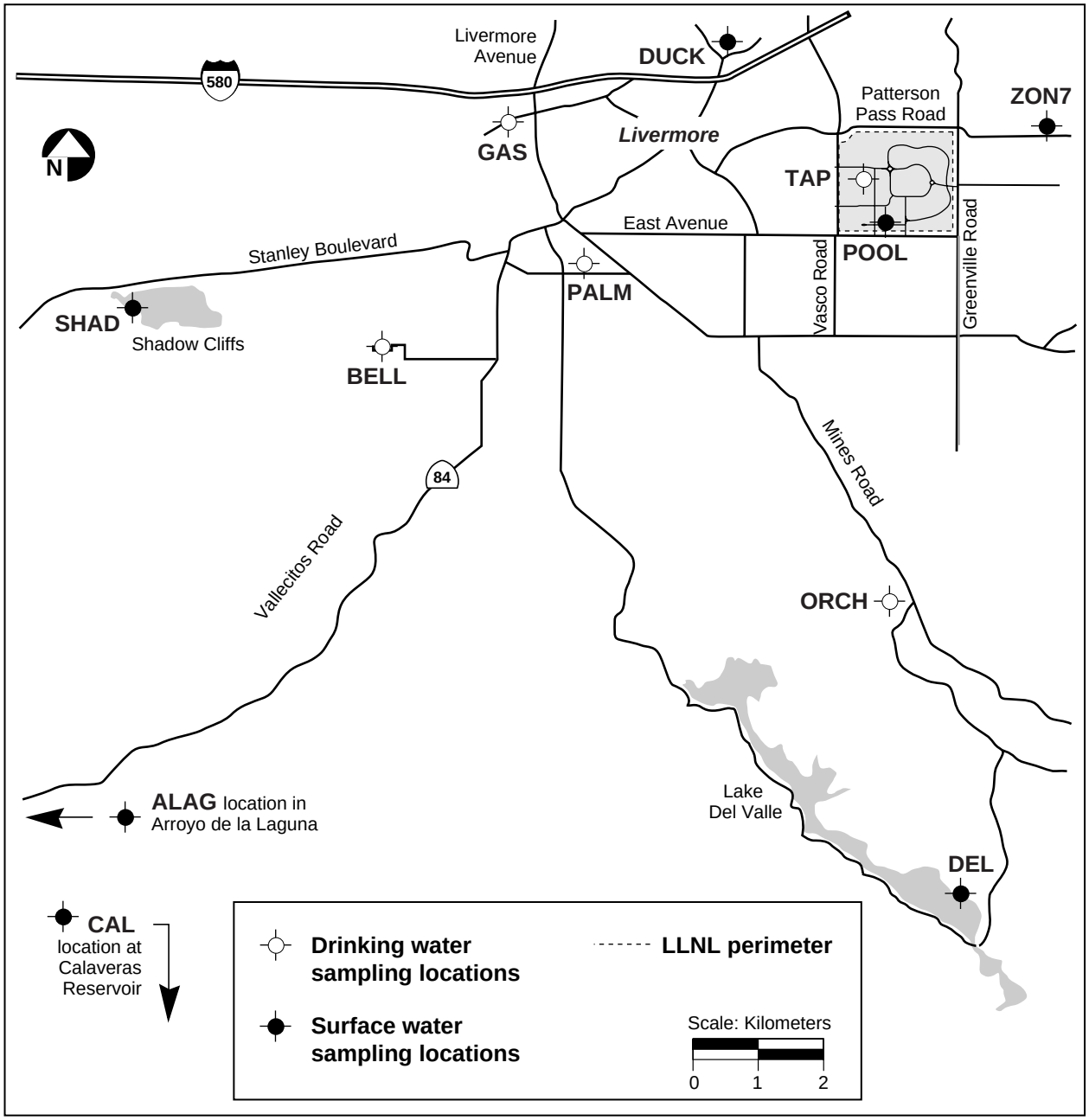

Figure 7-9. Surface and drinking water sampling locations, Livermore Valley

Domestic and surface water bodies are sampled semiannually, except for POOL, which is sampled quarterly. Sampling frequency was reduced from quarterly (monthly for POOL) because sufficient data have been collected to demonstrate a history of minimal impact from LLNL. Samples are collected more frequently at POOL than at other locations because of public concerns about water quality in the LLNL pool.

Surface water bodies near the Livermore site include the treatment tanks and reservoir of the Patterson Pass water treatment facility (ZON7) about 1.2 km east of the Livermore site, and the Springtown Pond (DUCK), an artificial decorative pond maintained in a community recreation area 2.6 km northwest of the Livermore site. Sampling location ALAG is in the Arroyo de la Laguna, 13 km southwest of LLNL. Lake Del Valle (DEL) and the Calaveras Reservoir (CAL) are water storage reservoirs 9 km south of the Livermore site and 21 km southwest of the Livermore site, respectively. Lake Del Valle is also used for aquatic recreation (swimming, boating, and fishing), as is the Shadow Cliffs Regional Park (SHAD), a water storage reservoir 11 km west of the Livermore site. Shadow Cliffs is a partially restored excavation produced by gravel quarry operations; additional pits in the same general area continue to mined. Locations DEL, CAL, and SHAD are used to evaluate background concentrations for environmental surface water monitoring. All three sites are generally upwind of LLNL and are not directly connected to LLNL runoff.

7.7.2.2 Site 300

Surface water adjacent to Site 300 is sampled at location GEOCRK (**Figure 7-2**). This location provides downstream samples of water in Corral Hollow Creek, which drains most of Site 300. It is also sampled as part of the storm water monitoring network.

7.7.3 Procedures for Laboratory Analysis

Radioactivity and radioisotope measurements are currently performed off site by contract analytical laboratories for analysis of tritium, gross alpha, and gross beta radiation.

7.7.4 QA Sampling and Requirements

Field duplicate samples are submitted on rotating quarters as intralaboratory and interlaboratory duplicates. Laboratory acceptance criteria determine the validity of the sample. Sampling does not include the use of field blanks or QA spikes and blanks. Quality control samples, as described in procedure EMP-W-S, are part of all monitoring activities.

7.7.5 Program Implementation Procedures

All domestic and surface water body sampling is conducted by LLNL technical staff according to procedure EMP-W-S, and samples are submitted for analyses using sample documentation and data management procedure EMP-QA-DM. Supplements to EMP-QA-DM specify procedures for completing field tracking forms (EMP-QAS-FTF), and chain-of-custody forms (EMP-QAS-COC). Sample bottle requirements and preservation requirements for each analyte are specified in procedure EMP-QA-BOT.

7.7.6 Action Levels

Tritium, gross alpha, and gross beta results from drinking water and surface water body samples are compared with their respective drinking water MCLs (740, 0.56, and 1.85 Bq/L, respectively). Other waters concentrations are generally below MCLs. If concentrations were to exceed an MCL or increase dramatically, a detailed investigation of the cause of the high result or results would ensue. A detailed investigation may include elements such as

- Management notification.
- Re-analysis of the samples.
- Additional sampling and analysis.
- Source investigation. (Results are compared with findings from other monitoring networks [e.g., air or rain], and LLNL activities that may have contributed to the result are investigated.)
- Expanded monitoring (more locations).
- Increased monitoring frequency.

7.7.7 Preparation and Disposition of Other Waters Reports

Drinking water and surface water body monitoring results are summarized and discussed in the surface water monitoring section of the *Environmental Report* (Biermann et al. 2001). All data are summarized and trends are discussed. Each report also includes a brief interpretation of the data.

7.7.8 Future Plans

No changes in other waters monitoring are planned at this time.

7.8 Livermore Site Arroyo Las Positas Maintenance Monitoring

7.8.1 Rationale and Design Criteria

LLNL performs annual maintenance activities within the flood control channel that transports the flows of the Arroyo Las Positas (ALP) around the northern perimeter of the LLNL Livermore site. Maintenance activities include phased desilting of a 7,000-linear-foot reach of the ALP over five years, trimming cattail heights, and conducting bank stabilization and erosion-control activities. Each year, up to 20 percent of the ALP is desilted. However, to avoid disturbing large continuous stretches of the arroyo and habitat features, this 20 percent is divided into segments. Where California red-legged frogs were present during surveys conducted in 1999, the length of the segment is approximately 100 feet; elsewhere, the segments are approximately 300 feet. These pre-identified zones are shown in **Figure 7-10**.

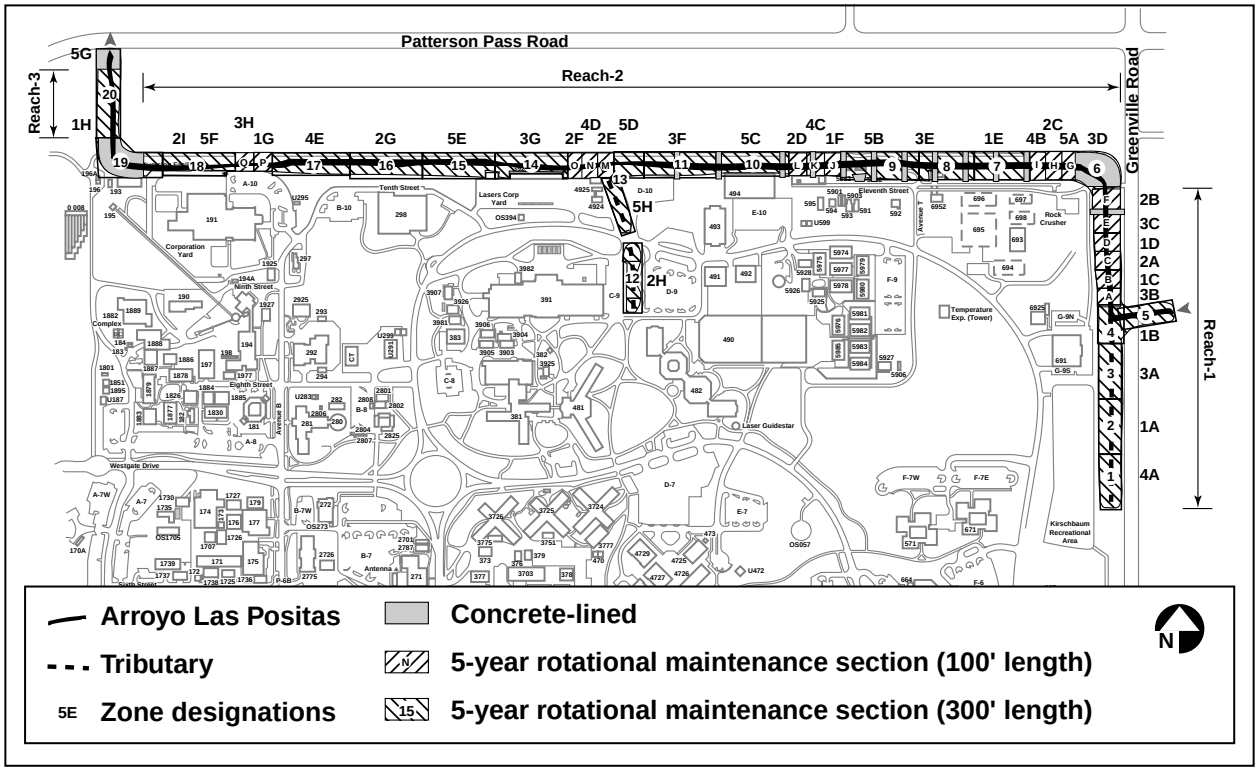

Figure 7-10. Arroyo Las Positas maintenance project map

7.8.1.1 Regulatory Drivers

The regulatory driver for ALP maintenance monitoring is Order No. 99-086, *Waste Discharge Requirements for Lawrence Livermore National Laboratory – 5-Year Maintenance Plan and Site Management Plan for Waters of the United States, Livermore, Alameda County*, issued by the San

Francisco Bay Regional Water Quality Control Board (SFRWQCB 1999). WDR 99-086 specifies that discharges cannot cause receiving water limits to be exceeded.

"1. The desilting activities shall not cause:

a. Floating, suspended, or deposited macroscopic particulate matter or foam in waters of the State at any place more than 50 feet from the point of discharge of diverted flow.

b. Alteration of apparent color beyond present natural background levels in water of the State at any place more than 50 feet from the point of discharge of diverted flow.

c. Visible floating, suspended, or deposited oil or other products of petroleum origin in waters of the State at any place more than 50 feet from the point of discharge of diverted flow.

d. The diverted flow shall not cause Waters of the State to exceed the following quality limits at any place more than 50 feet from the point of discharge of diverted flow:

i) Dissolved Oxygen: 5 mg/l minimum. When natural factors cause lesser concentrations, then this discharge shall not cause further reduction in the concentration of dissolved oxygen.

ii) pH: A variation of natural ambient pH by more than 0.5 pH units;

iii) Toxic or other deleterious substances: None shall be present in concentrations or quantities which may cause deleterious effects on aquatic biota, wildlife or waterfowl, or which render any of these unfit for human consumption either at levels created in the receiving waters or as a result of biological concentrations.

2. Turbidity of the waters of the State, as measured in NTUs, at any point beyond 50 feet downstream of the point of discharge of diverted flow shall not increase above background levels by more than the following:

Receiving Water Background	Incremental Increase
≥ 50 units	10% of background, maximum

3. The groundwater shall not be degraded as a result of the sediment disposal and handling operations."

The specifications for sampling and analysis and making observations are detailed in the *Self-Monitoring Program for Order 99-086*.

7.8.1.2 Monitoring Objectives

The primary objective of the ALP maintenance monitoring is to document compliance with effluent requirements and prohibitions established in WDR 99-086. The monitoring activities also facilitate LLNL in preventing and abating potential pollutant discharges when best management practices are not properly or effectively implemented.

7.8.1.3 Sources and Analytes

LLNL desilting activities involve removing sediment within the channel and minor grading to re-establish flow lines. To control sediment, no heavy equipment is allowed within the channel, spoils material are immediately transported from the project site, and water is diverted around the work section. Once water is diverted around the active project site, any remaining water within the active project site is pumped to the top of the bank; water from dewatering is not allowed to flow back to the ALP and evaporates or soaks into the ground.

WDR 99-086 specifically prohibits the direct discharge of wastes, including excavated sediment, from active desilting sites to surface waters or surface water drainage courses. To document compliance with the receiving water limits, LLNL analyzes diverted water flows for dissolved oxygen, pH, and turbidity. LLNL also conducts visual observations every day of operation when there is water present in the channel or there is a discharge of diverted flow.

7.8.1.4 Collection Methods

Prior to the start of any desilting at a certain segment, background samples are collected by grab sampling with a dip sampler no more than 50 feet downstream in the ALP from the point where the diverted water is discharged. Alternatively, background samples can be collected daily a minimum of 500 feet upstream of the active desilting site; background samples collected daily are valid for discharge occurring only in the same day. Receiving water samples are collected during active desilting by grab sampling with a dip sampler no more than 50 feet from the point where the diverted water is discharged.

A dip sampler, which consists of a 500-mL polypropylene beaker attached to an extension rod, is used to collect samples. The dip sampler is triple-rinsed with the water to be sampled, dipped or submerged into the water, and then withdrawn in a slow, smooth motion. Receiving water and upstream samples are measured in the field using meters. A duplicate of samples

from both the receiving water and upstream locations of the active desilting site is collected for quality assurance and sent to an off-site laboratory for analysis.

7.8.2 Extent and Frequency of Monitoring and Measurement

7.8.2.1 Routine Monitoring Requirements

WDR 99-086 requires that receiving water samples be collected and analyzed two times a day. The first sample is collected no earlier than one hour after desilting starts each day. The second sample is collected halfway between the time the first sample is collected and the time work is scheduled to end for the day. Samples are collected only on days when there is water present in the channel or when there is diverted flow. Upstream, background samples can also be collected daily.

If analytical results indicate that a receiving water sample exceeds any of the receiving water limits, confirmation samples are taken within two hours and every subsequent two hours until the exceedance has been corrected. The confirmation samples are analyzed for all constituents.

Duplicate samples are collected weekly. One set is analyzed onsite using field meters and the other set is submitted to a certified off-site laboratory for analysis.

7.8.2.2 Special Studies

No special studies are conducted as part of ALP maintenance monitoring.

7.8.3 Procedures for Laboratory Analysis

Quality assurance samples are shipped off-site to a certified laboratory immediately upon collection. Holding times for dissolved oxygen and pH are 4 hours and 24 hours, respectively. Because of the extremely short holding times, LLNL notifies the analytical laboratory in advance so that it can analyze the samples immediately upon receipt.

LLNL procedure EMP-QA-BOT describes the bottles to be used for each type of constituent. **Table 7-5** shows the methods used by off-site laboratories for ALP maintenance monitoring samples.

Table 7-5. ALP maintenance monitoring constituents

Analytical method	Description of analysis
EPA 150.1	pH
EPA 180.1	Turbidity
EPA 360.1	Dissolved oxygen

Off-site laboratories are required to follow all LLNL sample tracking procedures (contained in procedure EMP-QA-DM) when handling LLNL samples. LLNL must be notified of any problems immediately, including broken or damaged containers, discrepancies between sample bottles and/or labels and the CoC, broken seals on sample coolers, or any other compromises to the integrity of a sample. Identified problems must also be described in the case narrative that accompanies the final data report. Off-site laboratories must hold samples for a minimum of 30 days after the final report is generated and verified by LLNL. The laboratory must dispose of all unused sample portions in accordance with written procedures.

At a minimum, LLNL requires ongoing calibration checks from the offsite laboratory for each batch. A batch is defined as less than or equal to 20 samples. Initial calibration is available upon request. A summary of calibration sample results for each sample must be provided with the analytical data report. This summary must include the continuing calibration batch number, date and time of analysis, instrument ID number, analyst ID number, method number, theoretical result, actual result, percent recovery, and acceptable range. In addition, the laboratory must maintain initial instrument calibration data and make the data available upon request. The EPD Assurance Manager maintains copies of each laboratory's standard operating procedures for performing and tracking calibration activities on file. Each laboratory's calibration program and its implementation are verified at the annual facility audit.

7.8.4 Quality Assurance Procedures

As previously described, LLNL collects duplicate samples once per week.

7.8.5 Program Implementation Procedures

LLNL technical staff conduct ALP maintenance monitoring according to EMP-W-S and EMP-WSS-ALP. Duplicate samples are submitted to an offsite laboratory for analyses using sample control and documentation procedures (EMP-QA-SL and EMP-QA-DM). Sample bottle requirements and preservation requirements are specified in EMP-QA-BOT.

7.8.6 Action Levels

If any receiving water limit is exceeded, LLNL conducts activities to identify and correct the source of exceedance, then continues to resample to determine that the exceedance has been corrected. If any receiving water limit is exceeded for a 12-hour period, then the SFBRWQCB is notified by telephone.

Exceedance of a receiving water limit for a 24-hour period is a violation of WDR 99-086, and desilting activities are terminated until the cause of the violation is found and sampling

demonstrates that the exceedance has been corrected. Alternatively, desilting activities can resume when LLNL has provided the SFRWQCB with an acceptable corrective action plan. The corrective action plan must provide alternative methods of compliance that are acceptable to the SFBRWQCB's Executive Officer.

7.8.7 Preparation and Disposition of Reports

LLNL must submit self-monitoring reports to the SFBRWQCB annually when any receiving water limit is exceeded during ALP maintenance activities. The self-monitoring report must be submitted to the SFBRWQCB no later than 45 calendar days following the completion of desilting activities. In the event that a receiving water limit is exceeded for a 24-hour period and there is a violation of WDR 99-086, LLNL must submit a written report to the SFBRWQCB within 30 calendar days.

7.8.8 Future Plans

LLNL is reviewing the effectiveness of the ALP Maintenance Plan. If changes to the ALP Management Plan were proposed to the SFBRWQCB, there would be a large impact on WDR 99-086 and its *Self-Monitoring Program* requirements. The SFBRWQCB and U.S. Fish and Wildlife Service must first approve any changes to the ALP Management Plan.

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8 Groundwater Monitoring

Eric Christofferson • Richard A. Brown •Michael A. Revelli

8.1 Rationale and Design Criteria

8.1.1 Regulatory Drivers

This chapter of the *Environmental Monitoring Plan* (EMP) focuses on groundwater surveillance monitoring, driven primarily by U.S. Department of Energy (DOE) Order 5400.1, Change 2, Chapter IV paragraph 1a and paragraph 5 (see WSS B93 in Appendix B), and groundwater compliance monitoring, driven by various permit-granting regulatory agencies.

Groundwater surveillance and compliance monitoring programs at the Lawrence Livermore National Laboratory (LLNL) Livermore site and at the Experimental Test Site (Site 300) in the Altamont Hills are conducted in accordance with three types of regulatory drivers:

- DOE orders as adopted in Work Smart Standards (WSS)
- Written agreements with the California Environmental Protection Agency (Cal-EPA) issued under Resource Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)
- Permits and other controlling documents issued by the two responsible California Regional Water Quality Control Boards (RWQCBs): San Francisco Bay RWQCB (SFBRWQCB) and Central Valley RWQCB (CVRWQCB) under the Porter-Cologne Water Quality Control Act (California 1969)

8.1.1.1 Restoration Program

The following brief explanation of the LLNL environmental restoration program provides a context for CERCLA monitoring in relation to the surveillance and compliance programs described in this chapter.

The Laboratory's place on the National Priorities List mandates that groundwater cleanup at both the Livermore site and Site 300 conform with U.S. Environmental Protection Agency (EPA) guidance under CERCLA, as amended by the 1986 Superfund Amendments and Reauthorization Act (SARA), and negotiated Federal Facility Agreements (FFAs). Over several decades, LLNL's environmental restoration projects have investigated, evaluated, and

remediated potentially hazardous compounds that may have affected soil and groundwater at both the Livermore site and Site 300. Much of the groundwater monitoring at both sites is governed by CERCLA restoration program requirements. CERCLA monitoring is fully described in documents issued by the Site 300 Restoration Project and the Livermore site Groundwater Project (for references, see Chapter 8 of the sitewide *Environmental Report 2002* [Sanchez et al. 2003]).

8.1.1.2 Surveillance Program

Groundwater surveillance monitoring is carried out at both the Livermore site and Site 300. Applicable portions of DOE Order 5400.1, Chapter IV, paragraph 5b and Order 5400.5 (see WSS B93 and B94 in Appendix B) require that environmental surveillance monitoring programs be conducted at DOE sites. Surveillance monitoring complements restoration activities. At LLNL, the surveillance program emphasizes monitoring for possible contamination from present activities and operations, while restoration programs monitor contamination resulting from past operations. Surveillance monitoring also looks for constituents of concern (COCs), including radionuclides, that occur at levels below the restoration program's level of concern, and that may have been released to groundwater from LLNL operations.

Site-specific characteristics determine monitoring requirements. Groundwater monitoring programs are designed and implemented in accordance with Code of Federal Regulations (CFR), Title 4, Part 264, Subpart F or with of the CFR Title 40, Part 265 , Subpart F (see WSS A130 and A131 in Appendix B). Monitoring for radionuclides is performed in accordance with DOE orders in the 5400 series for radiation protection of the public and the environment.

8.1.1.3 Compliance Program

Compliance monitoring of groundwater is conducted only at Site 300, where the Porter-Cologne Water Quality Control Act requires a RWQCB to evaluate waste discharges and issue a Waste Discharge Requirements (WDR) order if the waste could adversely affect water quality in California. Porter-Cologne is the general regulatory driver behind the specific monitoring and reporting requirements at Site 300 that are described in the following documents:

- *Lawrence Livermore National Laboratory Site 300 Resource Conservation and Recovery Act Closure and Post-Closure Plans – Landfill Pits 1 and 7* (Rogers/Pacific Corporation 1990).

  This document contains specific requirements for groundwater monitoring, including the wells to be monitored at the closed waste management units (WMUs), the COCs and parameters to be measured, the frequency of sampling,

statistical analyses to be employed in the data analysis, and the contents and frequency of reports. Regulatory requirements are contained in Title 23 of the *California Code of Regulations* (23 CCR, Division 3, Chapter 15) and in 40 CFR 265, Subpart G, *Closure and Post-Closure*, concerning RCRA requirements.

The post-closure monitoring and reporting requirements in Rogers/Pacific Corporation (1990) are administered by the California Department of Toxic Substances Control (DTSC), a department of Cal-EPA. Administrative control was granted to Cal-EPA by EPA. RCRA is the regulatory driver behind Rogers/Pacific Corporation (1990).

- *Order No. 93-100, Waste Discharge Requirements for University of California, Lawrence Livermore National Laboratory Site 300 and U.S. Department of Energy, Landfill Pits 1 and 7, San Joaquin County, June 25, 1993* (CVRWQCB 1993).
- *Order No. 96-248, Waste Discharge Requirements for University of California, Lawrence Livermore National Laboratory Experimental Site (Site 300) and U.S. Department of Energy Evaporation and Percolation Ponds and Class II Surface Impoundments, Alameda and San Joaquin Counties, September 20, 1996* (CVRWQCB 1996).

  These WDRs specify monitoring requirements for the discharge of waste into land disposal facilities, and the monitoring of groundwater and other leak-detection systems. The WDR orders contain specific monitoring program requirements for the closed WMUs, including the wells to be monitored, COCs and parameters to be measured, frequency of sampling, statistical analyses to be used in the data analysis, and the contents and frequency of reports. WDR Order 93-100 and WDR Order 96-248 are administered by the CVRWQCB. Regulations pertaining to the issuance of such WDRs are contained in 23 CCR, Division 3, Chapter 9.
- *Post-Closure Plan for the Pit 6 Landfill Operable Unit, Lawrence Livermore National Laboratory, Site 300* (Ferry et al. 1998).

  The post-closure monitoring and reporting requirements in Ferry et al. (1998), which are administered under CERCLA, RCRA, and the California Porter-Cologne Water Quality Control Act of 1969 (Porter-Cologne), are the applicable, relevant, and appropriate requirements used to develop the post-closure plan. The CVRWQCB chose not to write a WDR order for the closed Pit 6 landfill.
- *Final Closure Plan for the High-Explosives Open Burn Treatment Facility at Lawrence Livermore National Laboratory Experimental Test Site 300* (Mathews and Taffet 1997).

The post-closure monitoring and reporting requirements for the former Building 829 (B829) burn facility are administered under RCRA by the DTSC. An application for a WDR permit is pending with the DTSC.

8.1.2 Monitoring Objectives

LLNL's groundwater monitoring program has both surveillance and compliance objectives. Surveillance monitoring requires continual assessment of all LLNL activities for their potential to release contaminants to groundwater. Surveillance monitoring programs are in place at both the Livermore site and Site 300. Compliance monitoring, currently conducted at Site 300 only, detects potential releases to groundwater of COCs that are contained in closed and active WMUs, such as landfill pits, surface water impoundments, and sewage ponds.

8.1.2.1 Surveillance Monitoring Objectives

DOE Order 5400.1, Chapter IV, paragraph 9a, is used as guidance for surveillance monitoring. It states that groundwater that is or could be affected by DOE activities shall be monitored to determine and document the effects of those activities on groundwater quality and quantity. DOE Order 5400.1 also mandates a groundwater monitoring plan that identifies all DOE requirements and regulations applicable to groundwater protection, and it includes a monitoring strategy. LLNL's program is designed to meet the following objectives identified in DOE Order 5400.1, Chapter IV, paragraph 9b:

- Obtain data for the purpose of determining baseline conditions of groundwater quality and quantity.
- Demonstrate compliance with and implementation of all applicable regulations and DOE orders.
- Provide data to permit the early detection of groundwater pollution or contamination.
- Furnish a reporting mechanism for detected groundwater pollution or contamination.
- Identify existing and potential groundwater contamination sources and maintain surveillance of these sources.
- Supply data to inform the decisions that should be made concerning land disposal practices and the management and protection of groundwater resources.

Groundwater surveillance monitoring primarily concerns overall groundwater quality beneath and adjacent to the LLNL Livermore site and Site 300. Groundwater plumes containing tritium

or halogenated organic compounds are monitored at LLNL and at Site 300. Surveillance monitoring examines an extensive suite of elements, radioisotopes, inorganic and organic compounds, and general contaminant indicators (**Tables 8-1**, **8-2**, and **8-3)**.[1] Existing contamination in groundwater caused by past operations is monitored for any significant increases that could signify new releases from remaining underground sources of COCs. Groundwater is also monitored in other areas, including off-site wells, where existing contamination could migrate under unusual circumstances. At Site 300, surveillance monitoring of additional closed WMUs (landfill Pits 2, 3, 4, 5, 8, and 9) is conducted. These landfills were closed before RCRA became effective and are not regulated by California-issued WDRs. The closed pits do contain COCs that, if released, would be detrimental to groundwater quality.

8.1.2.2 Compliance Monitoring Objectives

Compliance monitoring at Site 300 monitors for, detects, and reports any potential release of COCs to groundwater from two RCRA-closed landfills (Pits 1 and 7), from one CERCLA-closed landfill (Pit 6), from one RCRA-closed hazardous waste treatment facility (Building 829 Facility [B829]), from two active Class II water impoundments (surface impoundments), and from sewage generated at Site 300.

COCs for Pits 1 and 7 became effective upon RCRA closure of Pits 1 and 7 in 1993. COCs for Pit 6 became effective upon CERCLA closure of Pit 6 in 1998. COCs for B829 became effective upon RCRA closure in 1999. COCs associated with WDR Order 96-248 became effective in 1996.

WDR Order 96-248 specifies environmental compliance monitoring of the sewage ponds at Site 300 and the COCs to be measured in applicable groundwater samples (CVRWQCB 1996). A three-tiered groundwater compliance monitoring network detects any releases of COCs from the two surface impoundments at Site 300.

- Primary release detection is through weekly inspections for flow at the outfalls of leachate collection and removal systems (LCRSs) installed between the inner and outer liners of each of the impoundments.
- Secondary release detection is a quarterly operation of lysimeters installed in the vadose zone beneath the outer liners to collect any water present for analysis.
- Tertiary release detection is a quarterly sampling of groundwater in the vicinity of the impoundments via monitoring wells with examination of analytical data for specific COCs.

[1] The listed COCs are not all routinely monitored at every surveillance location.

Table 8-1. Groundwater monitoring, inorganic COCs, analytical methods, reporting limits, and action level concentrations

Constituent of concern (COC)	Analytical method	Reporting limit[a]	Action level concentration
Metals and minerals (mg/L)			
All alkalinities	EPA 310.1	1	TBD[b]
Aluminum	EPA 200.7 or 200.8	0.05	MCL[c]
Ammonia nitrogen (as N)	EPA 350.1, 350.2, or 350.3	0.025	RL[d]
Antimony	EPA 204.2 or 200.8	0.005	MCL
Arsenic	EPA 206.2 or 200.8	0.002	MCL
Barium	EPA 200.7 or 200.8	0.025	MCL
Beryllium	EPA 210.2 or 200.8	0.0002	MCL
Cadmium	EPA 213.2 or 200.8	0.0005	MCL
Calcium	EPA 200.7	0.5	TBD
Chloride	EPA 300.0	0.5	TBD
Chromium	EPA 218.2, 200.7, or 200.8	0.001	MCL
Chromium(VI)	EPA 218.4 or 7196	0.002	MCL
Cobalt	EPA 200.7 or 200.8	0.025	TBD
Copper	EPA 200.7, 220.2, or 200.8	0.001	MCL
Fluoride	EPA 340.1 or 340.2	0.05	MCL
Hardness, total (as $CaCO_3$)	SM2320B[e]	1	TBD
Iron	EPA 200.7 or 200.8	0.1	TBD
Lead	EPA 239.2 or 200.8	0.002	MCL
Magnesium	EPA 200.7 or 200.8	0.5	TBD
Manganese	EPA 200.7 or 200.8	0.03	RL
Mercury	EPA 245.1, 245.2, or 200.8	0.0002	MCL
Molybdenum	EPA 200.7	0.025	TBD
Nickel	EPA 249.2, 200.7, 200.8	0.002	MCL
Nitrate (as NO_3)	EPA 353.2, 354.1, or 300.0	0.5	MCL
Orthophosphate	EPA 300.0, 365.1, or 365.2	0.05	TBD
Perchlorate	EPA 314.0	0.004	TBD
Potassium	EPA 200.7 or 200.8	1	TBD
Selenium	EPA 270.2 or 200.8	0.002	MCL
Silver	EPA 272.2 or 200.8	0.0005	TBD
Sodium	EPA 200.7	1	TBD
Sulfate	EPA 300.0	1	TBD
Surfactants	EPA 425.1	0.5	TBD
Thallium	EPA 279.2 or 200.8	0.001	MCL
Total dissolved solids	EPA 160.1	1	TBD
Total Kjeldahl nitrogen	EPA 351.2 or 351.3	0.2	TBD
Vanadium	EPA 200.7 or 200.8	0.02	TBD
Zinc	EPA 200.7 or 200.8	0.02	TBD

(continued)

Table 8-1. Groundwater monitoring, inorganic COCs, analytical methods, reporting limits, and action level concentrations (concluded)

Constituent of concern (COC)	Analytical method	Reporting limit[a]	Action level concentration
General indicator parameters			
pH	EPA 150.1	none	TBD
Conductivity (µmho/cm)	EPA 120.1	none	TBD
Total organic carbon (mg/L)	EPA 9060	1.0	TBD
Total organic halides (mg/L)	EPA 9020	0.01	TBD
Explosive compounds (µg/L)			
HMX[f]	EPA 8330	1 or 5	TBD
RDX[g]	EPA 8330	1 or 5	TBD
TNT[h]	EPA 8330	5	TBD
Radioactivity (Bq/L)			
Gross alpha	EPA 900.0	0.074	MCL
Gross beta	EPA 900.0	0.111	MCL
Radioisotopes (Bq/L)			
Americium 241	U-NAS-NS-3050	0.0037	RL
Plutonium 238	U-NAS-NS-3050	0.0037	RL
Plutonium 239 + 240	U-NAS-NS-3050	0.0037	RL
Radon-222	EPA 913.0	3.7	TBD
Radium-226	EPA 903.1	0.009	MCL
Radium-228	EPA 904.0	0.037	MCL
Thorium-228	U-NAS-NS-3050	0.009	TBD
Thorium-232	U-NAS-NS-3050	0.006	TBD
Tritium	EPA 906.0	3.7	MCL
Uranium-234	EPA 907	0.0037	MCL
Uranium-235	EPA 907	0.0037	MCL
Uranium-238	EPA 907	0.0037	MCL

a The significant figures displayed in this table vary by COC. These variations reflect regulatory agency permit stipulations, or the applicable analytical laboratory contract under which the work was performed, or both. Reporting limits listed are lowest possible limits as of November 2001.

b TBD = To be determined

c MCL = Maximum contaminant level

d RL = Reporting limit

e SM = Standard Methods, rather than EPA Methods

f HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

g RDX = hexahydro-1,3,5-trinitro-1,3,5-triazine

h TNT = 2,4,6-trinitrotoluene

Table 8-2. Analytical methods and contractual reporting limits for organic constituents of concern in groundwater

Constituents of concern	Reporting limit (µg/L)[a,b]
EPA Method 420.1	
Phenolics	5
EPA Method 502.2 (or 524.2)	
1,1,1,2-Tetrachloroethane	0.2
1,1,1-Trichloroethane	0.2
1,1,2,2-Tetrachloroethane	0.2
1,1,2-Trichloroethane	0.2
1,1-Dichloroethane	0.2
1,1-Dichloroethene	0.2
1,1-Dichloropropene	0.2
1,2,3-Trichlorobenzene	0.2
1,2,3-Trichloropropane	0.2
1,2,4-Trichlorobenzene	0.2
1,2,4-Trimethylbenzene	0.2
1,2-Dichlorobenzene	0.2
1,2-Dichloroethane	0.2
1,2-Dichloropropane	0.2
1,3,5-Trimethylbenzene	0.2
1,3-Dichlorobenzene	0.2
1,3-Dichloropropane	0.2
1,4-Dichlorobenzene	0.2
2,2-Dichloropropane	0.2
2-Chlorotoluene	0.2
4-Chlorotoluene	0.2
Benzene	0.2
Bromobenzene	0.2
Bromochloromethane	0.2
Bromodichloromethane	0.2
Bromoform	0.2
Bromomethane	0.2
Carbon tetrachloride	0.2
Chlorobenzene	0.2
Chloroethane	0.2
Chloroform	0.2
Chloromethane	0.2
cis-1,2-Dichloroethene	0.2
cis-1,3-Dichloropropene	0.5
Dibromochloromethane	0.2
Dibromomethane	0.2
Dichlorodifluoromethane	0.2
Ethylbenzene	0.2
Freon 113	0.2
Hexachlorobutadiene	0.2
Isopropylbenzene	0.2
m- and *p*-Xylene isomers	0.2
Methylene chloride	0.2
n-Butylbenzene	0.2
n-Propylbenzene	0.2
Naphthalene	0.2
o-Xylene	0.2
Isopropyl toluene	0.2
sec-Butylbenzene	0.2
Styrene	0.2
tert-Butylbenzene	0.2
Tetrachloroethene	0.2
Toluene	0.2
trans-1,2-Dichloroethene	0.2
trans-1,3-Dichloropropene	0.2
Trichloroethene	0.2
Trichlorofluoromethane	0.2
Vinyl chloride	0.2
EPA Method 507 (or 525.2)	
Alachlor	0.5
Atraton	0.5
Atrazine	0.5
Bromacil	0.5
Butachlor	0.5
Diazinon	0.5
Dichlorvos	0.5
Ethoprop	0.5
Merphos	0.5
Metolachlor	0.5
Metribuzin	0.5
Mevinphos	0.5
Molinate	0.5
Prometon	0.5

(continued)

Table 8-2. Analytical methods and contractual reporting limits for organic constituents of concern in groundwater (continued)

Constituents of concern	Reporting limit (µg/L)[a,b]
EPA Method 507 (or 525.2) (continued)	
Prometryn	0.5
Simazine	0.5
Terbutryn	0.5
EPA Method 524.2	
1,1,1,2-Tetrachloroethane	1
1,1,1-Trichloroethane	1
1,1,2,2-Tetrachloroethane	1
1,1,2-Trichloroethane	1
1,1-Dichloroethane	1
1,1-Dichloroethene	1
1,1-Dichloropropene	1
1,2,3-Trichlorobenzene	1
1,2,3-Trichloropropane	1
1,2,4-Trichlorobenzene	1
1,2,4-Trimethylbenzene	1
1,2-Dibromo-3-chloropropane	2
1,2-Dichlorobenzene	1
1,2-Dichloroethane	1
1,2-Dichloropropane	1
1,3,5-Trimethylbenzene	1
1,3-Dichlorobenzene	1
1,3-Dichloropropane	1
1,4-Dichlorobenzene	1
2-Chlorotoluene	1
4-Chlorotoluene	1
Benzene	1
Bromobenzene	1
Bromodichloromethane	1
Bromoform	1
Bromomethane	2
Carbon tetrachloride	1
Chlorobenzene	1
Chloroethane	2
Chloroform	1
Chloromethane	2
cis-1,2-Dichloroethene	1
cis-1,3-Dichloropropene	1
Dibromochloromethane	1
Dibromomethane	1
Dichlorodifluoromethane	2
Ethylbenzene	1
Ethylene dibromide	1
Freon 113	1
Hexachlorobutadiene	1
Isopropylbenzene	1
m- and *p*-Xylene isomers	1
Methylene chloride	1
n-Butylbenzene	1
n-Propylbenzene	1
Naphthalene	1
o-Xylene	1
Isopropyl toluene	1
sec-Butylbenzene	1
Styrene	1
tert-Butylbenzene	1
Tetrachloroethene	1
Toluene	1
trans-1,2-Dichloroethene	1
trans-1,3-Dichloropropene	1
Trichloroethene	0.5
Trichlorofluoromethane	1
Vinyl chloride	2
EPA Method 547	
Glyphosate	20
EPA Method 601	
1,1,1-Trichloroethane	0.5
1,1,2,2-Tetrachloroethane	0.5
1,1,2-Trichloroethane	0.5
1,1-Dichloroethane	0.5
1,1-Dichloroethene	0.5
1,2-Dichlorobenzene	0.5
1,2-Dichloroethane	0.5

(continued)

Table 8-2. Analytical methods and contractual reporting limits for organic constituents of concern in groundwater (continued)

Constituents of concern	Reporting limit (µg/L)[a,b]
EPA Method 601 (continued)	
1,2-Dichloroethene (total)	0.5
1,2-Dichloropropane	0.5
1,3-Dichlorobenzene	0.5
1,4-Dichlorobenzene	0.5
2-Chloroethylvinylether	0.5
Bromodichloromethane	0.5
Bromoform	0.5
Bromomethane	0.5
Carbon tetrachloride	0.5
Chlorobenzene	0.5
Chloroethane	0.5
Chloroform	0.5
Chloromethane	0.5
cis-1,2-Dichloroethene	0.5
cis-1,3-Dichloropropene	0.5
Dibromochloromethane	0.5
Dichlorodifluoromethane	0.5
Freon 113	0.5
Methylene chloride	0.5
Tetrachloroethene	0.5
trans-1,2-Dichloroethene	0.5
trans-1,3-Dichloropropene	0.5
Trichloroethene	0.5
Trichlorofluoromethane	0.5
Vinyl chloride	0.5
EPA Method 602	
1,2-Dichlorobenzene	0.3
1,3-Dichlorobenzene	0.3
1,4-Dichlorobenzene	0.3
Benzene	0.4
Chlorobenzene	0.3
Ethylbenzene	0.3
m-Xylene isomers	0.4
o-Xylene	0.4
p-Xylene	0.4
Toluene	0.3
Total xylene isomers	0.4
EPA Method 608	
Aldrin	0.05
BHC, alpha isomer	0.05
BHC, beta isomer	0.05
BHC, delta isomer	0.05
BHC, gamma isomer (Lindane)	0.05
Chlordane	0.2
Dieldrin	0.1
Endosulfan I	0.05
Endosulfan II	0.1
Endosulfan sulfate	0.1
Endrin	0.1
Endrin aldehyde	0.1
Heptachlor	0.05
Heptachlor epoxide	0.05
Methoxychlor	0.5
4,4'-DDD	0.1
4,4'-DDE	0.1
4,4'-DDT	0.1
Toxaphene	1
EPA Method 615	
2,4,5-T	0.5
2,4,5-TP (Silvex)	0.2
2,4-D	1
2,4-Dichlorophenoxy acetic acid	2
Dalapon	10
Dicamba	1
Dichloroprop	2
Dinoseb	1
MCPA	250

(continued)

Table 8-2. Analytical methods and contractual reporting limits for organic constituents of concern in groundwater (continued)

Constituents of concern	Reporting limit (µg/L)[a,b]
EPA Method 615 (continued)	
MCPP	250
EPA Method 624	
1,1,1-Trichloroethane	1
1,1,2,2-Tetrachloroethane	1
1,1,2-Trichloroethane	1
1,1-Dichloroethane	1
1,1-Dichloroethene	1
1,2-Dichlorobenzene	1
1,2-Dichloroethane	1
1,2-Dichloroethene (total)	1
1,2-Dichloropropane	1
1,3-Dichlorobenzene	1
1,4-Dichlorobenzene	1
2-Butanone	20
2-Chloroethylvinylether	20
2-Hexanone	20
4-Methyl-2-pentanone	20
Acetone	10
Benzene	1
Bromodichloromethane	1
Bromoform	1
Bromomethane	2
Carbon disulfide	1
Carbon tetrachloride	1
Chlorobenzene	1
Chloroethane	2
Chloroform	1
Chloromethane	2
cis-1,2-Dichloroethene	1
cis-1,3-Dichloropropene	1
Dibromochloromethane	1
Dibromomethane	1
Dichlorodifluoromethane	2
Ethylbenzene	1
Freon 113	1
Methylene chloride	1
Styrene	1
Tetrachloroethene	1
Toluene	1
Total xylene isomers	2
trans-1,2-Dichloroethene	1
trans-1,3-Dichloropropene	1
Trichloroethene	0.5
Trichlorofluoromethane	1
Vinyl acetate	1
Vinyl chloride	1
EPA Method 625	
1,2,4-Trichlorobenzene	5
1,2-Dichlorobenzene	5
1,3-Dichlorobenzene	5
1,4-Dichlorobenzene	5
2,4,5-Trichlorophenol	5
2,4,6-Trichlorophenol	5
2,4-Dichlorophenol	5
2,4-Dimethylphenol	5
2,4-Dinitrophenol	25
2,4-Dinitrotoluene	5
2,6-Dinitrotoluene	5
2-Chloronaphthalene	5
2-Chlorophenol	5
2-Methylphenol	5
2-Methyl-4,6-dinitrophenol	25
2-Methylnaphthalene	5
2-Nitroaniline	25
3,3'-Dichlorobenzidine	10
3-Nitroaniline	25
4-Bromophenylphenylether	5
4-Chloro-3-methylphenol	10
4-Chloroaniline	10
4-Chlorophenylphenylether	5
4-Nitroaniline	25
4-Nitrophenol	25
Acenaphthene	25
Acenaphthylene	5
Anthracene	5

(continued)

Table 8-2. Analytical methods and contractual reporting limits for organic constituents of concern in groundwater (continued)

Constituents of concern	Reporting limit (µg/L)[a,b]
EPA Method 625 (continued)	
Benzo[*a*]anthracene	5
Benzo[*a*]pyrene	5
Benzo[*b*]fluoranthene	5
Benzo[*g,h,i*]perylene	5
Benzo[*k*]fluoranthene	5
Benzoic acid	25
Benzyl alcohol	10
Bis(2-chloroethoxy)methane	5
Bis(2-chloroisopropyl)ether	5
Bis(2-ethylhexyl)phthalate	5
Butylbenzylphthalate	5
Chrysene	5
Di-*n*-butylphthalate	5
Di-*n*-octylphthalate	5
Dibenzo[*a,h*]anthracene	5
Dibenzofuran	5
Diethylphthalate	5
Dimethylphthalate	5
Fluoranthene	5
Fluorene	5
Hexachlorobenzene	5
Hexachlorobutadiene	5
Hexachlorocyclopentadiene	5
Hexachloroethane	5
Indeno[*1,2,3-c,d*]pyrene	5
Isophorone	5
m- and *p*-Cresol	5
N-Nitroso-di-*n*-propylamine	5
Naphthalene	5
Nitrobenzene	5
Pentachlorophenol	5
Phenanthrene	5
Phenol	5
Pyrene	5
	5

Constituents of concern	Reporting limit (µg/L)[a,b]
EPA Method 632	
Diuron	0.1
EPA Method 8082	
Polychlorinated biphenyls	0.5
EPA Method 8140	
Bolstar	1
Chlorpyrifos	1
Coumaphos	1
Demeton	1
Diazinon	1
Dichlorvos	1
Disulfoton	1
Ethoprop	1
Fensulfothion	1
Fenthion	1
Merphos	1
Methyl Parathion	1
Mevinphos	1
Naled	1
Phorate	1
Prothiophos	1
Ronnel	1
Stirophos	1
Trichloronate	1
EPA Method 8260	
1,1,1,2-Tetrachloroethane	0.5
1,1,1-Trichloroethane	0.5
1,1,2,2-Tetrachloroethane	0.5
1,1,2-Trichloroethane	0.5
1,1-Dichloroethane	0.5
1,1-Dichloroethene	0.5
1,2,3-Trichloropropane	0.5
1,2-Dibromo-3-chloropropane	0.5
1,2-Dichloroethane	0.5
1,2-Dichloroethene (total)	0.5

(continued)

Table 8-2. Analytical methods and contractual reporting limits for organic constituents of concern in groundwater (concluded)

Constituents of concern	Reporting limit (µg/L)[a,b]
EPA Method 8260 (continued)	
1,2-Dichloropropane	0.5
2-Butanone	0.5
2-Chloroethylvinylether	0.5
2-Hexanone	0.5
4-Methyl-2-pentanone	0.5
Acetone	10
Acetonitrile	100
Acrolein	50
Acrylonitrile	50
Benzene	0.5
Bromodichloromethane	0.5
Bromoform	0.5
Bromomethane	0.5
Carbon disulfide	5
Carbon tetrachloride	0.5
Chlorobenzene	0.5
Chloroethane	0.5
Chloroform	0.5
Chloromethane	0.5
Chloroprene	5
Dibromochloromethane	0.5
Dichlorodifluoromethane	0.5
Ethanol	1000
Ethylbenzene	0.5
Freon 113	0.5
Methylene chloride	0.5
Styrene	0.5
Tetrachloroethene	0.5
Toluene	0.5
Total xylene isomers	0.5
Trichloroethene	0.5
Trichlorofluoromethane	0.5
Vinyl acetate	20
Vinyl chloride	0.5
cis-1,2-Dichloroethene	0.5
cis-1,3-Dichloropropene	0.5
trans-1,2-Dichloroethene	0.5
trans-1,3-Dichloropropene	0.5
EPA Method 8330	
HMX[c]	5 or 1
RDX[d]	5 or 1
TNT[e]	5

a The significant figures displayed in this table vary by constituents of concern. These variations reflect regulatory agency permit stipulations, the applicable analytical laboratory contract under which the work was performed, or both.

b Analytical reporting limits varied by laboratory used.

c HMX is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

d RDX is hexahydro-1,3,5-trinitro-1,3,5-triazine.

e TNT is 2,4,6-trinitrotoluene.

8.1.3 Livermore Site Groundwater Monitoring Program

8.1.3.1 Livermore Site Geology and Hydrogeology

The Livermore Valley is bordered on the east by the Altamont Hills, where Miocene Neroly and Cierbo Formations and rocks of the Late Cretaceous Great Valley sequence are exposed. Within the valley, lacustrine and fluvial valley fill deposits occur to depths in excess of 1 km. The oldest of these is the Lower Livermore Formation of late Tertiary age—a hard, locally lithified, predominantly fine-grained sedimentary sequence that is exposed in the hills south of the

Livermore Valley. This formation is encountered beneath the Livermore site at depths ranging from 7 m in the east to 119 m in the west. Above the Lower Livermore Formation are the heterogeneous, unconsolidated alluvial sediments of the Pleistocene Upper Livermore Formation, which consist of complexly interbedded layers of poorly sorted clay, silt, sand, and gravel. The late Pleistocene and Holocene alluvial deposits that form the uppermost sequence of valley sediments are virtually identical to the Upper Livermore Formation.

Table 8-3. Radioisotopes and reporting limits for gamma spectroscopic analysis of constituents of concern in groundwater[(a)]

Constituents of concern	Typical reporting limit (Bq/L)
Americum-241	1.3
Cesium-134	0.5
Cesium-137	0.4
Cobalt-60	0.4
Europium-152	1.0
Europium-154	1.2
Europium-155	1.0
Potassium-40	3.7
Radium-226	0.6
Thorium-228	0.9
Uranium-235	1.5

a The significant figures displayed in this table vary by constituents of concern. These variations reflect the applicable analytical laboratory contract under which the work was performed.

The Livermore Formation and overlying alluvial deposits contain the aquifers of the Livermore Valley groundwater basin. This is an important water-bearing formation. Natural recharge occurs primarily along the fringes of the basin and through the arroyos during periods of winter flow. The Zone 7 Water Agency conducts artificial recharge as needed to maintain groundwater levels. This recharge is done by releasing water from Lake Del Valle or from the South Bay Aqueduct into arroyo channels in the eastern portion of the valley. Groundwater flow in the Livermore Valley generally moves toward the central east-west axis of the valley and then westward through the central basin. Groundwater flow in the basin is generally assumed to be primarily horizontal, although a significant vertical component probably exists in fringe areas and under localized sources of recharge.

Beneath the Livermore site, depth to the water table varies from about 8 to 40 m. At the eastern edge of the Livermore site, groundwater gradients (changes in elevation per unit of horizontal distance) are quite steep, but under most of the site and farther to the west, the contours flatten to a gradient of approximately 0.003. Groundwater flow under the northern and western portions of the site is generally westward. Aquifer tests on monitoring wells in the vicinity of the Livermore site indicate that the hydraulic conductivity of the permeable sediments ranges from 1 to 16 m/day. This, in combination with observed water-table gradients, yields groundwater velocity estimates of 5 to 90 m/year. The range in these values reflects the heterogeneity typical of the alluvial sediments that underlie the area (Thorpe et al. 1990).

Figure 8-1 is an east-west cross-section along East Avenue showing the hydrostratigraphic units (HSUs) underlying the Livermore site. This cross section extends slightly past the western edge of LLNL at Vasco Road. The water table cuts across HSUs so that the shallowest water-saturated HSU (the uppermost aquifer) is HSU-6 at the southeastern corner of the site at Greenville Road and HSU-1B and HSU-2 along and toward the western site boundary (Vasco Road).

8.1.3.2 Livermore Site Existing Contamination

The requirements in DOE Order 5400.1 for a groundwater monitoring program include the identification of existing and potential groundwater contamination sources and surveillance of these sources. The following eight chlorinated solvents were detected in LLNL study area groundwater at concentrations exceeding federal or state MCLs: trichloroethene (TCE); tetrachloroethene (PCE); 1,1-dichloroethene (1,1-DCE); 1,2-dichloroethene (1,2-DCE); 1,2-dichloroethane (1,2-DCA); 1,1-dichloroethane (1,1-DCA); carbon tetrachloride; and chloroform. TCE and PCE are the predominant volatile organic compounds (VOCs) and are generally concentrated within HSUs 1B and 2. Tritium is present in groundwater near the East Taxi Strip Area mostly in HSU-3A and HSU-3B (Thorpe et al. 1990).

8.1.3.3 Livermore Site Potential Sources of Groundwater Contaminants

Surveillance monitoring of existing groundwater wells is performed at the Livermore site. This network monitors possible COCs other than the VOCs that are monitored under the restoration program's Livermore Site Groundwater Project. Groundwater from this area flows offsite toward the southwest (Hoffman et al. 1993; Macdonald et al. 1994). The list of potential sources is long and includes those described in the *CERCLA Remedial Investigations Report for the LLNL Livermore Site* (Thorpe et al. 1990). Wastes at the Livermore site that could potentially become pollutants to the groundwater include metals, VOCs, petroleum hydrocarbons, pesticides and herbicides, and radioactive wastes. Contamination sources (including leaking underground storage tanks and possibly leaking sanitary sewage pipes) were evaluated during the 1992–1996

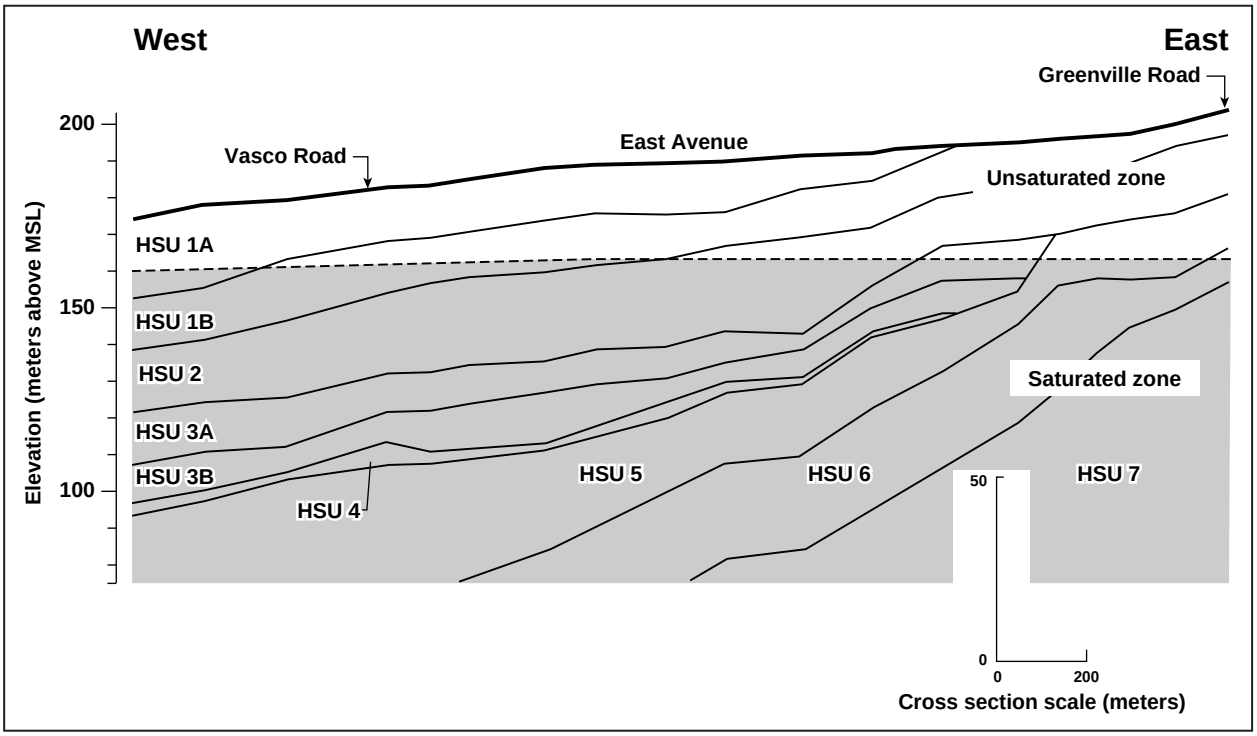

Figure 8-1. Livermore site hydrostratigraphic east-west cross-section along East Avenue

Tank Upgrade Project and the 1991–1995 Sanitary Sewer Rehabilitation Project, respectively. As a result of the Sanitary Sewer Rehabilitation Project, more than 6000 m of sanitary sewer pipes were lined to reduce exfiltration into the sediments and groundwater. The Building Drain Repair Project of 1994–1995 redirected funds from the Sanitary Sewer Rehabilitation Project to remove or redirect improper discharges that could also affect the groundwater (see *Environmental Report 1994* [Harrach et al. 1995]).

Two potential sources of groundwater contamination initially evaluated before the sitewide remedial investigation—the Taxi Strip Area and the East Traffic Circle Landfill—were further assessed for surveillance purposes through groundwater monitoring beginning in 1997. Radioactively contaminated liquid wastes had been deposited in four disposal pits in the Taxi Strip Area from 1953 through about 1976, according to the remedial investigation (Thorpe et al. 1990). Contaminants detected in the soil were VOCs, metals, and various radionuclides. The radionuclides initially detected in the soils and other materials were transuranics (unspecified), americium-241, uranium-235, and cesium-137 (Buerer 1983). The cleanup removed about 3000 cubic meters of contaminated soil and sediments.

At the East Traffic Circle Landfill, polychlorinated biphenyls (PCBs), metals, and various radionuclide contaminants were initially detected in the soil. The radionuclides detected by gamma spectroscopy in the soils and other materials were, in order of abundance: cesium-137, depleted uranium, radium-226, thorium-232, uranium-238, americium-241, and some cobalt-60 (McConachie et al. 1986). Cleanup involved the excavation and removal of 11,000 cubic meters of debris and soil with metal shavings, broken bottles, and capacitors. About 6 cubic meters of the total material excavated contained radioactive material (Thorpe et al. 1990; McConachie et al. 1986).

Although contaminated sediments were removed from both of these WMUs, and the depth to groundwater is greater than 20 m, LLNL continues the monitoring to determine that no hazardous materials have reached the groundwater. Monitoring wells downgradient from these two areas (already used for restoration monitoring for VOCs and tritium) were added to the surveillance monitoring network during 1997.

Although the National Ignition Facility (NIF) begins operations in 2003, it is prudent to obtain a baseline of groundwater quality prior to start of operations. Those operations will use significant quantities of tritium.

The hazardous waste/mixed waste storage facilities around Buildings 514 and 612 are a potential source of contamination for all types of radioactive and hazardous materials. Another potential source of groundwater contamination is the Decontamination and Waste Treatment Facility (DWTF) in the northeastern portion of LLNL that replaces the mixed waste storage areas of Buildings 514 and 612.

During the fourth quarter of 1999, LLNL began monitoring the uppermost saturated aquifers (HSU-1B and HSU-2) both hydrologically upgradient and downgradient from the Tritium and Plutonium Facilities (Buildings 331 and 332, respectively). This monitoring provides a baseline for any contamination that may be present, prior to expected increases in processing activities in both facilities and monitoring during those increased activities.

At the Livermore site, many utility vaults receive storm water runoff that can become contaminated from equipment and pollutants. These collected wastewaters are sampled and analyzed on a representative basis to determine proper disposal. It is expected that these utility vaults may have contributed some amount of hazardous wastes into the sediments and groundwater. This effort is discussed further in Chapter 7. Other sources of contamination are investigated on a case-by-case basis, as they are discovered, to determine whether further groundwater monitoring is warranted.

The COCs chosen for the surveillance sampling program are determined largely by knowledge of materials used at the Livermore site. All surveillance wells are now analyzed for general water quality parameters, usually called general minerals.

Tables 8-1, **8-2**, and **8-3** include the surveillance COCs at the Livermore site. Each surveillance monitoring well is analyzed for metals and minerals, gross alpha and beta, tritium, strontium-90, radium and uranium radioisotopes (**Table 8-1**), and herbicides (**Table 8-2**) currently used on site. Each perimeter surveillance monitoring well is also sampled and analyzed, annually at a minimum, for plutonium-238 and plutonium-239+240. Monitoring frequency and COCs are reviewed annually to determine whether they satisfy our surveillance needs. Additional radioisotopes (thorium-228, thorium-230, thorium-232, plutonium-238, plutonium-239+240, and americium-241) are measured by alpha spectroscopy (**Table 8-1**); cesium-137, cobalt-60, and potassium-40 are measured by gamma spectroscopy (**Table 8-3**), especially in the vicinity of the Taxi Strip and the East Traffic Circle Landfill areas. PCBs are measured by EPA Method 608 (**Table 8-2**) at monitoring wells downgradient from the Taxi Strip Area and downgradient from the East Traffic Circle Landfill, as discussed in the previous **Section 8.1.3.3**.

8.1.4 Site 300 Groundwater Monitoring Program

8.1.4.1 Site 300 Geology and Hydrogeology

Details of Site 300 geology and hydrogeology may be found in early studies edited by Raber and Carpenter (1983), and in subsequent CERCLA remedial investigations edited by Webster-Scholten (1994) and in Taffet et al. (1996). Site 300 is generally underlain by gently dipping sedimentary bedrock dissected by steep ravines. Topographic relief at the site is about 300 m. Elevations range from about 200 m in the southeast to more than 500 m in the northwest. The bedrock is formed primarily of interbedded sandstone, siltstone, and claystone. The Neroly Formation is the principal hydrologic unit. The Neroly Formation is about 150 m thick and consists of distinctive blue-gray to brown weathering volcaniclastic sandstone and sandy siltstone, interbedded with light gray weathering tuffaceous claystone and conglomerate. It is exposed extensively within the northern half of Site 300. The Neroly Formation is also present in the subsurface underlying the southeastern portion of the Site. **Figure 8-2** is a generalized stratigraphic diagram of Site 300 near-surface rocks and sediments. Surficial sediments have been derived from the underlying bedrock by weathering and mass wasting. They include alluvium, colluvium, valley-fill, and land-slide materials.

Groundwater recharge from rain at Site 300 occurs predominantly in locations where saturated alluvium valley fill contacts underlying permeable bedrock, or where bedrock strata crop out. Local recharge also occurs on hilltops, creating perched groundwater. Low rainfall, high

evapotranspiration, steep topography, and intervening aquitards generally preclude direct vertical recharge of the deeper bedrock. Unconfined groundwater resides mostly in the Tertiary Neroly Formation lower blue sandstone ($Tnbs_1$ in **Figure 8-2**). Significant unconfined groundwater is also locally present in permeable Quaternary valley fill and terrace sediments (Qal and Qt, respectively, in **Figure 8-2**). Much less groundwater is present in the unnamed Pliocene nonmarine unit (Tps in **Figure 8-2**), where it occurs as unconfined perched water. Tps is the youngest bedrock unit identified at Site 300 and is generally present only on hilltops. Where present, groundwater in Tps is frequently perched and is generally unconfined, although water under confined conditions occurs locally. Fine-grained siltstone and claystone interbeds ($Tnsc_1$ and $Tnsc_2$ in **Figure 8-2**) act as aquitards, confining layers, or perching horizons.

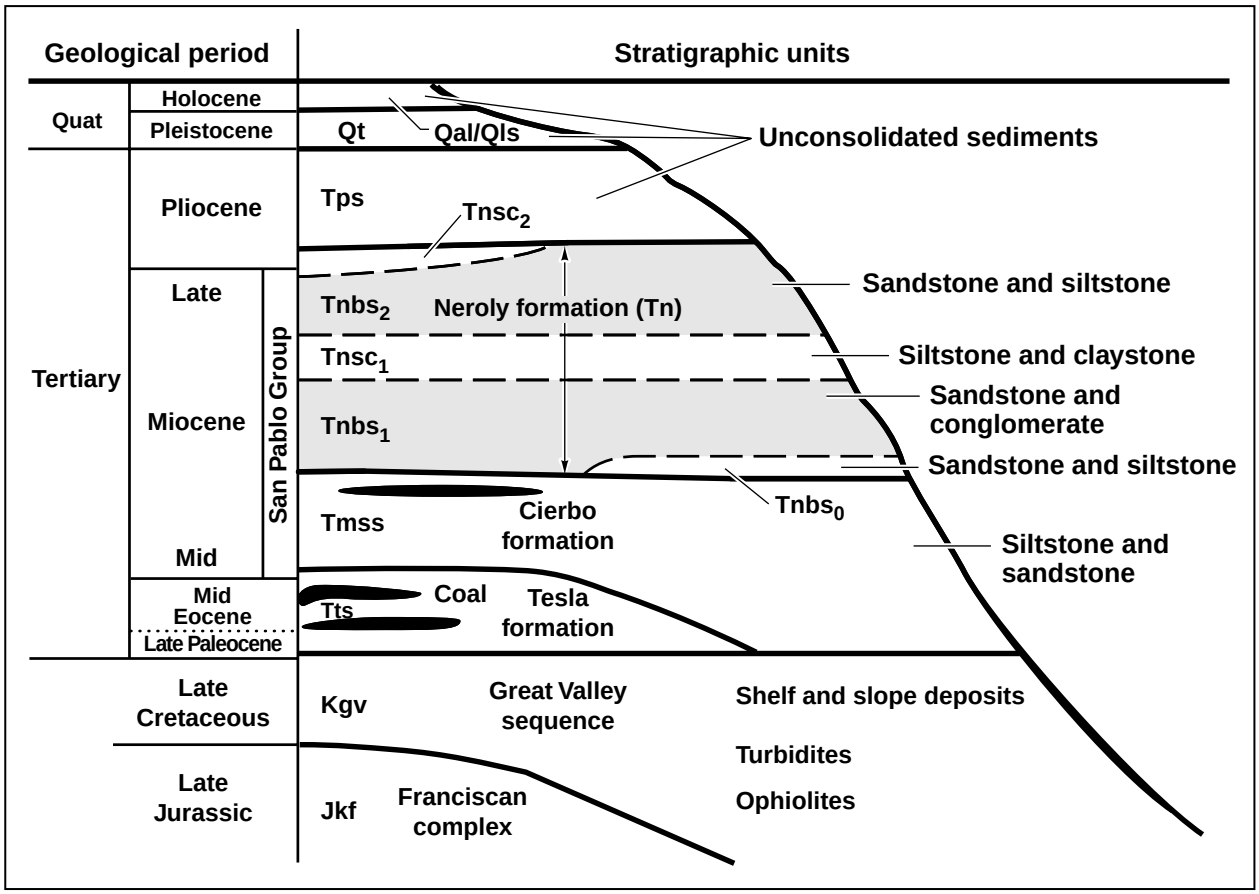

Figure 8-2. Site 300 stratigraphy

The bedrock sequence under Site 300 has been slightly deformed into several gentle, low-amplitude folds. The locations and characteristics of these folds, in combination with regional fault and fracture patterns, locally influence groundwater flow within the site. Groundwater flow follows the attitude (dip) of the bedrock. In the northern half of Site 300, north of the east-west trending Patterson anticline, groundwater flows generally east-northeast, except where it is locally influenced by groundwater in alluvium-filled ravines. In the southern half of the site, groundwater flows south-southeast. Knowledge of groundwater flow directions was used to place surveillance and compliance monitoring wells at Site 300.

Hydraulic conductivities in the water-bearing strata at Site 300 vary over three orders of magnitude, from 10^{-3} to 10^{-6} cm/s. Groundwater flow ranges from less than 1 to 40 m/year. Maximum flow rates occur in valley-fill deposits.

The uppermost, generally unconfined water-bearing zone is the primary target for groundwater monitoring at Site 300 because it contains most of the existing contamination, and it will be the first zone to be influenced by any new release of contaminants at or near the ground surface. Secondary targets are deeper, confined water-bearing zones. Multiple water-bearing zones are monitored using Barcad sampling devices at several locations in Doall Ravine and Elk Ravine to detect any downward movement of contaminated groundwater.

Confined groundwater is present mostly in the southern half of Site 300 where water supply Wells 18 and 20 are monitored. $Tnbs_2$ beds (**Figure 8-2**) are present throughout most of the southeastern part of Site 300 and locally in the northern part of the site. In the northern part of the Explosives Process Area, $Tnbs_2$ is unsaturated; but saturation increases downdip toward the south, resulting in local flowing artesian conditions in $Tnbs_2$ wells in the southern Explosives Process Area.

The Cierbo Formation (Tmss in **Figure 8-2**) of the Miocene age is saturated beneath Doall Ravine and the southern part of the East Firing Area. Tmss is unsaturated or does not otherwise yield water to wells in other parts of the East and West Firing Areas; this may be the result of swelling clays in pore spaces. The thickness of the Cierbo Formation is not well known because most boreholes are not deep enough to completely penetrate this formation. Some of the deeper wells in the General Services Area (GSA) penetrate the uppermost Tmss.

Alluvium of Quaternary age (Qal in **Figure 8-2**) is present as valley-fill in ravines throughout Site 300, but it is saturated only in the Corral Hollow Creek channel, in Doall Ravine in the West Firing Area, and in southern Elk Ravine in the East Firing Area near Spring 6 (location 812CRK). Saturated terrace deposits of Quaternary age (Qoa and Qt in **Figure 8-2**) are present in the Pit 6 area and in the GSA. Small quantities of groundwater are present in some local landslide deposits of Quaternary age (Qls in **Figure 8-2**).

8.1.4.2 Site 300 Existing Contamination in Groundwater

To determine the nature and extent of groundwater contamination at Site 300, approximately 450 groundwater monitoring wells have been installed since environmental investigations began in 1981. CERCLA site characterization studies took groundwater samples from numerous wells and springs. Samples of groundwater were analyzed for metals, inorganic compounds, organic compounds (including VOCs, BTEX,[2] high explosive [HE], total organic halides [TOX]), ions (including general minerals), phenols and phenolics, PCBs, and pesticides. Analytical methods used to detect organic compounds included EPA 524.2, EPA 601, EPA 602, EPA 604, EPA 608, EPA 624, Modified EPA 624, and EPA 625. Other EPA or standard methods were employed to detect HE compounds, Title 22 CCR metals, general minerals, tritium, gross alpha and beta, gamma, uranium isotopes, and radium isotopes. Sample data have revealed the limited extent of groundwater contamination (Webster-Scholten 1994; Taffet et al. 1996). CERCLA studies attribute many of the inorganic COCs detected, including some radioisotopes, to natural sources in the rocks and sediments.

Figure 8-3 shows the areas of groundwater contamination at Site 300 and identifies the main contaminants. Also identified are the names and area boundaries of operable units (OUs), where CERCLA remedial activities are currently focused. Contaminated groundwater is generally confined to the uppermost water-bearing zone in each area.

The highest tritium activity ever detected in groundwater was 44,000 Bq/L (1.2 μCi/L) in the northwestern part of the site in the Pit 7 Complex Area, which contains the closed landfill Pits 3, 4, 5, and 7 (where firing table gravel is buried). Tritium has been detected in groundwater in the vicinity of the Building 850 firing table. Three plumes of tritiated groundwater from Building 850 and Pits 3 and 5 in the Pit 7 Complex have commingled to form a continuous plume that extends northeast and southeast from the Pit 7 Complex, and from Building 850, northeast along Doall Ravine and southeast along Elk Ravine, approaching Buildings 801 and 802. During two periods of unusually high winter precipitation (1982–1983 and 1997–1998), tritium from buried gravel leached from Pits 3 and 5. Groundwater rose through the bottom of the pits and contacted tritiated gravel buried there. The infiltration of rain water and water used to prevent the resuspension of tritium-bearing dust in the vicinity of Building 850 resulted in the transfer of tritium from surface and subsurface soil moisture to groundwater beneath and downgradient of the building.

[2] The sum of benezene, ethylbenzene, toluene, and xylenen isomers.

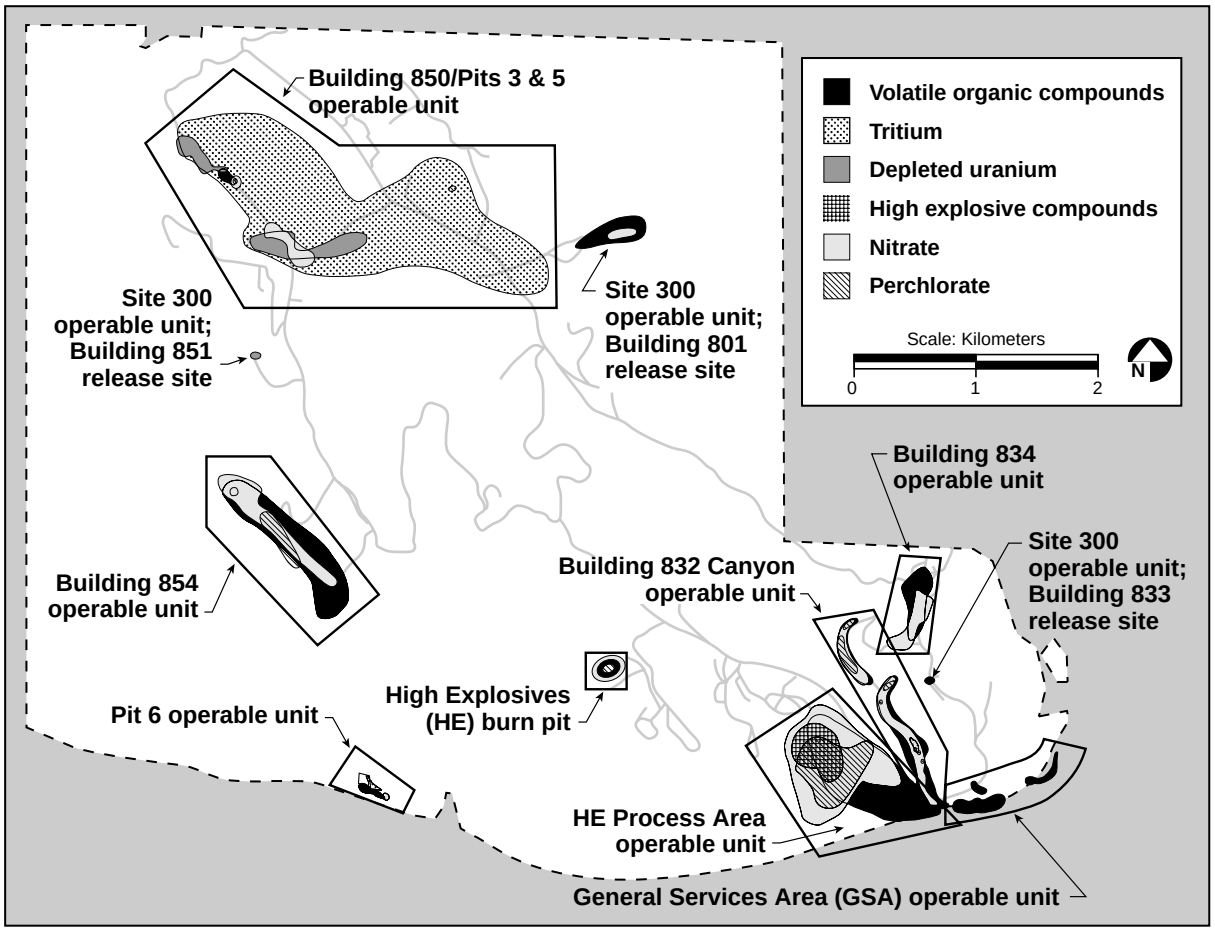

Figure 8-3. Boundaries of contaminated groundwater within building areas and operable units at Site 300

Three groundwater plumes of small extent contain depleted uranium released from Pit 5, Pit 7, and the Building 850 firing table area. Maximum detected groundwater uranium activity is 4.4 Bq/L (120 pCi/L), which represents the sum of depleted uranium and naturally occurring uranium (Taffet et al. 1996).

VOCs—including TCE; PCE; 1,2-DCE; chloroform; 1,1,1-trichloroethane (1,1,1-TCA); 1,1-DCE; 1,1-DCA; 1,2-DCA; Freon 11; and Freon 113—are detected at locations throughout Site 300. TCE is the primary VOC detected at the site. Samples from several monitoring wells in the East and West Firing Area (EWFA), including a well south of the Building 854 and 855 Complexes, contain trace concentrations of TCE. Distributions of tritium and TCE show generally declining trends since studies began in the early 1980s. Freon 113 is detected in three groundwater monitoring wells adjacent to closed landfill Pit 1. Historical evidence suggests that the Freon was released by means of spills, washdowns, and retention tank leaks at the Advanced Test

Accelerator (ATA Building 865), upgradient of Pit 1 (Webster-Scholten 1994). TCE is detected in samples from monitoring well K8-01 near Pit 8 (**Figure 8-7**). The TCE originates from historical discharges to the Building 801D dry well, upgradient of Pit 8.

TCE is detected in groundwater beneath several process and test complexes, maintenance facilities, and a few WMUs in the southern and southeastern portion of the site. The highest VOC concentration detected in groundwater is 0.5g/L of TCE beneath the Building 834 Complex (**Figure 8-3**) in the southeastern part of Site 300. CERCLA investigations detected VOCs (primarily TCE) in ephemeral perched groundwater below Building 833 (Webster-Scholten, 1994; Taffet et al. 1996). Groundwater in this hydrologic unit is present only briefly after significant precipitation and recharge. *Cis*-1,2-DCE; total-1,2-DCE; and toluene are also detected in samples from the shallow ephemeral perched groundwater zone.

Groundwater from several wells near Building 830 and Spring 3 in the Building 832 OU contains VOCs. Surface water samples from Spring 3, located downgradient (southwest) of Building 830, contain TCE. Although TCE is the primary contaminant of concern, *cis*-1,2-dichloroethene (*cis*-1,2-DCE); tetrachloroethene (PCE); chloroform; Freon 113; and methylene chloride have also been detected sporadically in groundwater samples.

CERCLA investigations indicate that VOCs (primarily TCE) exist in groundwater in the perched hydrologic units beneath the former HE burn pit, the HE Process Area, and downgradient (south) of the Building 834 Complex (Webster-Scholten 1994) (shown in **Figure 8-3**). The Building 834 Complex groundwater plume contains the highest TCE concentrations detected at Site 300. The plume extends nearly 500 m downgradient (south) of the Building 834 Complex. It varies from 50 to 150 m in width and is generally less than 2 m in thickness. Although TCE is the primary chemical of concern in this area, *cis*-1,2-DCE; PCE; diesel fuel; and tetra 2-ethylbutylorthosilicate (T-BOS) are also detected in groundwater samples. The presence of diesel fuel in the groundwater is attributed to overfilling of the Building 834 Complex underground diesel fuel tank.

TCE and the HE compounds, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are detected in groundwater beneath the HE Process Area. Dissolved zinc has also been detected at elevated concentrations in groundwater beneath the HE Process Area.

Environmental investigations in the GSA study area (**Figure 8-3**) identify VOCs in groundwater originating from several release locations (Webster-Scholten 1994). The primary chemical of concern detected in groundwater under the GSA is TCE. Between 1960 and 1986, VOCs were discharged to the environment from six dry wells, a steam-cleaning/sink area, and a solvent drum rack area in the central GSA. These releases resulted in two groundwater VOC plumes

along the southeastern Site 300 boundary. A TCE plume also was identified emanating from a debris burial trench in the eastern GSA. Although concentrations of TCE detected in the eastern GSA TCE plume are relatively low, the plume extends off site (east and north) along the Corral Hollow paleochannel from the debris burial trench.

CERCLA investigations identify the inactive Pit 6 WMU (**Figure 8-4**) as a confirmed release site for VOCs, and probably tritium (Webster-Scholten 1994; Ferry et al. 1998). VOCs (primarily TCE) are detected in groundwater from the first water-bearing zone present beneath Pit 6. The TCE plume is elongated at the southern Site 300 boundary, migrating east-southeast with the direction of groundwater flow. The shape of the plume is probably influenced by preferential groundwater flow within the Quaternary terrace gravel, which increases in thickness to the southeast. Surface water samples from two springs (Springs 7 and 15) in the vicinity of Pit 6 contain TCE. Since June 1991, concentrations of TCE in groundwater and the extent of the Pit 6 TCE plume have been decreasing. A small plume of tritium-bearing water has been identified adjacent to Pit 6 along its southeastern perimeter (Ferry et al. 1998).

8.1.4.3 Site 300 Potential Sources of Groundwater Contaminants

Site 300 operations historically used VOCs as solvents and as heat transfer fluids. HE compounds, metals, tritium, and depleted uranium were used in hydrodynamic tests conducted on open firing tables at Site 300. Fragments of these materials were released to gravel used on the firing tables and to soil and rock in the vicinity.

Present LLNL operations at Site 300 are designed and managed to minimize contamination of soil and bedrock. However, volumes of soil and rock were contaminated by historical LLNL operations, and some of the contaminants were released to groundwater beneath the site. Much of the contaminated soil and rock remains in place or is contained in landfills at the site. Removal actions, including the capping of four landfill pits, have significantly reduced the rates of contaminant migration to groundwater in those areas. However, other less contaminated volumes of soil and rock continue to release contaminants slowly to groundwater beneath Site 300. Under the unusual circumstance of excessive rainfall, rain infiltration, and water table rises, these sites could release additional contaminants to the underlying groundwater.

Compliance and surveillance groundwater monitoring programs implemented at Site 300 are capable of detecting small increases of COCs in groundwater. They provide LLNL management with critical information needed to evaluate the necessity of additional removal actions.

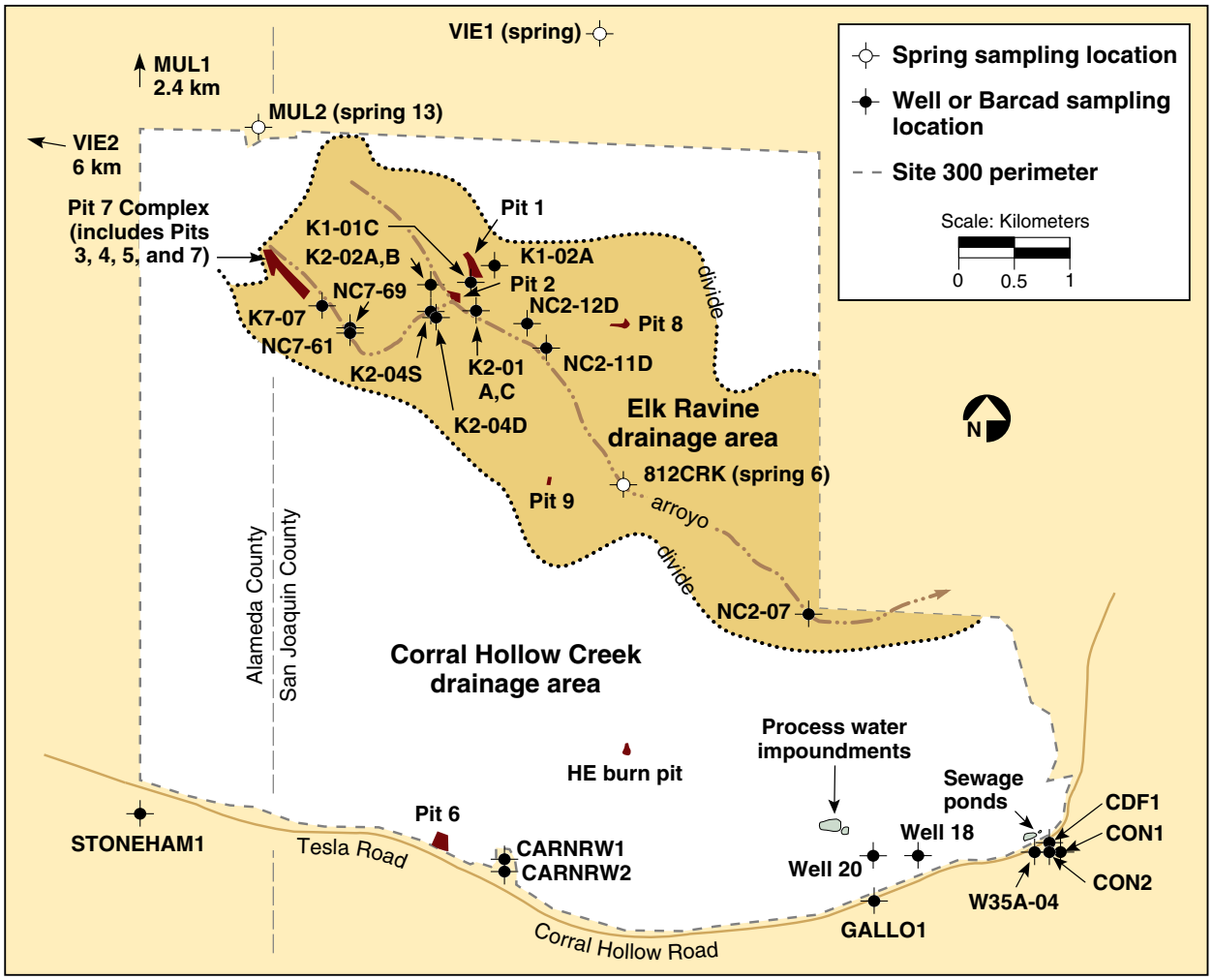

Figure 8-4. **Site 300 locations of pits (closed landfills), surface impoundments (process water), sewage ponds, and groundwater surveillance wells and springs**

Soil and rock analytic data were used to assess the nature and extent of contamination at Site 300. Initially, the site was divided into six study areas from which more than 4670 soil and rock samples were analyzed (Webster-Scholten 1994). Samples were collected at depths ranging from ground surface to 158 m. Most soil and rock samples were obtained during the drilling of exploratory and pilot boreholes. Analytic and historic data indicate that solvents and other VOCs were released at Site 300 via surface spills, discharges to disposal lagoons, dry wells, and pipe leaks. In general, the highest concentrations and greatest extent of soil and rock contamination coincide with areas of known surface or near-surface releases. A few of the more mobile COCs have migrated to groundwater.

Two VOCs (TCE and PCE), HE compounds, and tritium are the most prominent compounds detected in soil and rock at Site 300. Specifically, TCE and PCE are detected largely in the southern and southeastern portions of the site, whereas tritium is confined to the EWFA in the northern portion of Site 300. HE compounds are found primarily at decommissioned rinsewater lagoons in the Explosives Process Area. The highest VOC concentrations in soil and rock are present in the GSA and the Building 834 areas.

Environmental investigations of the Building 833 area identified TCE as the primary chemical of concern in soil and rock (Webster-Scholten 1994). Soil and rock samples collected in the vicinity of Buildings 830 and 833 and at Spring 3 suggest that TCE was released to the environment via surface spills near test cells and by discharges to septic systems and disposal lagoons.

From 1963 to 1978, tritium, depleted uranium, cadmium, copper, and other elements and compounds were used in hydrodynamic experiments conducted at some of the seven firing tables. Trace amounts of tritium were used through 1990. As a result of these experiments, tritium and other components of the experiments were released to surface and subsurface soil and rock in the vicinity of the firing tables. In addition, pea gravel that was placed on top of the firing tables to absorb the shock from explosive blasts frequently became contaminated with tritium. Because of compaction and accumulations of tritium radioactivity, the pea gravel was periodically removed and deposited in several landfills in the northern portion of Site 300.

Environmental investigations indicate that surface soil (less than 0.15 m) samples collected in the vicinity of the Buildings 801, 850, and 851 firing tables contain concentrations of cadmium, copper, and depleted uranium. In addition, surface soil collected in the vicinity of the Buildings 801 and 850 firing tables contain concentrations of beryllium. Soil samples collected from the Building 851 firing table also contain concentrations of zinc. These metals were probably released during hydrodynamic experiments on the firing tables.

Subsurface (0.15–3.6 m) and deeper soil and rock core, lysimeter soil moisture, and soil vapor moisture sample analyses from the EWFA indicate that tritium is the primary COC in soil. These data also identify the firing table, sand pile, and lower corporation yard at Building 850 and disposal Pits 3 and 5 at the Pit 7 Complex as primary tritium release sites in the EWFA.

More than 95 percent of the approximately 840 TBq (22,670 Ci) of tritium shipped to Site 300 was used in hydrodynamic experiments conducted on the Building 850 firing table between 1963 and 1978. Most of the firing table gravel from the Building 850 and other EWFA firing tables is buried in the Pit 7 Complex. As a result, the Building 850 and Pit 7 Complex areas contain most of the tritium contamination remaining at the site. Prior to disposal at the Pit 7 Complex, firing table gravel was stored in an exposed area east of Building 850. Gravel from the firing table was frequently soaked to reduce airborne dust. The combination of the open

storage and frequent washdowns resulted in the mobilization of tritium into the vadose and saturated zones, and the subsequent contamination of subsurface and deeper soil beneath the Building 850 firing table area. Although the Buildings 802 and 851 firing tables are also confirmed sites of tritium releases to soil, the extent of soil contamination at these firing tables appears to be relatively localized.

Although tritium is the primary COC in the EWFA, other COCs—depleted uranium, thorium, VOCs, PCBs, dioxins, furans, and several metals—also were released to soil, rock, and groundwater as a result of firing table experiments and subsequent debris disposal in the Pit 7 Complex landfills (Taffet et al. 1996).

Low concentrations of PCBs, dioxins, depleted uranium, thorium, and several metals exist in surface soil around Building 850, while subsurface soil shows low concentrations of PCBs, dioxins, furans, and thorium (Taffet et al. 1996).

Analyses of soil and rock samples collected in the vicinity of the Building 854 Complex and the ATA Building 865 areas confirm these locations as VOC release sites. From 1965 to 1989, the Building 854 area housed two TCE brine systems for vibration, thermal, and shock experiments. These systems were similar to the TCE brine system in use at the Building 834 Complex. TCE is reported to have been released to the environment from the Building 854 area via surface spills, pipe leaks, valve leaks, and pump leaks, primarily between 1967 and 1984.

The ATA Building 865 area, located in the northeastern portion of the EWFA, housed a linear accelerator. Until 1988, solvents (primarily Freon 113) and oils were stored and used at this facility. Historical information indicates that insulating oil, used as a heat-transfer medium, and Freon 113 were used to clean accelerator modules and other experimental apparatus. Oils and Freon 113 were released to the environment by means of spills, washdown operations, and wastewater retention tank leaks.

Analyses of soil and rock samples from the Explosives Process Area confirm 20 chemical release sites and identify TCE and the HE compounds HMX and RDX as the primary chemicals of potential concern. HE compounds were released to the environment in process rinse water that was discharged to 11 unlined disposal lagoons from the late 1950s to 1984. HE compounds were also released at a dry well and at the former Building 829 HE Open Burn Treatment Facility (where HE waste was destroyed by burning).

Since 1985, HE process rinsewater has been discharged to two surface impoundments that are double-lined to prevent releases to the environment. VOCs, primarily TCE, were released to the environment by:

- Surface spills south of the former Building 815 HE Process Area steam plant
- Minor spills near a few drum rack dry wells
- A minor septic system release at Building 827

In addition, dilute concentrations of a few VOCs may have been released inadvertently to some of the unlined disposal lagoons. The Building 829 HE Open Burn Treatment Facility has the largest single area of HE-contaminated soil. However, the lateral extent of HE compounds in soil and rock in the area is limited primarily to the vicinity of the disposal lagoons and a former dry well.

In the GSA, borehole data verify seven VOC release sites: four dry wells, a solvent drum rack, a steam-cleaning/sink discharge, and a debris burial trench. Historic information and analytic data indicate that VOCs were discharged to the GSA dry wells from the 1960s to 1986 (Webster-Scholten 1994). TCE is identified as the primary chemical of potential concern; but other chemicals of potential concern include PCE; 1,1-DCE; and *cis*-1,2-DCE.

Pit 6 consists of three large disposal trenches and six smaller animal burial pits, which were used to contain solid waste from 1964 to 1973. Leakage from the landfill resulted in minor releases of VOCs, primarily TCE, and tritium. From 1964 to 1973, about 1529 m^3 of solid waste were buried in nine separate trenches within the landfill. Three larger trenches contain about 1300 m^3 of solid waste, including empty drums, glove boxes, lumber, ducting, and capacitors. Six smaller trenches contain about 229 m^3 of biomedical waste, including animal carcasses and animal waste.

8.2 Extent and Frequency of Monitoring and Measurements

8.2.1 Livermore Site Extent and Frequency of Monitoring and Measurements

8.2.1.1 Livermore Site Criteria for Sampling Location Selection

As part of its ongoing groundwater monitoring, LLNL has drilled and now monitors more than 400 wells on and in the vicinity of the Livermore site. Although the primary function of these monitoring wells is environmental restoration monitoring, data from a subset of these wells also fulfill the surveillance monitoring mandates of DOE Orders 5400.1 and 5400.5.

DOE Order 5400.1 requires LLNL, in part, to obtain data that establish baseline conditions of groundwater quality and quantity. Likewise, 40 CFR 265, Subpart F, G*roundwater Monitoring*, details requirements for RCRA Interim Status facilities, including locating at least one monitoring well upgradient of the facility to represent background groundwater quality in the uppermost aquifer. This upgradient well is to be monitored quarterly until background water quality is established. LLNL's program employs two upgradient monitoring wells (W-008 and W-221) in the eastern and northeastern portions of the site (**Figure 8-5**), and seven downgradient monitoring wells located just inside and beyond the western boundary of the site (**Figure 8-5**). These wells are located downgradient from Treatment Facility B (W-571 and W-1012) and Treatment Facility C (W-373 and W-556); three of the downgradient wells (W-121, W-151, and W-14B1) are located downgradient from, but near the zone of influence of, Treatment Facility A. This configuration of monitoring wells was implemented in 1996 to monitor the uppermost aquifers (HSUs designated as 1B and 2) for COCs that could leave the site to the west beneath Vasco Road, the predominant direction of groundwater flow (**Figure 8-1**).

In 1997, the groundwater surveillance network was expanded to incorporate monitoring wells downgradient from the Taxi Strip Area, from the East Traffic Circle Landfill, from two hazardous and mixed-waste storage areas on site, and from two areas of documented releases of metals to ground. Both the Taxi Strip Area and the East Traffic Circle Landfill WMUs were identified in the remedial investigation (Thorpe et al. 1990) and are discussed briefly in **Section 8.1.3**. **Figure 8-5** shows seven downgradient monitoring wells (W-119, W-204, W-363, W-906, W-1303, W-1306, and W-1308) that form the monitoring network for the Taxi Strip and the East Traffic Circle WMUs.

Analyses are conducted on groundwater samples collected from wells W-653 and W-1207 (screened in HSUs 3A and 2, respectively) hydrologically downgradient from NIF for minerals, selected metals, gross alpha and beta radiation, radium-226, and tritium.

The hazardous waste/mixed waste storage facilities around Buildings 514 and 612 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 are sampled and analyzed for selected trace metals, general minerals, americium-241, plutonium-238, plutonium-239, radium-226, and tritium in 2002. Likewise, samples are obtained downgradient of DWTF from wells W-007, W-593 (screened in HSU 3A, and W-594 and analyzed for minerals, selected metals, and radioactive constituents—americium-241, plutonium-238, plutonium-239, radium-226, and tritium. monitoring wells W-007 and W-594 (screened in HSUs 2/3A and 2, respectively) were added to this monitoring network in 2002.

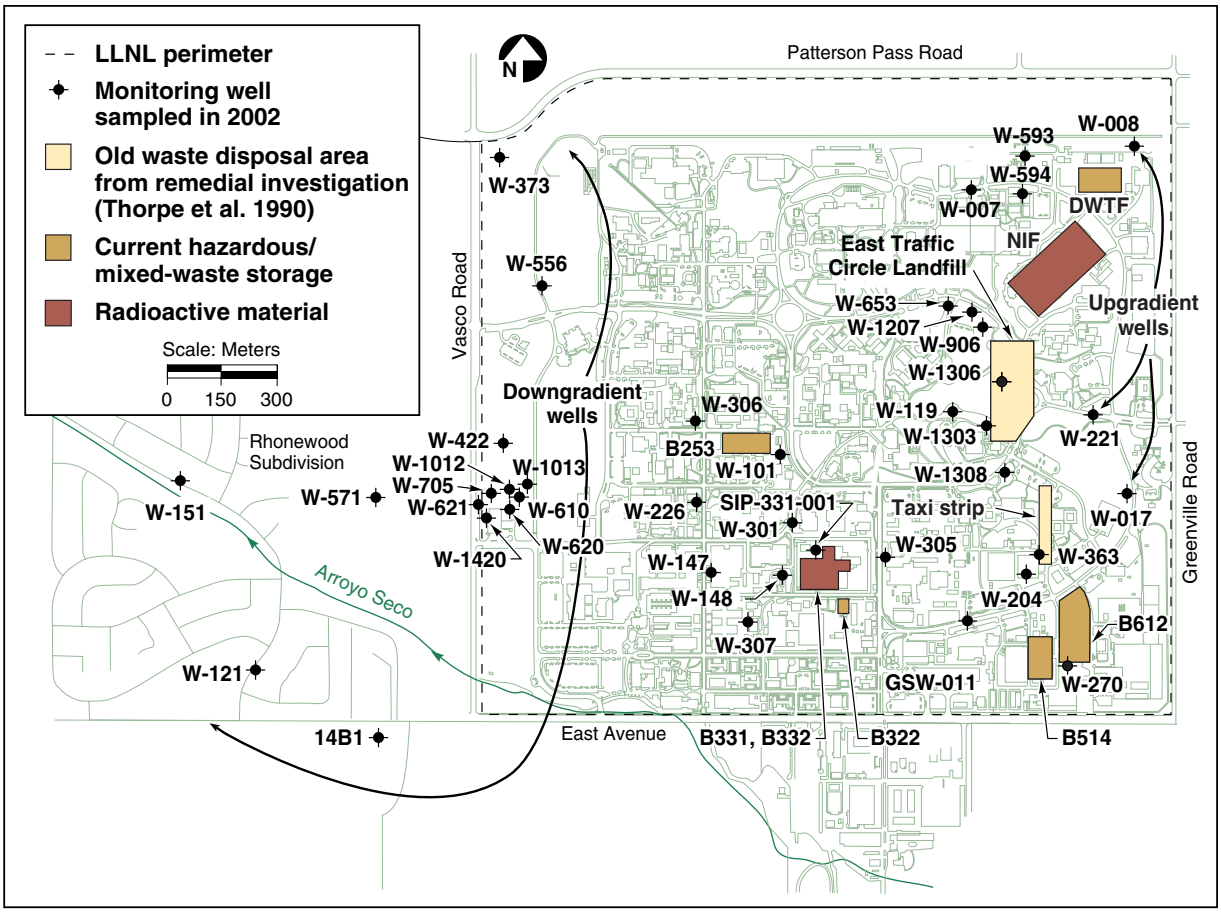

Figure 8-5. Livermore site groundwater surveillance monitoring well locations, 2002

Groundwater samples are collected annually and analyzed for metals from monitoring well W-307, downgradient from where a fume hood on Building 322 released metals to ground. Groundwater samples are also collected annually and analyzed for metals from monitoring wells W-226 and W-306. These wells are downgradient from sediments containing elevated metals that accumulated in a storm water catch basin (**Figure 8-5**).

In 1999, LLNL began monitoring well W-305 upgradient from the Building 332 and well W-148 hydrologically downgradient from Buildings 331 and 332 (**Figure 8-5**). Well W-305 is screened in HSU-2, and well W-148 is screened in HSU-1B. (The locations of Buildings 331 and 332 are not shown in **Figure 8-5**.)

LLNL continues to monitor 23 off-site water wells, approximately downgradient from LLNL, for tritium activity at distances of 3.5 to 16 km to the west of the Livermore site (**Figure 8-6**).

8.2.1.2 Livermore Site Sampling Frequency

The groundwater surveillance network of 25 wells (on or very near the site) established for the Livermore site is sampled quarterly at the two upgradient wells and at least annually at the 23 downgradient surveillance wells. Generally, these downgradient wells are sampled after periods of the heaviest winter rains. Heavy winter rains have been seen to wash some metals out of the vadose zone and into the groundwater. Retest samples are taken subsequent to analytical results that are elevated above background concentrations or above concentrations of concern for human health. Wells used to characterize groundwater quality adjacent to the Livermore site (for the Groundwater Project) are sampled annually, biannually, or quarterly, based on criteria in the CERCLA Work Plan. All groundwater sampling at and adjacent to the Livermore site is conducted by EPD's Environmental Restoration Division (ERD) technical staff or contract staff.

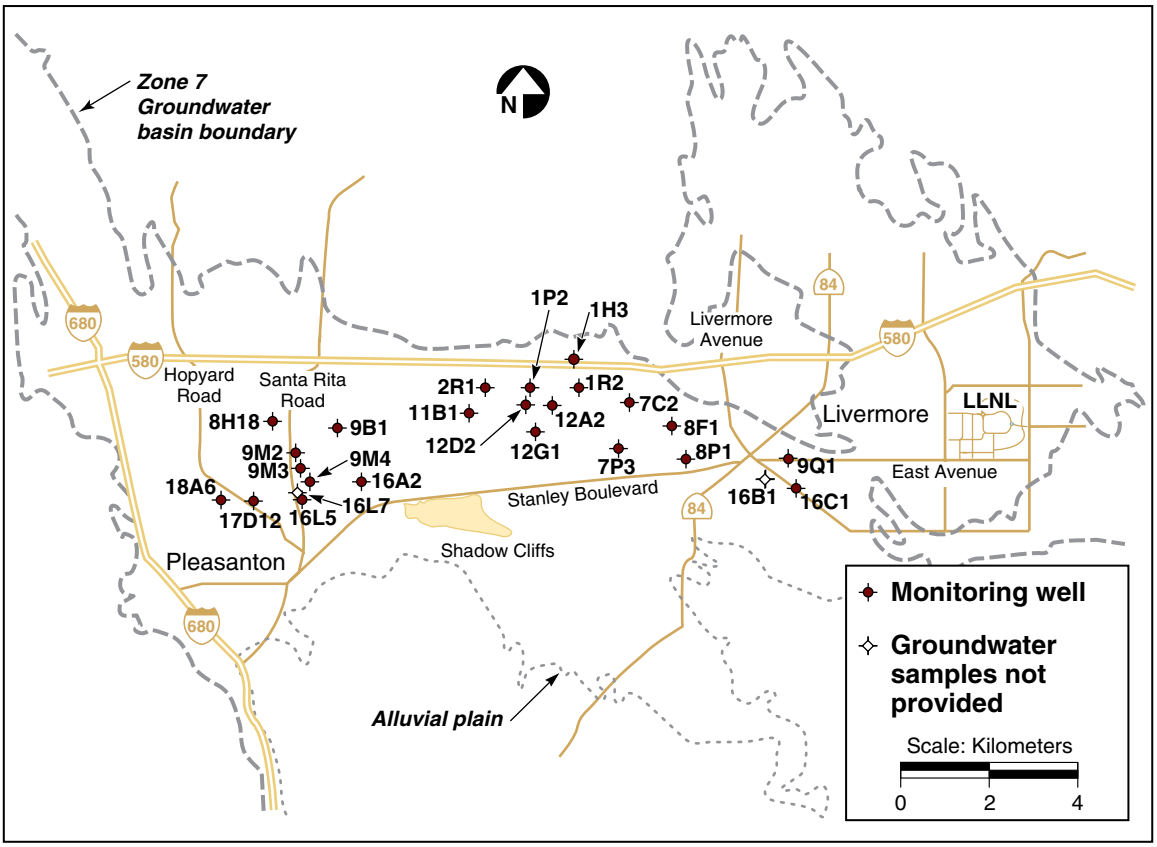

Figure 8-6. Livermore Valley groundwater surveillance monitoring well locations, 2002

The 23 downgradient wells associated with the tritium monitoring in the Livermore Valley are sampled annually. Groundwater samples are obtained in LLNL-supplied bottles by personnel at these facilities:

- California Water Service (five wells)
- City of Livermore (nine wells)
- City of Pleasanton (three wells)
- Zone 7 Water Agency (six wells)

8.2.2 Site 300 Extent and Frequency of Monitoring and Measurements

8.2.2.1 Site 300 Criteria for Sampling Location Selection

Groundwater monitoring locations within Site 300, including compliance and surveillance wells and Barcad samplers, have been selected from a large array of CERCLA installations that were initially used for site characterization. Selections were made that could detect releases of COCs from closed landfill Pits 1, 2, 3, 4, 5, 6, 7, 8, and 9, the former HE burn pit, and from active WMUs. Groundwater flow directions beneath Site 300 are known from area-wide measurements of water table elevations in the CERCLA wells. For compliance purposes, detection monitoring wells both upgradient and downgradient from the WMUs were selected.

The selected wells are typically screened in the uppermost water-bearing zone beneath the units in order to provide the earliest warning of COC releases to groundwater. Other wells are screened in the regional aquifer and are used to detect any degradation of drinking water supplies. Some wells within Site 300 (**Figure 8-4**) were selected to follow surface water courses, such Elk Ravine, where contaminant plumes caused by past operations have been detected by exhaustive remedial investigation studies (Webster-Scholten 1994; Taffet et al. 1996). These wells were optimally located to monitor the concentrations of COCs within contaminant plumes and to monitor the fate and transport of contaminant plumes. The surveyed locations and engineering specifications of the Site 300 groundwater monitoring installations, including wells, Barcads, and lysimeters, are maintained in the LLNL computer database EPDBS::EPDData.

For surveillance monitoring purposes, the number and locations of sampling wells, the COCs, and frequency of sampling are prerogatives of LLNL, allowing the Laboratory to devise a comprehensive, cost-effective monitoring program. Because the flow rates of groundwater beneath Site 300 rarely exceed 40 m/year, quarterly, semiannual, and annual sampling frequencies are deemed appropriate for data trending and meet annual reporting requirements.

Surveillance monitoring at Site 300 analyzes groundwater samples from on-site DOE CERCLA wells and from private off-site production wells and springs. Sampling is coordinated to prevent interference with compliance monitoring and remediation activities at the site. Although surveillance monitoring uses on-site wells that were placed for the purpose of site characterization under CERCLA, it is conducted independently of other monitoring. COCs of many types are monitored in groundwater samples to accomplish several important goals. Surveillance monitoring provides independent checks of findings from site characterization studies and remediation efforts. It detects (down to detection limits) any slow-to-develop releases of COCs to groundwater at the site. This program also detects any increases in existing contamination that could indicate accelerated COC releases from remaining buried sources. Chemical data from groundwater samples obtained through both surveillance and remediation monitoring at Site 300 are added continually to the EPDBS::EPDData database.

8.2.2.2 Site 300 Groundwater Surveillance Monitoring Networks

Brief descriptions of the Site 300 surveillance areas and their monitoring wells are given below. Detailed descriptions of the geology, hydrogeology, and the nature and extent of groundwater contamination in the surveillance areas can be found in the site-wide remedial investigation (SWRI) reports (Webster-Scholten 1994; Taffet et al. 1996).

Figure 8-4 displays the groundwater surveillance sampling locations, which include 24 wells and 3 springs. Although most of the locations provide representative samples of groundwater from the shallowest water-bearing zone, four multiple completion installations (K1-01, K1-02, K2-01, and K2-02) are fitted with a total of ten Barcad devices that provide water samples from deeper water-bearing zones. Barcad samplers are identified by letters A, B, and C at the end of a well's ID code. Barcad A designates the deepest water-bearing zone.

8.2.2.2.1 Off-Site Surveillance Monitoring Network. Twelve surveillance locations for groundwater monitoring are off site. Four are to the north, and eight are to the south of Site 300 (**Figure 8-4**). Three locations, the MUL2 and VIE1 springs, and the cattle watering well, MUL1, are adjacent to Site 300 on the north, where the Altamont Hills slope down to the San Joaquin Valley. VIE2 represents a background well, typical of drinking water supplies in the Altamont hills. It lies 6 km northwest of Site 300 in the upper reaches of the Livermore Valley watershed. Eight off-site surveillance locations are located immediately south of Site 300 in the Corral Hollow Creek drainage area. These are wells CARNRW1, CARNRW2, CDF1, CON1, CON2, GALLO1, STONEHAM1, and W35A-04. Of these southern wells, STONEHAM1 is monitored primarily to provide upgradient background data for water supply wells in Corral Hollow Creek. The remaining off-site surveillance wells, which are used to water cattle or suppress fires, monitor for VOCs beyond the southern boundary of Site 300.

Of the 12 off-site groundwater surveillance wells sampled, water samples are taken quarterly from CARNRW1 and CON2 and are analyzed for VOCs only (EPA Method 601). Samples from the remaining ten wells are taken either quarterly (CARNRW2, CON1, CDF1, and GALLO1), or annually (MUL1, MUL2, VIE1, VIE2, STONEHAM1, and W35A-04). The samples are analyzed for 17 elements (mostly metals), HE compounds, VOCs (EPA Method 502.2), extractable organic compounds (EPA Method 625), pesticides and PCBs (EPA Method 608), herbicides (EPA Method 615), nitrate, general radioactivity (gross alpha and gross beta), tritium, and uranium isotopes.

8.2.2.2.2 On-Site Surveillance Monitoring Networks. Nine on-site surveillance wells and one spring (812CRK) are located along the system of fault-marked ravines and arroyos that constitute the Elk Ravine drainage area (**Figure 8-4**). Nine on-site surveillance locations are used to monitor three closed landfills (Pits 2, 8, and 9 in the Elk Ravine drainage area). CERCLA Barcads and wells, both upgradient and downgradient from the closed landfills, were selected for monitoring. Three Barcads at three locations are used at Pit 2 (K2-01A and K2-02A and B).

Five wells monitor Pit 8 (**Figure 8-7**). Four wells monitor Pit 9 (**Figure 8-8**). Surveillance monitoring also includes two on-site water production wells, Well 18 and Well 20 (**Figure 8-4**). Well 20 provides potable water for use at Site 300. Well 18 is a standby supply well.

<u>Elk Ravine Surveillance Monitoring Network</u>

Elk Ravine drains most of northern Site 300 in the area between the drainage divides shown in **Figure 8-4**. Surface runoff from closed WMUs within the drainage area (Pits 1, 2, 3, 4, 5, 7, and 9) is collected in arroyos. With sufficient seasonal rainfall, unconfined groundwater can flow southeast on and within the valley-fill deposits that floor the Pit 7 Complex valley. Surface runoff from the Pit 7 Complex valley (containing the most elevated landfills) can flow southeast to Doall Road, where it is deflected northeastward into Doall Ravine by a landslide deposit. At the northeastern end of Doall Ravine, this runoff combines with channeled runoff from the ATA Building 865 area. From this confluence point, the arroyo trends southeasterly within Elk Ravine. Near Well NC2-07, channeled runoff turns easterly, away from the trend of the Elk Ravine Fault, and flows off site for approximately 2 km to its confluence with Corral Hollow Creek. Except for Doall Ravine, the arroyos and valley-fill deposits traverse and follow faults, especially the extensive Elk Ravine Fault, that may provide pathways to the underlying groundwater. Thus, groundwaters from wells that lie within the Elk Ravine drainage area are monitored. The monitored wells are (from highest to lowest elevation) K7-07, NC7-61, NC7-69, K2-04D, K2-04S, K2-01C, NC2-12D, NC2-11D, and NC2-07. The 812CRK sampling location is a natural spring (also identified as Spring 6), located in the main Elk Ravine arroyo on the Elk Ravine Fault. Individual well locations are discussed below.

Well K7-07 is located in the Pit 7 Complex valley. It is a shallow well that is screened in both $Tnbs_1$ and Qal. It is downgradient from Pits 3, 4, 5, and 7 with respect to unconfined flow in the valley-fill deposits and to surface runoff. Wells NC7-61 and NC7-69 are screened in separate water-bearing zones beneath the upper reaches of Doall Ravine. Well NC7-61 is screened in $Tnbs_1$ (shallower zone), and Well NC7-69 is screened in Tmss (deeper zone). Wells K2-04D and K2-04S and Barcad K2-01C are located near the join between Elk Ravine and Doall Ravine. They are all screened in $Tnbs_1$. Wells NC2-12D and NC2-11D are located in Elk Ravine below its join with Doall Ravine. Well NC2-11D is screened at the contact between $Tnbs_1$ and Tmss. Well NC2-07 is the farthest downstream surveillance well in the Elk Ravine drainage area and is screened in $Tnbs_1$.

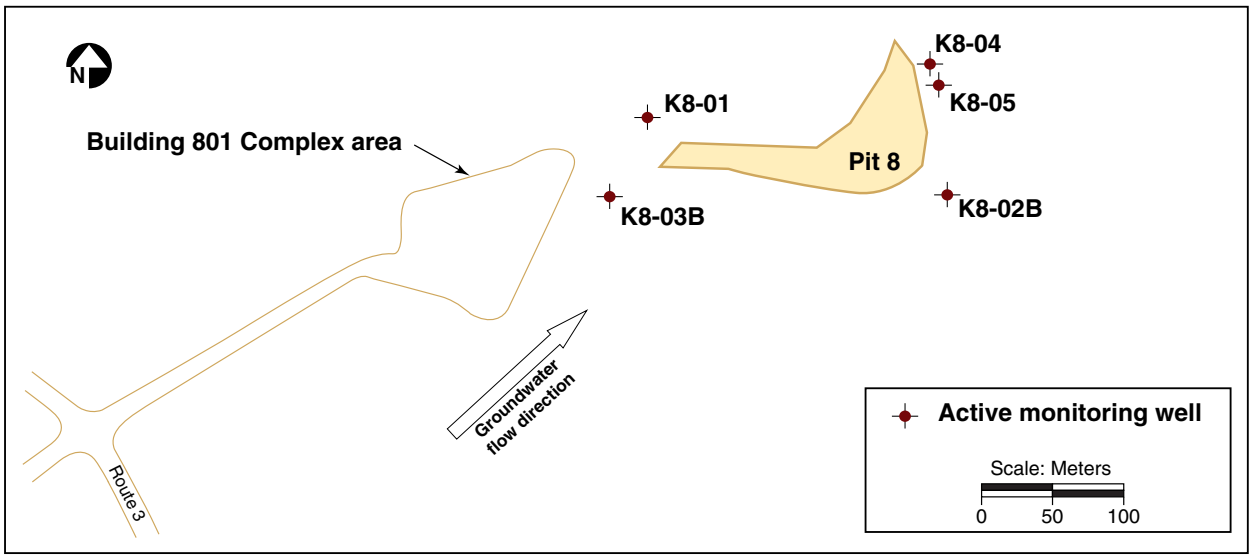

Figure 8-7. Site 300 Pit 8 groundwater surveillance monitoring wells

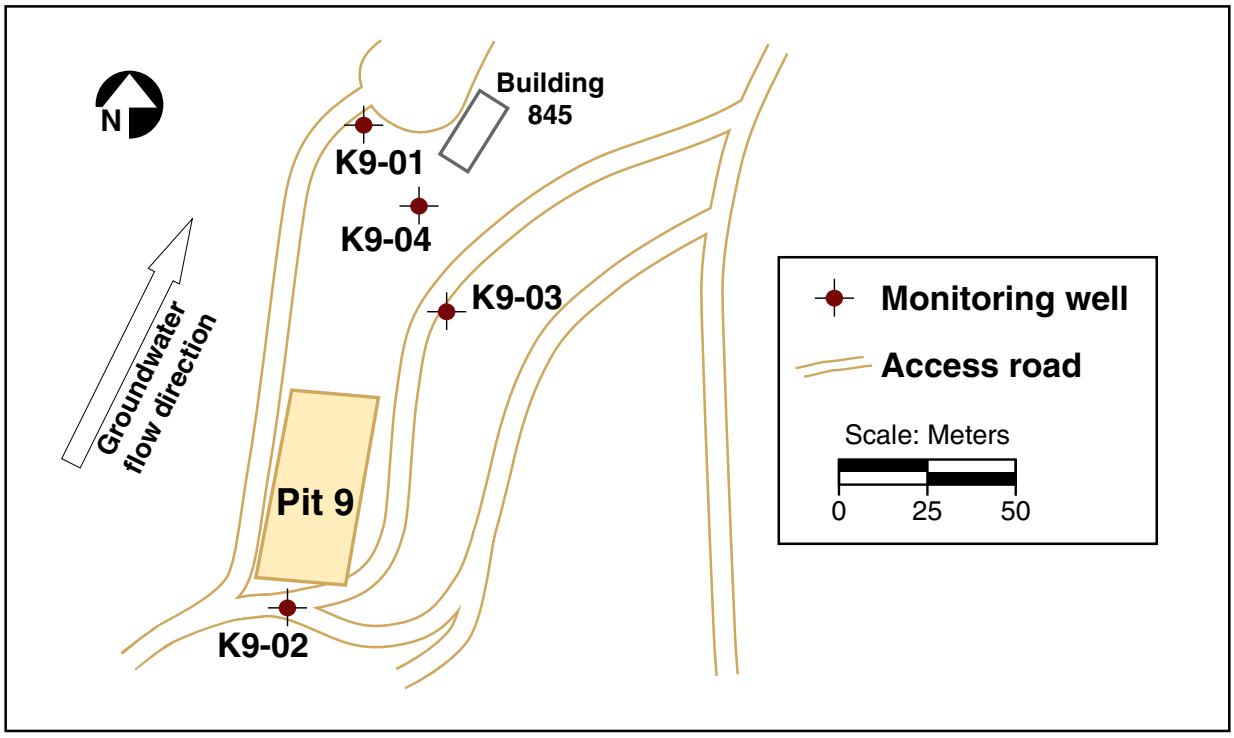

Figure 8-8. Site 300 Pit 9 groundwater surveillance monitoring wells

Groundwater samples are taken semiannually from the nine wells and one spring in Elk Ravine and are analyzed for 17 elements (mostly metals), HE compounds, VOCs (EPA Method 601), nitrate, general radioactivity (gross alpha and gross beta), tritium, and uranium isotopes.

Pit 2 Surveillance Monitoring Network

Closed Pit 2 is shown in **Figure 8-9**. Pit 2 lies about 320 m above sea level within the upper reaches of the Elk Ravine drainage area. Surface runoff from the area is southerly. Subsurface water flow beneath the pit is eastward, following the local inclination of the underlying Miocene $Tnbs_1$ and Tmss sedimentary strata. Pit 2 primarily contains waste gravel and debris from explosives experiments conducted on the Buildings 801 and 802 firing tables. The waste contains depleted uranium and trace amounts of beryllium and thorium. Tritium, in the form of tritiated water moisture (HTO), may also be present. Pit 2 is unlined.

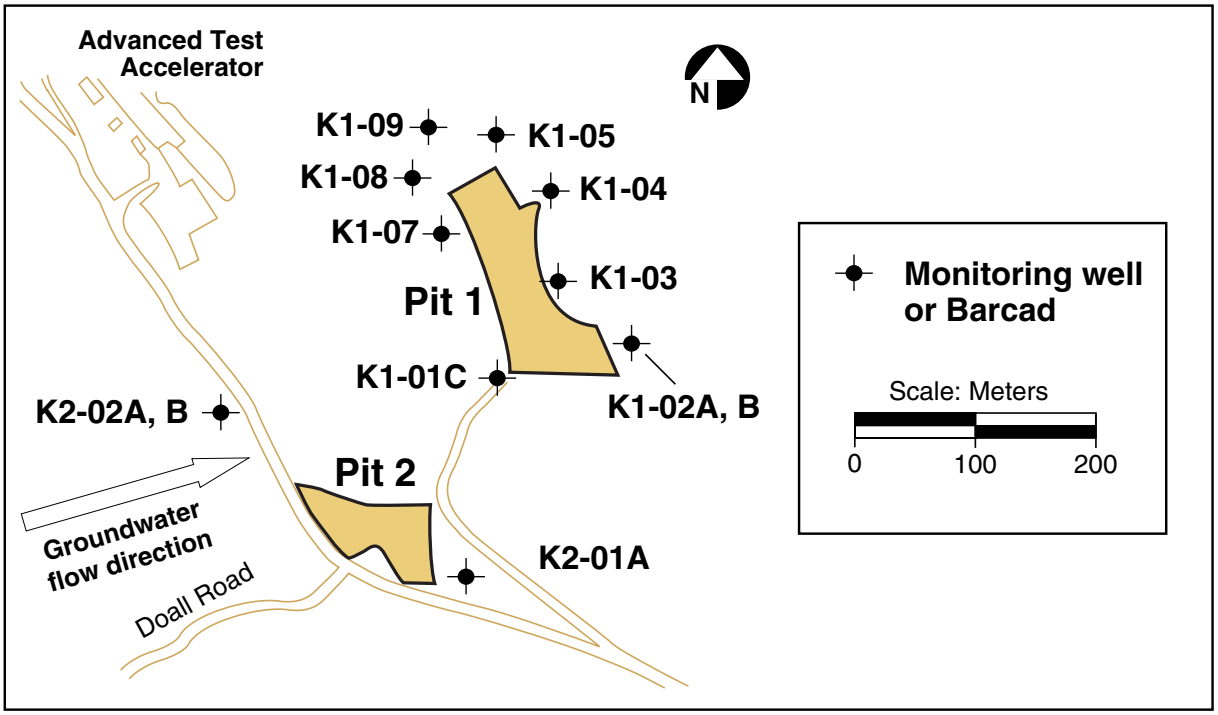

Figure 8-9. **Site 300 Pit 2 surveillance monitoring Barcads and Pit 1 groundwater compliance monitoring wells**

Well K1-01C, in the shallowest water-bearing zone, also serves as one of two upgradient groundwater monitoring points for Pit 1, northeast of Pit 2. Barcads K2-01A, K2-02A, and K2-02B are screened in Tmss. Barcad K2-01B is screened in $Tnbs_1$. Multiple completion installation K2-02 is hydrologically cross-gradient from Pit 2. Groundwater samples from it represent upgradient groundwater.

Groundwater samples are taken quarterly from the Barcads and wells and are analyzed for 17 elements (mostly metals), HE compounds, nitrate, general radioactivity (gross alpha and gross beta), tritium, and uranium isotopes. Because volatiles are typically lost during extraction of groundwater from Barcad devices, the Barcad samples are not analyzed for volatile COCs.

Pit 8 Surveillance Monitoring Network

Pit 8 (**Figure 8-7**) is located adjacent to the Building 801 firing table, where explosive experiments were conducted from 1958 to 1974. Approximately 40 m^3 of untreated debris from the firing table were placed in the pit during that time, and a final cover was installed in 1974. Debris may contain HTO, depleted uranium, lead, and beryllium. The debris was originally dumped on the ground surface and was later leveled and compacted by bulldozer. It was

covered with about 1 m of locally obtained silt with lesser clay, sand, and gravel. A drainage ditch was constructed around the landfill to protect the cover from erosion.

Figure 8-7 shows the Building 801 and Pit 8 areas. The pit is located in a narrow ravine at an average elevation of 330 m within the Elk Ravine drainage area. It is bordered by an earthen dam on its western side at the locations of monitoring wells K8-01 and K8-03. Surficial materials at Pit 8 consist of colluvial soils and shallow ravine fills. The landfill was constructed in the unconsolidated Tps formation. Blue sandstone and interbedded siltstones and claystones of the Neroly Formation underlie the landfill area. The landfill is about 0.5 km northeast of the Elk Ravine fault shear zone, 1.2 km northeast of the Patterson anticline, and 0.5 km southwest of a subparallel syncline that plunges southeast. At the landfill, outcropping beds strike N25°W and dip slightly northeast. Chemical analysis of soil and rock samples taken from this area during CERCLA remedial investigations showed no elevated concentrations of COCs (Webster-Scholten 1994). However, low concentrations of TCE have been detected in groundwater samples from upgradient well K8-01 since 1987.

Depth to water beneath the landfill area varies from 40 to 50 m below the ground surface. A hydraulic test indicates that groundwater flows at a rate of about 20 m/year. Monitoring wells K8-01, K8-02, K8-03, K8-04, and K8-05 were drilled in 1987 and 1988 for remedial investigations and are now used for surveillance purposes. Well K8-05 is screened in a perched water-bearing zone that has not yielded sufficient water for sampling.

Groundwater samples are collected annually from three Pit 8 monitoring wells. Samples are analyzed for 17 elements (mostly metals), VOCs (EPA Method 601), nitrate, general radioactivity (gross alpha and gross beta), tritium, and uranium isotopes.

Pit 9 Surveillance Monitoring Network

Pit 9 (**Figure 8-8**) is centrally located within the Elk Ravine drainage area at an average elevation of 340 m above sea level. It contains waste gravel and debris from the Building 845 firing table. Surface runoff from Pit 9 is northward into Elk Ravine. Subsurface groundwater flow is north-northeast in the Neroly $Tnbs_1$ lower blue sandstone. **Figure 8-8** shows the locations of the four surveillance wells used to monitor the groundwater in the vicinity of Pit 9. Monitoring Well K9-02 is hydrologically upgradient from Pit 9. Wells K9-01, K9-03, and K9-04 are downgradient. Well K9-02 is screened at the contact between $Tnbs_1$ and Tmss. Wells K9-01, K9-03, and K9-04 are screened in Tmss, just below its contact with $Tnbs_1$.

Groundwater samples are taken annually from the four Pit 9 monitoring wells. Samples are analyzed for 17 elements (mostly metals), HE compounds, VOCs (EPA Method 601), nitrate, general radioactivity (gross alpha and gross beta), tritium, and uranium isotopes.

Potable Water Surveillance Monitoring Network

Well 20 supplies potable water for Site 300, and Well 18 serves as a standby water supply well. Both are located in the southeastern part of Site 300 (**Figure 8-4**). They are deep, high-production water wells screened in $Tnbs_1$. The Well 18 screen extends upward into a fine-grained aquitard ($Tnsc_1$) in the Neroly Formation that separates $Tnbs_1$ from the overlying $Tnbs_2$. Each well can produce up to 1500 L/min.

Groundwater samples are taken monthly from supply Well 20 and are analyzed for VOCs (EPA Method 502.2). Every three months (quarterly), the samples are analyzed additionally for 17 elements (mostly metals), HE compounds, nitrate, general radioactivity (gross alpha and gross beta), tritium, and uranium isotopes. Groundwater samples are taken quarterly from the backup supply Well 18 and are analyzed for 17 elements (mostly metals), HE compounds, VOCs (EPA Method 601), nitrate, general radioactivity (gross alpha and gross beta), tritium, and uranium isotopes.

8.2.2.3 Site 300 Groundwater Compliance Monitoring

Compliance monitoring at Site 300 involves analysis of groundwater drawn from 30 wells associated with the two RCRA-closed landfills (17 wells), two active surface impoundments (4 wells), and one sewage evaporation pond and a connected overflow percolation pond (9 wells). **Figure 8-4** shows the locations of the closed landfills (Pits 1 and 7), surface impoundments, and sewage ponds.

Groundwater samples for compliance monitoring are routinely collected quarterly to meet quarterly and annual reporting requirements. Samples may be taken more frequently to satisfy mandated statistical methodology, such as analysis of variance (ANOVA), which requires a minimum of three independent COC measurements (samples taken at least one week apart) each quarter. Sampling frequencies may include four per quarter (four independent samples taken one week apart), three per quarter (monthly), four per year (quarterly), two per year (semiannually), or one per year (annually). All COCs are measured in groundwater samples at least once each year.

8.2.2.3.1 Pits 1 and 7 Compliance Monitoring Network. The compliance monitoring program for Pits 1 and 7 includes groundwater sampling and analysis, visual inspections, elevation surveys, and quarterly and annual reporting of work performed. Post-closure monitoring of Pits 1 and 7 was implemented upon RCRA closure in 1993. Samples of groundwater are obtained quarterly from monitoring wells upgradient and downgradient from the two closed landfills. COCs for monitoring were selected based on knowledge of materials deposited in the landfills. Typically, this material was gravel from firing tables containing debris from explosive experiments,

including depleted uranium, tritium, metals, plastic, and wood. COCs required for monitoring by Cal-EPA are listed in **Table 8-4** for Pit 1 and **Table 8-5** for Pit 7 (Rogers/Pacific Corporation 1990). Additional COCs required by CVRWQCB are listed in **Table 8-6** for Pit 1 and **Table 8-7** for Pit 7 (CVRWQCB 1993). The statistical limits (SLs) for the COCs shown in **Tables 8-6** and **8-7** were updated in 1998 (CVRWQCB 1998).

In order to maintain the physical integrity of the two pits, LLNL technical staff inspect them at least once a quarter and after major rainstorms. Each year LLNL hires an independent Professional Engineer to inspect Pits 1 and 7 and provide a written report of those findings. LLNL surveyors annually measure the elevations of fixed markers on the two caps. These measurements are made to locate any settling that could adversely affect the integrity of the caps.

Table 8-4. Site 300 Pit 1 post-closure plan COCs

Constituent of concern (COC)	Samples per year per well
Groundwater elevation	4
Temperature	4
pH	2
Specific conductance (µS/cm)	2
Total organic carbon	2
Total organic halides (TOX)	2
Arsenic	2
Barium	2
Beryllium	2
Cadmium	2
Chloride	1
Chromium	2
HMX[(a)]	1
Iron	2
Lead	2
Manganese	2
Mercury	2
Nickel	2
Nitrate	2
RDX[(b)]	1
Selenium	2
Silver	2
Sodium	2
Sulfate	1
Pesticides	1
Volatile organic compounds	1
Extractable organic compounds	1
Tritium	2
Gross alpha	2
Gross beta	2

a HMX is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

b RDX is hexahydro-1,3,5-trinitro-1,3,5-triazine.

Table 8-5. Site 300 Pit 7 post-closure plan COCs

Constituent of concern (COC)	Samples per year per well
Groundwater elevation	4
Temperature	4
Beryllium	4
Lead	4
Volatile organic compounds	4
Tritium	4
Gross alpha	4
Gross beta	4

Table 8-6. WDR 93-100 COCs, wells, statistical methods, concentration limits, and statistical limits for Pit 1[a]

Constituent of concern (COC)[b]	Well	Statistical method	Concentration limit[c]	Statistical limit
Arsenic (µg/L)	K1-02B	Control chart	12	20
	K1-03	Control chart	13	19
	K1-04	Control chart	10	19
	K1-05	Control chart	14	24
	K1-08	Control chart	14	21
	K1-09	Control chart	13	19
Barium (µg/L)	K1-02B	Control chart	<25	25
	K1-03	Control chart	<25	25
	K1-04	Control chart	25	32
	K1-05	Control chart	30	41
	K1-08	Control chart	33	51
	K1-09	Control chart	33	46
Beryllium (µg/L)	All	Prediction limit	<0.5	0.5
Cadmium (µg/L)	All	Prediction limit	<0.5	0.5
Cobalt (µg/L)	All	Prediction limit	<25	25
Copper (µg/L)	All	Prediction limit	21	34
Lead (µg/L)	All	Prediction limit	<2	2
Nickel (µg/L)	All	Prediction limit	<5	12
Vanadium (µg/L)	K1-02B	Control chart	47	78
	K1-03	Control chart	44	72
	K1-04	Control chart	32	48

(continued)

Table 8-6. WDR 93-100 COCs, wells, statistical methods, concentration limits, and statistical limits for Pit 1 (concluded)

Constituent of concern (COC)[b]	Well	Statistical method	Concentration limit[c]	Statistical limit
Vanadium (µg/L) (continued)	K1-05	Control chart	67	97
	K1-08	Control chart	64	100
	K1-09	Control chart	58	92
Zinc (µg/L)	All	Prediction limit	29	94
HMX (µg/L)[d]	All	Prediction limit	<5	5
RDX (µg/L)[e]	All	Prediction limit	<5	5
Radium 226 (Bq/L)	All	Prediction limit	0.006	0.044
Tritium (Bq/L)	K1-03	Control chart	17.2	23.4
	K1-04	Control chart	0.00	3.70
	K1-05	Control chart	0.00	3.70
	K1-08	Control chart	0.10	3.70
Uranium (total, Bq/L)	K1-02B	Control chart	0.102	0.192
	K1-03	Control chart	0.064	0.145
	K1-04	Control chart	0.070	0.124
	K1-05	Control chart	0.072	0.109
	K1-08	Control chart	0.072	0.120
	K1-09	Control chart	0.062	0.109
Thorium 228 (Bq/L)	All	Prediction limit	0.002	0.023
Thorium 232 (Bq/L)	All	Prediction limit	0.002	0.009

a Revision to MRP 93-100 (CVRWQCB 1998)

b The significant figures displayed in this table vary by COC. These variations reflect regulatory agency permit stipulations, or the applicable analytical laboratory contract under which the work was performed, or both.

c Background concentration

d HMX is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

e RDX is hexahydro-1,3,5-trinitro-1,3,5-triazine.

Table 8-7. WDR 93-100 COCs, wells, statistical methods, concentration limits, and statistical limits for Pit 7[a]

Constituent of concern (COC)[b]	Well	Statistical method	Concentration limit[c]	Statistical limit
Arsenic (µg/L)	K7-01	Control chart	8.9	14
	K7-03	Control chart	2.1	3.2
	K7-09	Control chart	<2.0	2.0
	K7-10	Control chart	2.3	4.2
	NC7-25	Control chart	5.3	8.6

(continued)

Table 8-7. WDR 93-100 COCs, wells, statistical methods, concentration limits, and statistical limits for Pit 7 (continued)

Constituent of concern (COC)[b]	Well	Statistical method	Concentration limit[c]	Statistical limit
	NC7-26	Control chart	2.2	3.6
	NC7-47	Control chart	13	17
	NC7-48	Control chart	7.1	19
Barium (µg/L)	K7-01	Control chart	170	230
	K7-03	Control chart	63	85
	K7-09	Control chart	<25	25
	K7-10	Control chart	49	120
	NC7-25	Control chart	68	140
	NC7-26	Control chart	25	39
	NC7-47	Control chart	42	63
	NC7-48	Control chart	140	400
Beryllium (µg/L)	All	Prediction limit	<0.5	0.5
Cadmium (µg/L)	K7-01	Control chart	<0.5	0.5
	K7-03	Control chart	<0.5	0.5
	K7-09	Control chart	<0.5	0.5
	K7-10	Control chart	<1.6	1.6
	NC7-25	Control chart	<0.5	0.6
	NC7-26	Control chart	<0.5	0.5
	NC7-47	Control chart	<0.5	0.5
	NC7-48	Control chart	<1.2	1.2
Cobalt (µg/L)	All	Prediction limit	<25	25
Copper (µg/L)	K7-01	Control chart	15	40
	K7-03	Control chart	71	140
	K7-09	Control chart	<10	10
	K7-10	Control chart	<10	10
	NC7-25	Control chart	<10	10
	NC7-26	Control chart	<10	10
	NC7-47	Control chart	<10	10
	NC7-48	Control chart	<10	10
Lead (µg/L)	K7-01	Control chart	1.4	6.0
	K7-03	Control chart	1.3	6.1
	K7-09	Control chart	<5.9	5.9
	K7-10	Control chart	<2.0	2.0
	NC7-25	Control chart	<2.0	2.0
	NC7-26	Control chart	1.1	5.1
	NC7-47	Control chart	1.5	7.6
	NC7-48	Control chart	<2.0	2.0
Nickel (µg/L)	K7-01	Control chart	<5	25
	K7-03	Control chart	5	26
	K7-09	Control chart	<5	29
	K7-10	Control chart	<5	13

(continued)

Table 8-7. WDR 93-100 COCs, wells, statistical methods, concentration limits, and statistical limits for Pit 7 (continued)

Constituent of concern (COC)[b]	Well	Statistical method	Concentration limit[c]	Statistical limit
	NC7-25	Control chart	1.7	13
	NC7-26	Control chart	<5	5
	NC7-47	Control chart	2.5	14
	NC7-48	Control chart	6.5	48
Vandium (µg/L)	K7-01	Control chart	<25	25
	K7-03	Control chart	<25	25
	K7-09	Control chart	<25	25
	K7-10	Control chart	<25	25
	NC7-25	Control chart	<25	25
	NC7-26	Control chart	<25	25
	NC7-47	Control chart	54	79
	NC7-48	Control chart	33	110
Zinc (µg/L)	K7-01	Control chart	6.3	52
	K7-03	Control chart	41	72
	K7-09	Control chart	<20	20
	K7-10	Control chart	<20	20
	NC7-25	Control chart	<36	36
	NC7-26	Control chart	<20	20
	NC7-47	Control chart	9.2	50
	NC7-48	Control chart	17	44
HMX (µg/L)[d]	All	Prediction limit	<25	25
RDX (µg/L)[e]	All	Prediction limit	<5	5
Radium-266 (Bq/L)	K7-01	Control chart	0.038	0.080
	K7-03	Control chart	0.001	0.030
	K7-09	Control chart	0.008	0.023
	K7-10	Control chart	0.011	0.032
	NC7-25	Control chart	0.023	0.054
	NC7-26	Control chart	0.016	0.034
	NC7-47	Control chart	0.005	0.022
	NC7-48	Control chart	0.014	0.040
Tritium (Bq/L)	K7-09	Control chart	4.7	4.7
	K7-10	Control chart	4.7	4.7
	NC7-47	Control chart	4.7	4.7
	NC7-48	Control chart	4.0	16.4
Uranium (total, Bq/L)	K7-01	Control chart	0.455	0.636
	K7-03	Control chart	0.142	0.224
	K7-09	Control chart	0.017	0.035
	K7-10	Control chart	0.036	0.083
	NC7-25	Control chart	0.814	1.262

(continued)

Table 8-7. WDR 93-100 COCs, wells, statistical methods, concentration limits, and statistical limits for Pit 7 (concluded)

Constituent of concern (COC)[b]	Well	Statistical method	Concentration limit[c]	Statistical limit
	NC7-26	Control chart	0.016	0.034
	NC7-47	Control chart	0.090	0.178
	NC7-48	Control chart	0.858	2.327
Thorium (Bq/L)	All	Prediction limit	0.000	0.024
	All	Prediction limit	0.001	0.014

a Revision to MRP 93-100 (CVRWQCB 1998)

b The significant figures displayed in this table vary by COC. These variations reflect regulatory agency permit stipulations, or the applicable analytical laboratory contract under which the work was performed, or both.

c Background concentration

d HMX is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

e RDX is hexahydro-1,3,5-trinitro-1,3,5-triazine.

Figure 8-9 shows Pit 1, the ATA Building 865 area, the adjacent closed Pit 2, and the eight groundwater wells used to monitor Pit 1. Pit 1 lies at an average elevation of 330 m in the upper reaches of the Elk Ravine drainage area. Groundwater flows east-northeast beneath the pit following the dip of the underlying sedimentary rocks. Wells K1-01C and K1-07 are upgradient from Pit 1; K1-02B, K1-03, K1-04, and K1-05 are downgradient; and K1-08 and K1-09 are cross-gradient. Wells K1-03 and K1-07 are screened in $Tnbs_1$. The remaining wells are screened across or at the $Tnbs_1$–Tmss formation contact. Pit 2 is hydrologically upgradient from Pit 1 with respect to groundwater flow, but it is downgradient from Pit 1 with respect to surface water (rain) runoff.

For compliance monitoring purposes, groundwater samples are collected quarterly from Pit 1 monitoring wells and are analyzed for the COCs listed in **Tables 8-4** and **8-6**.

Figure 8-10 shows the locations of the nine groundwater wells used to monitor RCRA-closed Pit 7 (and Pits 3, 4, and 5) in the Pit 7 Complex. The complex of four closed landfills lies in the uppermost reaches of the Elk Ravine drainage area at an average elevation of 425 m above sea level. Groundwater can flow in several directions in this area. With sufficient seasonal rainfall, a shallow, unconfined, southeastward flow develops in the surficial valley-fill deposits. Groundwater also flows year-round to the east-northeast, following the down dip direction of the $Tnbs_1$ and Tmss formations. The network of compliance monitoring wells is oriented in the east-northeast flow direction. Well K7-06 is upgradient; Wells K7-09 and K7-10 are cross-gradient; and Wells K7-01, K7-03, NC7-25, NC7-26, NC7-47, and NC7-48 are downgradient. Wells K7-01, K7-10, and NC7-26 are screened in $Tnbs_1$. The remaining wells are screened in Tmss. Well K7-09 samples a separate, deeper water-bearing zone in Tmss.

For compliance monitoring purposes, groundwater samples are collected quarterly from Pit 7 monitoring wells and are analyzed for the COCs listed in **Tables 8-5** and **8-7**.

9.2.2.3.2 Pit 6 Compliance Monitoring Network. Pit 6, an unlined, closed WMU, lies at an average elevation of 210 m above sea level and covers an area of about 1 hectare adjacent to the southern boundary of Site 300 (**Figures 8-4** and **8-11**). Pit 6 is cut into Quaternary terrace deposits (Qt) above and north of the Corral Hollow Creek flood plain. $Tnbs_1$ lies beneath the terrace deposits. Surface runoff from the pit area is southward to Corral Hollow Creek. Groundwater flows southward beneath the pit, following the south-dipping sedimentary rocks. Flow abruptly turns eastward beneath the landfill where movements along the Carnegie Fault have brought vertically dipping strata on the south into contact with the gently southward dipping strata to the north. Terrace gravel in a trough within the vertically dipping strata immediately south of the landfill acts as a channel for groundwater to flow eastward after it passes below Pit 6 (Webster-Scholten 1994).

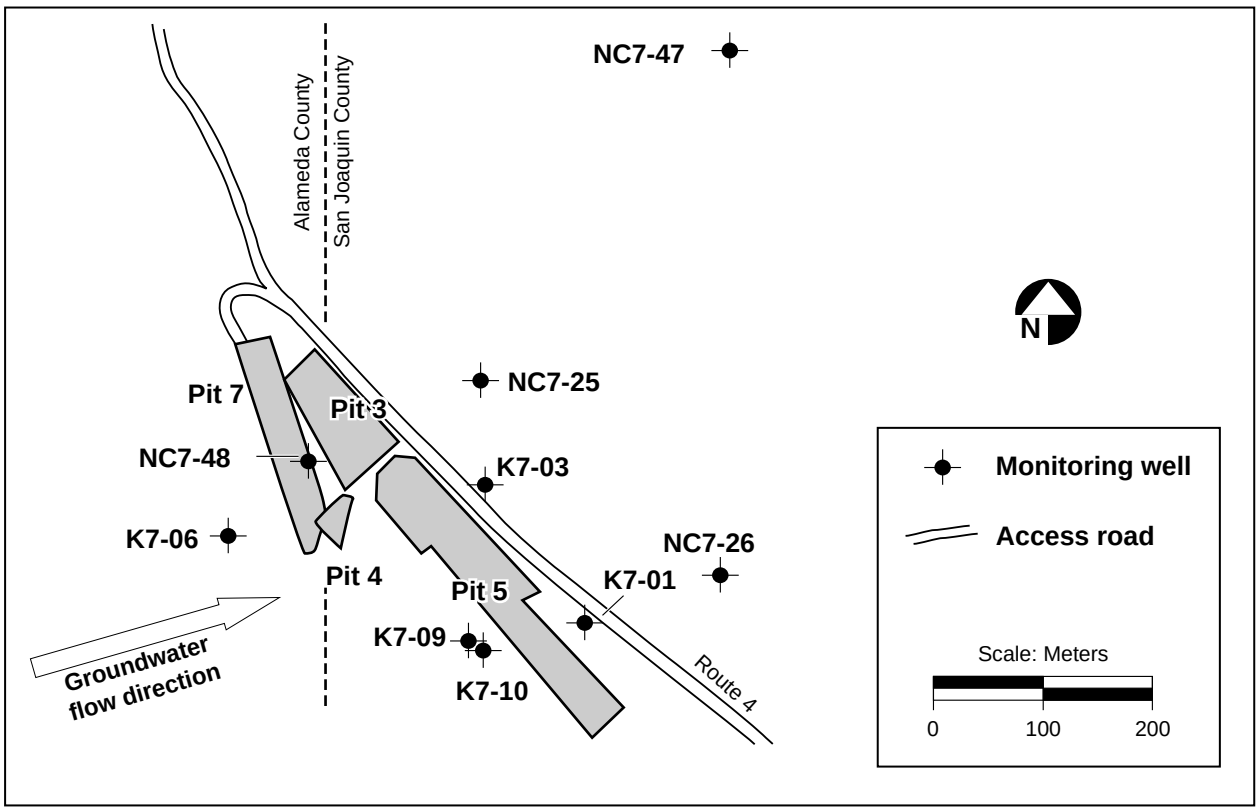

Figure 8-10. Site 300 Pit 7 Complex groundwater compliance monitoring wells

Closure and post-closure of Pit 6 are being conducted as a non-time-critical removal action under CERCLA, part of the overall remediation of Site 300. The initial component of this

removal action was construction of an impermeable cap and associated drainage controls to prevent infiltration of surface water that could mobilize contaminants. Reduced groundwater recharge in the area of the VOC plume will further lessen the potential for off-site migration of VOCs. Other components of the removal action include groundwater monitoring and administrative controls.

Post-closure groundwater monitoring began during the second quarter of 1998 to detect any releases of contaminants from the buried waste. Monitoring is also used to evaluate the natural attenuation of the VOC plume, assess the effectiveness of the corrective action, and trigger evaluation of the need for contingency actions. Groundwater monitoring is conducted at six detection monitoring wells (EP6-06, EP6-08, EP6-09, K6-01S, K6-36, and K6-19), all located hydrologically downgradient of Pit 6 along the point of compliance; and at four upgradient wells (K6-03, K6-04, K6-15, and K6-32), as shown in **Figure 8-11**. (Corrective action monitoring points consist of all monitoring wells.)

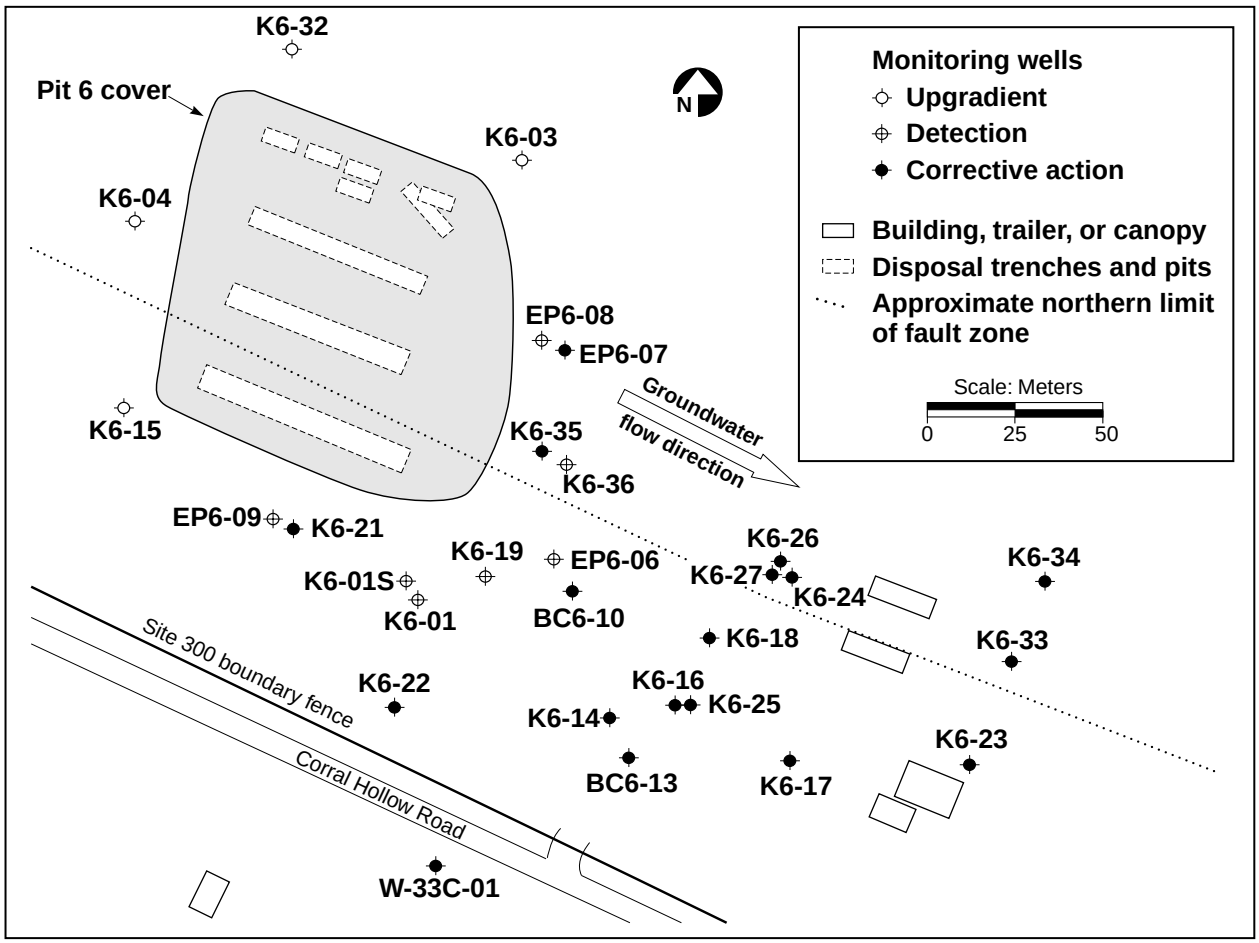

Figure 8-11. Locations of Pit 6 compliance monitoring wells and northern limit of fault zone

The Post-Closure Monitoring Plan (PCMP) for Pit 6 identifies potential contaminants to groundwater (Ferry et al. 1998). These COCs, as defined by Title 22 CCR, Chapter 15, are waste constituents, their reaction products, or hazardous constituents that are reasonably expected to be in or derived from the buried waste. COCs for monitoring at Pit 6 are listed in **Table 8-8**.

Although not specifically identified as contaminants disposed of in Pit 6, several chlorinated VOCs (including TCE, PCE, 1,2-DCA, 1,1,1-TCA, methylene chloride, and chloroform) have been detected in soil or groundwater samples, indicating a release to the subsurface. In addition, benzene, toluene, ethylbenzene, and total xylenes have been detected in groundwater. Therefore, these contaminants are also COCs.

Beryllium and mercury are COCs because they are listed in the waste disposal records as being associated with the buried waste.

Table 8-8. Pit 6 COCs, their typical analytical reporting limits (RL), and their statistical limits of concentration (SL), for each detection monitoring well

Constituent of concern (COC)	Typical analytical RL (units)	Well EP6-06 SL	Well EP6-08 SL	Well EP6-09 SL	Well K6-01S SL	Well K6-19 SL	Well K6-36 SL
1,1,1-TCA	0.5 µg/L	RL	RL	RL	RL	RL	TBD[a]
1,2-DCA	0.5 µg/L	RL	RL	RL	RL	RL	TBD
Cis-1,2-DCE	0.5 µg/L	RL	RL	RL	7.0	RL	TBD
Chloroform	0.5 µg/L	RL	1.0	RL	RL	1.5	TBD
Methylene chloride	0.5 µg/L	RL	RL	RL	RL	RL	TBD
PCE	0.5 µg/L	RL	1.6	RL	RL	RL	TBD
TCE	0.5 µg/L	RL	RL	17	1.5	13	TBD
Benzene	0.5 µg/L	RL	RL	RL	RL	RL	TBD
Ethylbenzene	0.5µg/L	RL	RL	RL	RL	RL	TBD
Toluene	0.5 µg/L	RL	RL	RL	RL	RL	TBD
Total xylenes	1 µg/L	RL	RL	RL	RL	RL	TBD
Beryllium	0.5 µg/L	RL	RL	RL	RL	RL	TBD
Mercury	0.2 µg/L	RL	RL	RL	RL	RL	TBD
Carbon disulfide	5.0 µg/L	RL	RL	RL	RL	RL	TBD
Perchlorate	4 µg/L	RL	RL	RL	RL	27.5	14.4
Tritium	100 pCi/L	RL	RL	RL	RL	RL	TBD
Uranium	0.3 pCi/L	3.6	1.5	3.7	27	7.2	TBD
Gross alpha	1 pCi/L	7.7	4.0	4.9	26	9.2	TBD
Gross beta	1 pCi/L	21	21	21	58	21	TBD

a TBD = to be determined

Nine radionuclide COCs are associated with waste buried in Pit 6: antimony-125, cesium-137, cobalt-60, sodium-22, strontium-90, thallium-204, thorium-232, uranium-238, and tritium. Gross alpha and gross beta data are used as surrogates for seven radionuclides other than uranium and tritium.

Sampling is conducted quarterly for all COCs at monitoring wells for which backgrounds are known from existing data, and from which SLs can be determined.

Samples are submitted for analysis to an analytical laboratory certified by the California Department of Health Services. Analyses use EPA methods or other appropriate standard methods.

The data gathered through the Pit 6 monitoring program are reported quarterly to the Site 300 Remedial Project Managers. An annual report, in lieu of a fourth quarter report, is due March 1 of the following calendar year.

8.2.3 Building 829 Monitoring Network at Site 300

8.2.3.1 Rationale and Design Criteria

8.2.3.1.1 Regulatory Drivers. During early 1999, LLNL closed the HE Open Burn Treatment Facility within the Building 829 Complex in the south-central portion of Site 300. The facility was operated as an interim status thermal treatment unit under RCRA (40 CFR 265, Subpart P, *Thermal Treatment*; and 22 CCR, Division 4.5, Chapter 15, Article 16). Provisions for the post-closure monitoring of such hazardous waste treatment facilities are identified in the governing regulations. 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).

The former High-Explosives (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 (1050 ft) (see **Figure 8-12**). The facility included three shallow unlined pits constructed in unconsolidated sediments that cap the ridge (Tps formation). The former burn facility was covered with an impervious cap during 1998 following RCRA guidance. The facility was used to thermally treat explosives waste generated by research operations at Site 300. Surface water drains southward from the facility toward Corral Hollow Creek. The nearest site boundary lies about 1.6 km (4500 ft) 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 (100 ft), is perched within the Neroly upper siltstone/claystone aquitard ($Tnsc_2$). The deeper zone, at a depth of about 120 m (400 ft), represents a regional aquifer within the Neroly upper sandstone member ($Tnbs_2$). The design of the post-closure monitoring plan (PCMP) is described in Chapter 2 of 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).

8.2.3.1.2 Monitoring Objectives. The primary monitoring objective of the PCMP is to detect any release of COCs from the treatment facility.

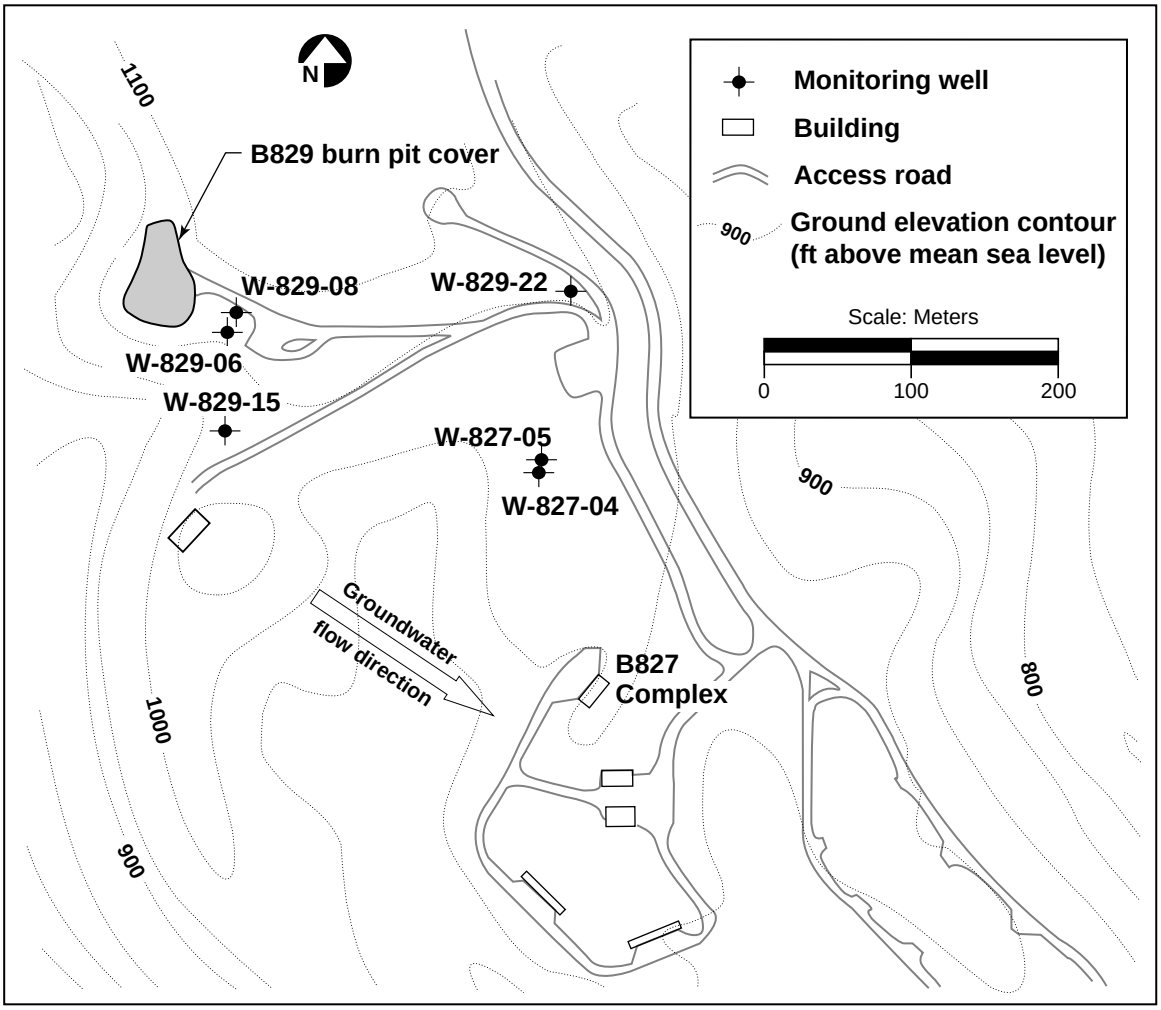

Figure 8-12. Site 300 Building 829 HE Open Burn Treatment Facility groundwater compliance monitoring wells

8.2.3.2 Potential Sources and Contaminants.

The PCMP identified the wastes treated at the HE Open Burn Treatment Facility as potential groundwater contaminants. LLNL used treatment records, analyses of waste ash from the treatment process, and analyses of groundwater and soil samples from beneath the facility to identify the COCs listed in **Table 8-9** for this monitoring network.

8.2.3.3 Extent and Frequency of Monitoring and Measurements

8.3.3.3.1. Criteria for Sampling Location Selection. LLNL established a point of compliance (POC) approximately 274 m downgradient of the edge of the HE Open Burn Treatment Facility. Four monitoring wells (W-827-04, W-827-05, W-829-15, and W-829-22 shown in **Figure 8-12**) are located along the POC and are completed in the regional aquifer, which is the uppermost aquifer beneath the Open Burn Treatment Facility.

In addition to the above wells, two boreholes screened in a shallow, perched, water-bearing zone were converted to monitoring wells, identified as wells W-829-06 and W-829-08 in **Figure 8-12**. LLNL plans to monitor the perched water-bearing zone from these two monitoring wells throughout the post-closure period.

8.2.3.3.2 Sampling Frequency. Groundwater monitoring of the water-bearing zones beneath the HE Open Burn Treatment Facility include quarterly sampling of wells W-829-06 and W-829-08 (screened in the perched water-bearing zone beneath the facility) for VOCs and HE compounds HMX, RDX, and TNT, and quarterly sampling of wells W-827-05, W-829-15 and W-829-22 (screened in the deep regional aquifer) for the COCs listed in **Table 8-9**. COCs were selected based on the potential contaminants associated with the operation of the treatment facility. As in past years, it has not been possible to obtain groundwater samples from monitoring well W-827-04 because it is screened above the present elevation of the water table in the deep regional aquifer.

8.2.3.3.3 Quality Assurance/Quality Control (QA/QC) Sampling. Elements of the QA/QC sampling program are consistent with Dibley and Depue (2002), including the collection of duplicates, field blanks, and trip blanks. QA sampling requirements are specified on field tracking forms (FTFs) for each sampling event.

8.2.3.4 Constituents of Concern

The Post-Closure Monitoring Plan (PCMP) for Building 829 identifies potential contaminants to groundwater (Mathews and Taffet 1997). **Table 8-9** lists the COCs identified in the PCMP, their typical analytical reporting limits (RLs), and their statistical limits of concentration (SLs) as presented in Revelli (2003).

8.2.3.4.1 Class II Surface Water Impoundments Compliance Monitoring Network. The main purpose of compliance monitoring of the two surface impoundments is to detect any release of COCs contained in process water to ground. The COCs for analysis are specified in WDR Order 96-248 (CVRWQCB 1996).

Figure 8-13 shows Building 817, the two surface impoundments, and the groundwater wells used for compliance monitoring in the Explosives Process Area. (Not shown are the locations of the five lysimeters installed beneath the surface impoundments.)

Four groundwater monitoring wells, screened in the $Tnbs_2$, are used. The direction of groundwater flow is southeast, following the local dip of the underlying sedimentary formations. Well W-817-01 is hydrologically upgradient of the surface impoundments. Wells W-817-02, W-817-03, and W-817-04 are downgradient.

Table 8-9. Constituents of concern, their typical analytical reporting limits (RLs), and their statistical limits of concentration (SLs) for the Building 829 Facility deep monitoring wells W-827-05, W-829-15, and W-829-22

Constituent of concern	Typical analytical RL (µg/L)	Well W-827-05 SL	Well W-829-15 SL	Well W-829-22 SL
HMX	5	RL	RL	RL
RDX	5	RL	RL	RL
TNT	5	RL	RL	RL
Chromium	1	3.7	7.8	1.5
Cobalt	25	RL	RL	RL
Copper	10	30	RL	RL
Antimony	5	RL	RL	RL
Arsenic	2	4.1	22	2.9
Barium	25	RL	75	RL
Lead	2	RL	RL	RL
Manganese	10	300	RL	RL
Mercury	0.2	RL	RL	RL

(continued)

Table 8-9. Constituents of concern, their typical analytical reporting limits (RLs), and their statistical limits of concentration (SLs) for the Building 829 Facility deep monitoring wells W-827-05, W-829-15, and W-829-22 (concluded).

Constituent of concern	Typical analytical RL (µg/L)	Well W-827-05 SL	Well W-829-15 SL	Well W-829-22 SL
Molybdenum	25	31	27	RL
Nickel	5	RL	RL	RL
Selenium	2	RL	RL	RL
Silver	1	RL	RL	RL
Beryllium	0.5	RL	RL	RL
Vanadium	25	RL	RL	RL
Zinc	20	RL	RL	RL
Cadmium	0.5	RL	RL	RL
Chloroform	0.5	RL	RL	RL
Dichlorodifluoromethane	0.5	RL	RL	RL
1,2-Dichloroethane	0.5	RL	RL	RL
1,1-Dichloroethene	0.5	RL	RL	RL
1,2-Dichloroethene (total)[(a)]	1	RL	RL	RL
Ethylbenzene	0.5	RL	RL	RL
Freon 113	0.5	RL	RL	RL
Benzene	0.5	RL	RL	RL
Phenols	2	RL	RL	RL
Tetrachloroethene	0.5	RL	RL	RL
Toluene	0.5	RL	RL	RL
1,1,1-Trichloroethane	0.5	RL	RL	RL
Trichloroethene	0.5	RL	RL	RL
Trichlorofluoromethane	0.5	RL	RL	RL
Total xylene isomers	1	RL	RL	RL
Bis (2-ethylhexyl) phthalate	5	RL	RL	RL
Carbon disulfide	5	RL	RL	RL
Gross alpha (pCi/L)	2	6.0	3.3	RL
Gross beta (pCi/L)	3	41.6	102	11.5

a Includes *cis*- and *trans*-1,2-dichloroethene.

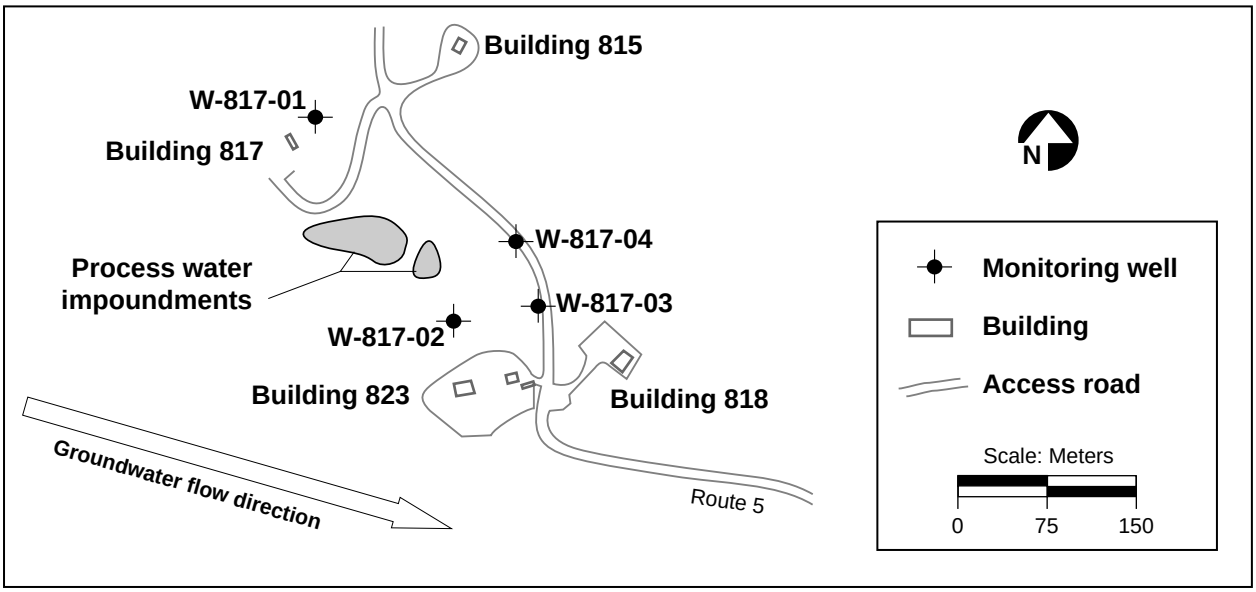

Figure 8-13. Site 300 Explosives Process Area groundwater compliance monitoring wells

Effluent rinsewater from the photographic processes is sampled and analyzed for total metals and pH. Effluent wastewater from the chemistry processes is sampled and analyzed for RDX; HMX; 2,4,6-trinitro-1,3,5-benzenetriamine (TATB); VOCs; and dimethyl sulfoxide (DMSO). Effluent wastewater from the explosives processes is sampled and analyzed for total metals; RDX; HMX; TATB; 2,4,6-trinitrotoluene (TNT); pentaerythritol tetranitrate (PETN); VOCs; and extractable organic compounds. COCs and their effluent limits for water discharged to the surface impoundments are listed in **Table 8-10**. Wastewater COCs, sampling frequencies, and the analytical methods used to detect them are listed in **Table 8-11**.

Figure 8-14 is a schematic diagram of the wastewater sampling locations.

For compliance monitoring purposes, groundwater samples are collected quarterly from the four monitoring wells and are analyzed for the COCs listed in **Table 8-12**.

Influent samples are collected whenever a discharge occurs from retention tanks that collect photographic process rinsewater (from retention tanks at Buildings 801, 823, and 851) or whenever discharges of Chemistry Area wastewater occur (from retention tanks at Buildings 825 and 826 and from the Building 827 Complex). These samples are analyzed for COCs that are likely to be found in process water discharging to the surface impoundments. Because rinse water from the Building 823 retention tank is discharged automatically to the surface impoundments, samples are collected on a quarterly basis. Process wastewater generated from the Explosives Process Area (Buildings 806/807, 809, and 817) also discharges

automatically and is sampled annually to verify compliance with WDR Order 96-248 (CVRWQCB 1996).

The outflows of the two LCRSs are visually monitored once a week for the presence of water that would indicate a leak in a surface impoundment liner. Five lysimeters installed beneath the liners of the impoundments are operated quarterly. Any water flowing from an LCRS or extracted from a lysimeter is presumed to be leachate. Proof is obtained by analyzing the presumed leachate for the COCs and parameters listed in **Table 8-13**. For additional proof, samples from the surface impoundment are collected and analyzed for the COCs and parameters listed in **Table 8-13**.

Sewage Evaporation and Percolation Ponds Compliance Monitoring Network

Environmental monitoring is specified in the Monitoring and Reporting Plan (MRP) part of WDR Order 96-248 for the sewage evaporation and percolation ponds (sewage ponds). In response to this permit, a new compliance network was formed in 1996 to analyze both wastewater and groundwater at the sewage ponds.

Table 8-10. COCs, processes generating discharges, and discharge limits for wastewater entering the Site 300 surface impoundments

Constituent of concern (COC)	Discharge limit (mg/L)
Acid and bases	2 < pH < 12.5
Halocarbons	
1,1,1-Trichloroethane	100
Bromoform	100
Chlorobenzene	100
1,2-Dichloroethane (1,2-DCA)	0.5
Methylene chloride	100
Tetrachloroethene (PCE)	0.7
Trichlorotrifluoroethane (Freon 113)	100
Hydrocarbons	
Napthalene	200
Toluene	200
Metals	
Aluminum	None
Arsenic	5
Barium	100
Cadmium	1
Chromium	5
Cobalt	80
Copper	25

(continued)

Table 8-10. COCs, processes generating discharges, and discharge limits for wastewater entering the Site 300 surface impoundments (concluded)

Constituent of concern (COC)	Discharge limit (mg/L)
Lead	5
Manganese	None
Molybdenum	350
Nickel	20
Potassium	None
Silver	5
Zinc	250
Photographic chemicals	
m- & *p*-Cresol	50
Benzyl alcohol	1000
Salts	
Ammonia (as N)	None
Bicarbonate	None
Bromide	None
Chloride	None
Nitrate	None
Orthophosphate	None
Silver thiosulfate	5
Sulfate	None
Volatile/semivolatile compounds	
Acetone	1000
Methyl ethyl ketone (2-butanone)	200
Dimethyl sulfoxide (DMSO)	1000
Ethyl alcohol (Ethanol)	1000
Methyl isobutyl ketone	1000
Energetic materials	
HMX[(a)]	None
PETN[(b)]	None
RDX[(c)]	None
TATB[(d)]	None
TNT[(e)]	None
Additives to energetic materials	
Bis(2-ethylhexyl) phthalate	None
Unreactive polymers	
Vinyl chloride	0.2
Styrene	None

a HMX is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

b PETN is pentaerythritol tetranitrate.

c RDX is hexahydro-1,3,5-trinitro-1,3,5-triazine.

d TATB is 1,3,5-triamine-2,3,6-trinitobenzene.

e TNT is 2,4,6-trinitrotoluene.

Table 8-11. COCs, sampling frequencies, and EPA methods for influent entering the Site 300 surface impoundments

Constituent of concern (COC)	EPA method
Photographic processing (B801,[a] B823,[b] B850,[a] B851[a]) wastewater	
Antimony	204.2 or 200.8
Barium	200.7 or 200.8
Beryllium	210.2 or 200.8
Cadmium	213.2 or 200.8
Chromium	218.2 or 200.8
Cobalt	200.7 or 200.8
Copper	220.2, 200.7, or 200.8
Lead	239.2 or 200.8
Manganese	200.7 or 200.8
Molybdenum	200.7
Nickel	249.2, 200.7, or 200.8
Silver	272.2, 200.7, or 200.8
Thallium	279.2 or 200.8
Vanadium	200.7 or 200.8
Zinc	200.7 or 200.8
Chemistry Area (B825,[a] B826,[a] B827A,[a] B827C,[a] B827E[a])	
DMSO	625
RDX and HMX	8330
TATB[c]	Ion chromatography[c]
Volatiles	8021, 8260 or 624
Explosives Process Area (B806/807,[d] B809,[d] B817[a])	
Aluminum	200.7 or 200.8
Arsenic	206.2 or 200.8
Barium	200.7 or 200.8
Cadmium	213.2 or 200.8
Chromium	218.2 or 200.8
Cobalt	200.7 or 200.8
Copper	220.2, 200.7, or 200.8
Lead	239.2 or 200.8
Manganese	200.7 or 200.8
Molybdenum	200.7
Nickel	249.2, 200.7, or 200.8
PETN[e]	8330
RDX[f] and HMX[g]	8330
Semivolatiles	625
Silver	272.2, 200.7, or 200.8
TATB[h]	Ion chromatography[c]
TNT[i]	8330

(continued)

Table 8-11. COCs, sampling frequencies, and EPA methods for influent entering the Site 300 surface impoundments (concluded)

Constituent of concern (COC)	EPA method
Volatiles	8021, 8260 or 624
Zinc	200.7 or 200.8

a Each batch

b Quarterly

c There is no standard analytical method to analyze for TATB.

d Annually

e PETN is pentaerythritol tetranitrate.

f RDX is hexahydro-1,3,5-trinitro-1,3,5-triazine.

g HMX is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

h TATB is 1,3,5-triamino-2,4,6-trinitobenzene.

i TNT is 2,4,6-trinitrotoluene.

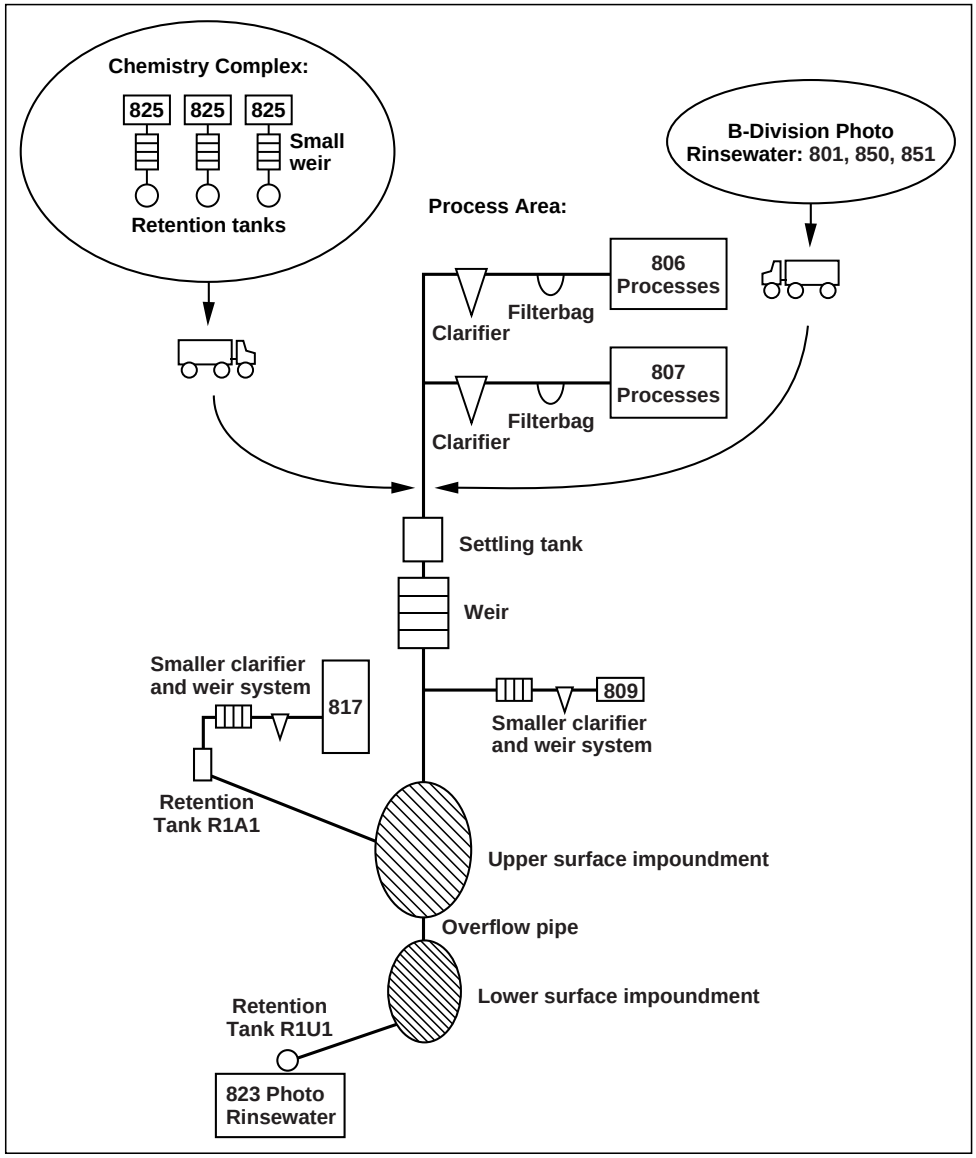

Figure 8-14. Schematic representation of wastewater inputs entering the Site 300 Class II surface water impoundments

Table 8-12. WDR 96-248 COCs, wells, and statistical limits for groundwater beneath the Site 300 surface impoundments

Constituent of concern (COC)	Well	Statistical limit[a]
Halocarbons (µg/L)		
1,1,1 Trichloroethane	All	1.0
Bromoform	All	1.0
Chlorobenzene	All	1.0
1,2-Dichloroethane (1,2 DCA)	All	1.0
Methylene chloride	All	1.0
Tetrachloroethene (PCE)	All	1.0
Trichlorotrifluoroethane (Freon 113)	All	1.0
Hydrocarbons (µg/L)		
Napthalene	All	5
Toluene	All	1.0
Metals (mg/L)		
Aluminum	All	0.2
Arsenic	W-817-02	0.073
	W-817-03	0.072
	W-817-04	0.077
Barium	All	0.025
Cadmium	W-817-02	0.0016
	W-817-03	0.001
	W-817-04	0.001
Chromium	W-817-02	0.003
	W-817-03	0.0042
	W-817-04	0.0098
Cobalt	All	0.05
Copper	All	0.02
Lead	All	0.0099
Manganese	All	0.010
Molybdenum	W-817-02	0.073
	W-817-03	0.060
	W-817-04	0.054
Nickel	All	0.044
Potassium	W-817-02	18.6
	W-817-03	14.6
	W-817-04	13.7
Silver	All	0.001
Zinc	W-817-02	0.24
	W-817-03	0.0099
	W-817-04	0.055
Photographic chemicals (µg/L)		
m- & *p*-Cresol	All	2
Benzyl alcohol	All	2

(continued)

Table 8-12. WDR 96-248 COCs, wells, and statistical limits for groundwater beneath the Site 300 surface impoundments (concluded)

Constituent of concern (COC)	Well	Statistical limit
Salts (mg/L)		
Ammonia (as N)	All	0.02
Bicarbonate	All	277
Bromide	W-817-02	1.46
	W-817-03	1.18
	W-817-04	1.49
Chloride	W-817-02	388
	W-817-03	302
	W-817-04	296
Nitrate	All	110
Ortho-phosphate	All	0.19
Perchlorate	W-817-02	0.044
	W-817-03	0.050
	W-817-04	0.049
Sulfate	W-817-02	512
	W-817-03	233
	W-817-04	284
Volatile/semivolatile compounds (µg/L)		
Acetone	All	10
Methyl ethyl ketone (2-butanone)	All	20
Dimethyl sulfoxide (DMSO)	All	10
Ethyl alcohol (ethanol)	All	1000
Methyl isobutyl ketone	All	20
Energetic materials (µg/L)		
HMX	All	1.0
PETN	All	1.0
RDX	W-817-02	0.85
	W-817-03	9.3
	W-817-04	9.68
TATB	All	20
Tetryl	All	1.0
TNT	All	0.26
4-Amino-2,6-dinitrotoluene	W-817-02	0.26
	W-817-03	1.22
	W-817-04	1.08
Additives to energetic materials (µg/L)		
Bis(2-ethylhexyl) phthalate	All	5
Unreactive polymers (µg/L)		
Vinyl chloride	All	1.0
Styrene	All	1.0

a The significant figures displayed in this table vary by **COC**. These variations reflect regulatory agency permit stipulations, or the applicable analytical laboratory contract under which the work was performed, or both. The statistical limits may be updated annually. The present limits are for calendar year 2001.

Table 8-13. Site 300 leachate collection and removal system (LCRS) effluent monitoring program

Constituent of concern (COC) or parameter	Analytical method[a]	Upper pond LCRS	Lower pond LCRS	Upper pond[b]	Lower pond[b]
Aluminum	EPA 200.7 or 200.8	I/Q[c]	I/Q	As needed	As needed
Arsenic	EPA 206.2 or 200.8	I/Q	I/Q	As needed	As needed
Barium	EPA 200.7 or 200.8	I/Q	I /Q	As needed	As needed
Bicarbonate alkalinity (as $CaCO_3$)	EPA 310.1	I/Q	I/Q	As needed	As needed
Cadmium	EPA 213.2 or 200.8	I/Q	I/Q	As needed	As needed
Calcium	EPA 200.7	I/Q	I/Q	As needed	As needed
Carbonate alkalinity (as $CaCO_3$)	EPA 310.1	I/Q	I/Q	As needed	As needed
Chloride	EPA 300.0	I/Q	I/Q	As needed	As needed
Chromium	EPA 218.2 or 200.8	I/Q	I/Q	As needed	As needed
Cobalt	EPA 200.7 or 200.8	I/Q	I/Q	As needed	As needed
Copper	EPA 220.2, 200.7, or 200.8	I/Q	I/Q	As needed	As needed
Fluoride	EPA 340.2 or 300.0	I/Q	I/Q	As needed	As needed
Hydroxide alkalinity (as $CaCO_3$)	EPA 310.1	I/Q	I/Q	As needed	As needed
Iron	EPA 200.7 or 200.8	I/Q	I/Q	As needed	As needed
Lead	EPA 239.2 or 200.8	I/Q	I/Q	As needed	As needed
Magnesium	EPA 200.7 or 200.8	I/Q	I/Q	As needed	As needed
Manganese	EPA 200.7 or 200.8	I/Q	I/Q	As needed	As needed
Molybdenum	EPA 200.7	I/Q	I/Q	As needed	As needed
Nickel	EPA 249.2, 200.7, or 200.8	I/Q	I/Q	As needed	As needed
Nitrate (as NO_3)	EPA 345.1 or 300.0	I/Q	I/Q	As needed	As needed
pH	EPA 150.1	I/Q	I/Q	As needed	As needed
Potassium	EPA 200.7 or 200.8	I/Q	I/Q	As needed	As needed
RDX[d]	EPA 8330	I/Q	I/Q	As needed	As needed
HMX[e]	EPA 8330	I/Q	I/Q	As needed	As needed

(continued)

Table 8-13. Site 300 leachate collection and removal system (LCRS) effluent monitoring program (concluded)

Constituent of concern (COC) or parameter	Analytical method[(a)]	Upper pond LCRS	Lower pond LCRS	Upper pond[(b)]	Lower pond[(b)]
Silver	EPA 272.2 or 200.8	I/Q	I/Q	As needed	As needed
Sodium	EPA 200.7	I/Q	I/Q	As needed	As needed
Specific conductance	EPA 120.1	I/Q	I/Q	As needed	As needed
Sulfate	EPA 300.0	I/Q	I/Q	As needed	As needed
TDS[f]	EPA 160.1	I/Q	I/Q	As needed	As needed
Total alkalinity (as $CaCO_3$)	EPA 310.1	I/Q	I/Q	As needed	As needed
Total hardness (as $CaCO_3$)	SM 2320B	I/Q	I/Q	As needed	As needed
Zinc	EPA 200.7 or 200.8	I/Q	I/Q	As needed	As needed

a Or other approved method

b Samples are collected from the surface impoundment where leachate is found in the collection system. Samples are analyzed for the same parameters.

c I/Q = Initial discharge/quarterly = Sample upon initial discovery, and quarterly thereafter until discharge has stopped.

d RDX is hexahydro-1,3,5-trinitro-1,3,5-triazine.

e HMX is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

f TDS = Total dissolved solids

Quarterly samples of wastewater flowing into the sewage evaporation pond are collected and analyzed. Samples of wastewater flowing into the sewage evaporation pond are collected and analyzed for pH (limit 6.5<pH<10), specific conductance (EC), and biochemical oxygen demand (BOD). Samples of water in the pond are analyzed for pH, specific conductivity (SC), and dissolved oxygen (DO) (limit not less than 1.0 mg/L for more than 24 hours). The pond's condition is observed at least monthly for freeboard, color, odor, and levee condition. All overflow discharges to the percolation pond are sampled and analyzed for BOD, SC, total and fecal coliform, and pH.

Figure 8-15 locates the nine monitoring wells and the wastewater sampling points. Groundwater monitoring includes semiannual sampling and analysis of upgradient monitoring wells W-7E, W-7ES, and W-7PS; cross-gradient groundwater monitoring well W-35A-04; and downgradient groundwater monitoring wells W-7DS, W-25N-20, W-26R-01, W-26R-11, and W-26R-15. Monitoring wells W-7ES, W-7PS, W-26R-11, and W-35A-04 are screened in Quaternary alluvium (Qal); wells W-7E and W-26R-01 are screened in $Tnbs_1$. The three remaining wells are screened in both Qal and $Tnbs_1$. The COCs for sewage pond monitoring are listed in **Table 8-14.**

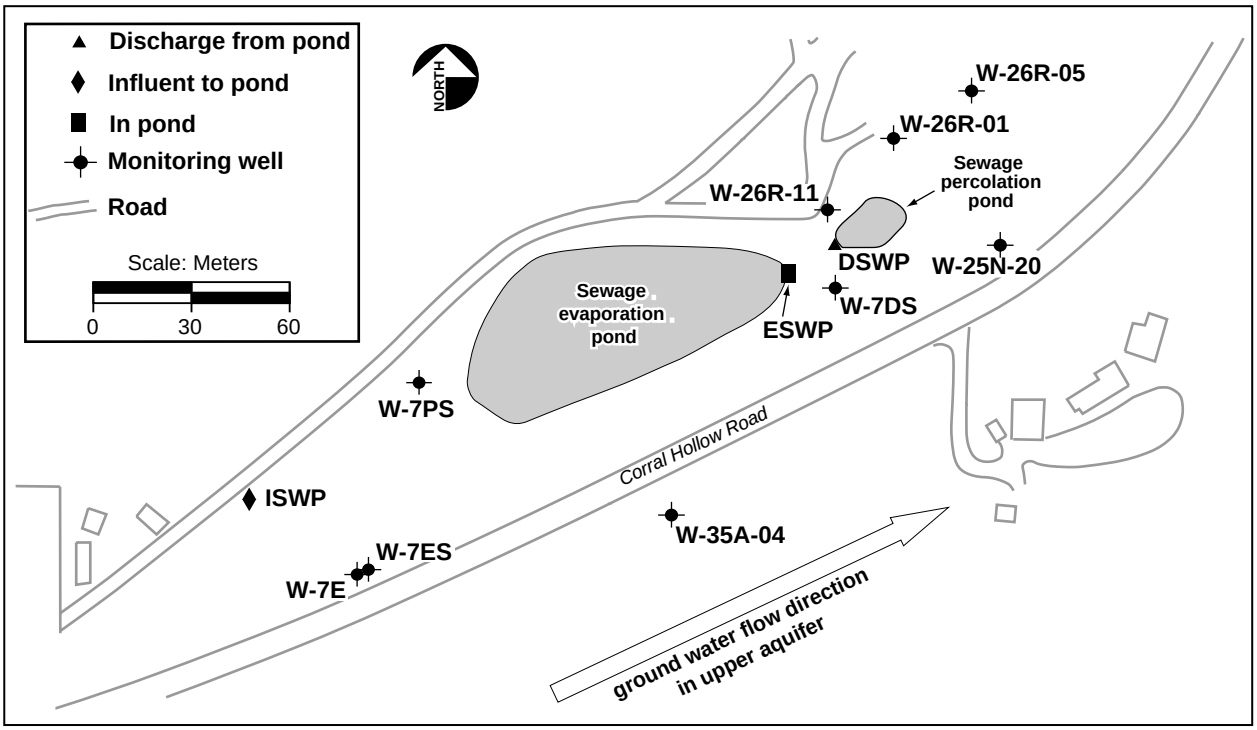

Figure 8-15. Site 300 sewage ponds groundwater compliance monitoring wells and wastewater sampling locations

Table 8-14. WDR 96-248 COCs and concentration limits for the groundwater beneath the Site 300 sewage evaporation and percolation ponds

Constituent of concern (COC)	Concentration limit
Groundwater elevation[a]	None
Biological:	
Total coliform bacteria	None
Fecal coliform bacteria	2.2 MPN[b] /100 mL
General:	
pH	None
Nitrate	None
Specific conductivity	None

a Groundwater elevation is monitored to calculate groundwater flow.

b MPN = most probable number of organisms

8.3 Procedures for Laboratory Analysis

Tritium analysis and other routine radioactivity and radioisotope measurements are performed offsite by certified contract laboratories. LLNL analytical laboratories are occasionally used for nonroutine measurements of various radioisotopes.

Tables 8-1, **8-2**, and **8-3** list the COCs for groundwater surveillance, the EPA or Standard Method used to measure each constituent, a typical reporting detection limit expected for each method, and action level concentrations. (No EPA or Standard Method exists for the explosive compound triaminotrinitobenzene [TATB]; it is measured using ion chromatography.) COC concentrations in groundwater are monitored down to their analytical reporting limits (RLs), which are equivalent to practical quantitation limits (PQLs). The RL (PQL) for a COC can vary depending upon the presence of interfering substances dissolved in the water. For an analytical method to meet LLNL data quality objectives (DQOs), RLs must be at or below EPA or California maximum contaminant levels (MCLs) for drinking water, or be below any permitted statistical limits of concentration (SLs) for COCs. Analytical laboratories must be California-certified in order to meet LLNL's quality assurance and compliance monitoring requirements.

8.4 Quality Assurance Procedures

Tables 8-1, **8-2**, and **8-3** list DQOs for analyses of various chemicals and radionuclides in groundwater samples. Where California or federal MCLs have been established for drinking water, the DQOs are below the MCLs.

8.4.1 Analytical Precision

Field duplicate (collocated) samples, about 10 percent or more in frequency, are collected and submitted to the analytical laboratories with fictitious identifiers and are processed in batches of routine samples. Additional samples are split at the analytical laboratory and are analyzed separately. Matrix spike and matrix spike duplicate samples are included with each batch of samples analyzed. Results from these additional samples provide a measure of analytical precision.

8.4.2 Analytical Bias

Laboratory control samples are prepared and analyzed at the analytical laboratory to determine the existence of systematic errors, that is, analytical biases related to calibrations of measuring instruments. Matrix spike and matrix spike duplicate sample results may also indicate analytical bias.

8.4.3 Field Sampling Assessments

Annual assessments of groundwater sampling are scheduled for all groundwater networks, according to the applicable ERD standard operating procedures (SOPs); each assessment covers a portion of those SOPs. Assessments are scheduled every three years for the other water monitoring networks.

8.4.4 Quality Assurance/Quality Control Sampling

For purposes of quality assurance/quality control (QA/QC), groundwater and leachate collection and removal system (LCRS) samples are collected according to ERD SOP 4.9, "Collection of Field QC Samples." Specifically, QC duplicate or collocated samples are collected for about 10 percent of the routine samples for QA/QC purposes. Field blank samples are also collected and analyzed, one for every field grouping of samples. ERD SOP 4.6, "QA/QC Objectives for Nonradiological Data Generated by Analytical Laboratories," describes in detail the objectives of analyses of these samples for the groundwater and LCRS media (Dibley and Depue 2000). The same QA/QC objectives are applied to all monitoring of influent entering the surface impoundments.

QA/QC requirements for monitoring sewage influent into and effluent from the sewage evaporation pond are discussed briefly in procedure EMP-W-S and supplements and are similar to those in the ERD SOPs.

8.5 Program Implementation Procedures—Sample Collection Methods

Sampling, testing, and screening procedures for all groundwater and lysimeter sampling are covered in the *Livermore Site and Site 300 Environmental Restoration Projects Quality Assurance Project Plan* (QAPP), Chapter 5 (Sampling Procedures), Chapter 7 (Calibration Procedures), and Chapter 8 (Analytical Procedures) (Dibley 1997), as well as in *LLNL Livermore Site and Site 300 Environmental Restoration Project Standard Operating Procedures* (SOPs) (Dibley and Depue 2000). The safety of technicians who perform sampling tasks in the field is covered by Integrated Work Sheet 529. Details of these procedures are not included in this document. Groundwater and lysimeter samples are collected in the field and sent to the analytical laboratory(ies) with their chain-of-custody documentation by trained technicians with the Environmental Restoration Division (ERD). The SOPs listed in **Table 8-15** are followed to ensure consistent groundwater monitoring results that accurately represent groundwater quality at all monitoring points. Monitoring networks are individually assigned to an Operations and Regulatory Affairs Division (ORAD) analyst or analyst assistant, who directs groundwater monitoring on a day-to-day basis and prepares quarterly sampling plans.

Table 8-15. Groundwater standard operating procedures (SOPs) used by ERD at LLNL in groundwater monitoring

SOP	Title
1.9	Lysimeter Soil Moisture Sampling
1.10	Soil Vapor Surveys
2.1	Presample Purging of Wells
2.2	Field Measurements on Surface and Groundwaters
2.3	Sampling Monitor Wells with Bladder and Electric Submersible Pumps
2.4	Sampling Monitor Wells with a Bailer
2.6	Sampling for Volatile Organic Compounds
2.7	Presample Purging and Sampling of Low Yielding Monitor Wells
2.8	Installation of Dedicated Sampling Pumps
2.9	Sampling for Tritium in Groundwater
2.10	Well Disinfection and Coliform Bacteria Sampling
2.12	Groundwater Monitor Well and Equipment Maintenance
3.1	Water-Level Measurement
3.2	Pressure Transducer Calibration
4.1	General Instructions for Field Personnel
4.2	Sample Control and Documentation
4.3	Sample Containers and Preservation
4.4	Guide to Handling, Packaging, and Shipping of Samples
4.5	General Equipment Decontamination
4.6	QA/QC Objectives for Nonradiological Data Generated by Analytical Laboratories
4.7A	Livermore Site Treatment and Disposal of Well Development and Well Purge Fluids
4.7B	Site 300 Treatment and Disposal of Well Development and Well Purge Fluids
4.8	Calibration/Verification and Maintenance of Field Instruments Used in Measuring Parameters of Surface Water, Groundwater, and Soils
4.9	Collection of Field QC Samples
4.15	ERD Self-Assessments and Walk-Abouts
5.1	Data Management Printed Analytical Result Receipt and Processing
5.2	Data Management Chain-of-Custody Receipt and Processing
5.3	Data Management Electronic Analytical Result Receipt and Processing for Sample and Analysis Data
5.4	Data Management Hand Entry of Analytical Results
5.5	Data Management Revision, Receipt, and Processing

Written procedures detailing sampling for all water media except groundwater are contained in LLNL ORAD procedure EMP-W-S. This procedure describes the methods ORAD field technicians use to collect samples from surface water bodies (such as the Site 300 surface impoundments and the sewage ponds) and from influent into (including with ISCO samplers)

and effluent from these ponds. An SOP supplement EMP-WSS-PPT was developed and is being followed for sampling of wastewater discharges from retention tanks from photographic process operations. SOP supplement EMP-WSS-HEP was developed and is being followed for sampling of wastewater discharges from the Explosives Process Area. SOP supplement EMP-WSS-SWEP was developed and is being followed for sewage pond sampling. ORAD IWS 674 was developed for sampling activities conducted under SOP EMP-W-S. EMP-QA-BOT further describes requirements for sample bottles, sample preservation, special sampling techniques, and other analyte-specific information for all COCs in aqueous media routinely sampled by LLNL. Quarterly sampling schedules (Analysis Request Sheets) detail the routine and QA/QC sample plans for each medium, including WDR 96-248 related retention tank discharge sampling.

Written procedures (**Table 8-16**) govern ORAD's water sampling operations other than groundwater and ensure their compliance with DOE and other regulatory requirements.

Table 8-16. Water monitoring procedures used at LLNL by ORAD to ensure data quality

Procedure and Supplements	Title
EMP-QA-BOT	Aqueous Sample Bottle Requirements
EMP-QA-DM	Data Management
EMP-W-S	Water Sampling Procedure
(supplements to SOP EMP-W-S)	
EMP-WSS-PPT	Site 300 Photo Process Retention Tank Sampling
EMP-WSS-HEP	Site 300 HE Process Wastewater Discharge Sampling
EMP-WSS-SWEP	Site 300 Sewage Evaporation Pond Wastewater Sampling

The collection of samples from retention tanks not equipped with ISCO samplers in the Chemistry Area at Site 300 is described in the LLNL Radioactive and Hazardous Waste Management (RHWM) Division's Procedure 411 (Rev. 1), "Sampling Containerized Liquids" (LLNL 1997b). These samples are collected and sent to the analytical laboratory(ies) with chain-of-custody documentation attached by RHWM field technicians, as directed by the responsible ORAD analyst or analyst assistant.

8.6 Action Levels

Environmental action levels are COC concentration levels in groundwater above which certain responses are automatic. These action level concentrations can be the analytical reporting limits (for compounds that are not typically detected), WDR permit limits, or drinking water MCLs. Action level concentrations for groundwater COCs at LLNL are listed in **Tables 8-1**, **8-2**, and **8-3**.

Automatic responses to exceedences of action level concentrations include the following actions:

- Assess QA/QC data from the analytical laboratory reporting the COC "hit."
- Notify LLNL management.
- Resample the monitoring point twice. Samples are taken at least one week apart to ensure independence.
- If either retest is another "hit," the initial result is confirmed. If neither retest is a "hit," the initial result is invalidated. LLNL management is notified of the retest results.
- For compliance monitoring, if retesting confirms the initial "hit," notify state regulators in writing within seven days of the finding.

Some COCs do not yet have action level concentrations established, because of a lack of sufficient data. These are listed as TBD (to be determined) in **Tables 8-1**, **8-2**, and **8-3**. Once sufficient analytical data have been analyzed, COC action level concentrations listed as TBD will be set using California-approved statistical methods.

LLNL uses SLs to detect significant increases of COC concentrations in groundwater. The control chart (CC) statistical method is preferred to generate SLs used as action level concentrations. This method is sensitive to COC concentration increases, and a single measurement of a COC concentration is sufficient, minimizing monitoring costs. Because concentrations of COCs are typically spatially variable, a control chart for each COC is developed for each monitoring well. Each new COC measurement is compared with its historical concentrations for that well.

When sufficient data are analyzed during the next 2 years, an action level concentration will be calculated for the few remaining COCs such that future measurements each have approximately a 1-in-100 chance of exceeding the action level concentration when no change in concentration has actually occurred. This yields a statistical test with a significance level of approximately 0.01.

8.7 Preparation and Disposition of Reports

The following reports document monitoring results from both the compliance and the surveillance networks.

- The annual *Environmental Report*—Groundwater monitoring data and significant results for a calendar year are summarized in a chapter of the LLNL site annual *Environmental Report* (e.g., Biermann et al. 2001) that is widely distributed to state

and federal agencies and to the public. Surveillance groundwater monitoring data are included in tables in the Data Supplement volume that accompanies the annual report.

- Occurrence Reports—An occurrence report may be required when a permitted COC concentration is exceeded, if it entails nonroutine reporting to a regulatory agency.
- *LLNL Experimental Test Site 300 Compliance Monitoring Program for RCRA-Closed Landfill Pits 1 & 7* (e.g., Christofferson and MacQueen 2001)—These quarterly and annual reports are submitted to CVRWQCB. Required contents are tables of measurements made during a quarter or year, a summary of the measurement data with regard to compliance, and a short discussion of monitoring results, including any water quality violations.
- *LLNL Experimental Test Site 300 Compliance Monitoring Program for the CERCLA-Closed Pit 6 Landfill* (e.g., Christofferson et al. 2001)—These quarterly and annual reports are submitted to Site 300 Remedial Program Managers. Required contents are tables of measurements made during a quarter or year, a summary of the measurement data with regard to compliance, and a short discussion of monitoring results, including any water quality violations.
- *LLNL Experimental Test Site 300 Compliance Monitoring Report for Waste Discharge Requirements 96-248* (e.g., Brown 2001b)—These quarterly and annual reports are also submitted to CVRWQCB. Contents of the reports are similar to the reports outlined above for closed landfills.
- *LLNL Experimental Test Site 300 Compliance Monitoring Program for the Closed Building 829 Facility Annual Report* (e.g., Revelli and Christofferson 2001, Revelli 2003)—This annual report is submitted to DTSC. Report contents are similar to the reports outlined above for closed landfills. The monitoring data are also included in the LLNL site annual *Environmental Report* (e.g., Biermann et al. 2001, Gallegos 2002).

8.8 Plans for the Future

8.8.1 Existing Monitoring Network at Livermore Site

Immediate short-term plans include sampling and analyzing the 25 monitoring wells on and adjacent to the Livermore Site and the 23 off-site tritium wells described in this plan for the next few years. These analyses will confirm present baseline conditions and detect any possible

additional contamination (particularly radiological) that may leach into groundwater and migrate off site.

Ongoing analyses will determine the need for long-term additions to the groundwater surveillance monitoring program and will determine sampling frequencies. Many sampling frequencies have been reduced to annual for surveillance monitoring. The groundwater surveillance plan will be updated on a site-specific basis, taking into consideration facility characteristics, applicable regulations, hazard potentials, quantities and concentrations of materials released, extent and use of local water resources, and specific local public interests and concerns. The objectives of the surveillance program are the following:

- Verify compliance with applicable environmental laws and regulations.
- Verify compliance with environmental commitments made in environmental impact statements, environmental assessments, safety analysis reports, and other official DOE documents.
- Characterize and define trends in the physical, chemical, and biological condition of environmental media.
- Further establish baselines of environmental quality.
- Provide a continuing assessment of pollution-abatement programs.
- Identify and quantify existing or new environmental quality problems.

The plan will be modified as site operations and/or new pollution discoveries warrant.

8.8.2 Existing Monitoring Network at Site 300

Future expectations for compliance groundwater monitoring at Site 300 include further consolidation of the separate, but overlapping, monitoring plans for Pits 1 and 7 currently being followed (Rogers/Pacific Corporation 1990; CVRWQCB 1993).

An expansion of surveillance monitoring is anticipated that will include random sampling of the more than 400 operational CERCLA wells at Site 300. Wells will be sampled at a rate of ten wells per quarter. Baseline analyses will be performed on random groundwater samples. CERCLA baseline surveys are typically conducted once, upon installation of a new well. COCs detected at that time continue to be monitored, but those COCs that are not detected by the baseline survey are eliminated from further monitoring. The object of this surveillance monitoring is to detect any new or slow-to-develop contamination by COCs that were not detected when the initial baseline surveys were completed.

8.8.3 Long-Term Groundwater Monitoring

Long-range monitoring at both the Livermore site and Site 300 is presented in the LLNL *Groundwater Protection Management Program* (Brown 2001a). Long-range monitoring evaluates the potential for groundwater contamination and projects the migration of contaminants during a 50-year timeframe, in conjunction with existing land use development plans in the vicinity of both sites. Long-range monitoring seeks to detect groundwater contamination at an early stage so that appropriate remedial steps can be considered in time to be effective. The long-range monitoring plan in this EMP will be assessed to determine whether the existing groundwater network is adequate for detecting current releases that, although not necessarily of concern today, could be of concern within the 50-year timeframe.

For the Livermore site, documents key to this assessment provide two types of information. First, they estimate the growth patterns and population concentrations expected in the Livermore Valley over the next 50 years. Second, they describe LLNL's plans for long-range groundwater monitoring and site progress during the same period. The following documents are the most informative:

- *South Livermore Valley Area Plan* (Livermore 1996) describes the developments planned for the South Livermore agricultural and residential corridors.
- *Livermore Community General Plan, 1976–2000* (Livermore 1975).
- *North Livermore Valley Area Plan* (Livermore and Alameda County 1997). This draft joint working paper describes the developments planned for the Las Positas Valley. The Las Positas Valley will not be within Livermore City boundaries.
- *LLNL Comprehensive Site Plan* (LLNL 1997a).
- *CERCLA Remedial Investigation Report for the LLNL Livermore Site* (Thorpe et al. 1990).

For Site 300, the process is much the same. Community growth expectations for Tracy and unincorporated areas of San Joaquin and Alameda Counties will be examined. These expected population and developmental pressures will be studied as they relate to LLNL's continuing remediation and monitoring activities in adjacent areas. The following documents are vital to this assessment:

- Tracy, *General Plan* (Tracy 1997a) describes residential and other development within the City of Tracy sphere of influence.
- Tracy, *Tracy Hills Preliminary Environmental Impact Statement and Final Environmental Impact Report* (Tracy, 1997b) describes the effects and extent of mixed-use development in the South Tracy area.

- *Final Site-Wide Remedial Investigation Report, LLNL Site 300* (Webster-Scholten 1994).
- *LLNL Comprehensive Site Plan* (LLNL 1997a).

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9 Soil Monitoring

Gretchen M. Gallegos • Richard A. Brown

9.1 Introduction

Soil is an integrating medium that can contain pollutants originally released directly to the ground, to the air, or through liquid effluents. For the purpose of surveillance monitoring, "soil" is defined as the top layer of earth, suitable for the growth of plants; and "sediment" is defined as recently deposited, finely divided solid material that has settled out of a liquid stream in an arroyo or other storm water drainage. In a geologic sense, all Livermore site soils are sediment.

Sedimentary materials in active streambeds can accumulate contaminants. Sampling and analysis of these sediments can provide a measure of waterborne radionuclides not available from direct water sampling because of the potential accumulation of contaminants in sediment.

9.2 Rationale And Design Criteria

9.2.1 Regulatory Drivers

Lawrence Livermore National Laboratory (LLNL) implements the environmental monitoring requirements in the applicable portions of U.S. Department of Energy (DOE) Orders 5400.1 and 5400.5 (see WSS B93 and B94 in Appendix B). Soil and sediment are specifically mentioned in DOE monitoring guidance for implementing these orders (*Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* [DOE 1991]) as environmental media that should be analyzed to determine the impacts of facility operations. DOE states that "periodic sampling and analysis of indicator materials, such as soil . . . should be performed to determine if there is measurable long-term buildup of radionuclides in the terrestrial environment. . . . Soil sampling and analysis should be used to evaluate the long-term accumulation trends and to estimate environmental radionuclide inventories" (DOE 1991).

According to DOE, "the sampling of sedimentary material from streams or ponds can provide an indication of the accumulation of undissolved radionuclides in the aquatic environment. The accumulation of radioactive materials in sediment can lead to exposure of humans through ingestion of aquatic species, through sediment resuspension into drinking water supplies, or as an external radiation source. . . ." (DOE 1991).

Contaminated sedimentary materials are regulated by a number of federal laws, such as, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); Resource Conservation and Recovery Act (RCRA); Clean Water Act; Toxic Substances Control Act; and Oil Pollution Act. These laws generally address the cleanup of contaminated sediments but do not specifically address routine sediment monitoring.

No specific guidance or regulations requiring or recommending soil monitoring for surveillance of the nonradiological environmental effects of ongoing operations have been identified. However, explicit regulatory requirements are not the sole basis for monitoring. Monitoring is carried out where there is a high level of public interest or concern, or where best management practices indicate monitoring is appropriate. Best management practice evaluations have indicated that vadose zone soil samples should be evaluated for metals and organic compounds, and that soil samples at Site 300 should be evaluated for beryllium.

9.2.2 Monitoring Objectives

LLNL conducts soil and sediment surveillance monitoring to evaluate the long-term accumulation trends and to estimate environmental radionuclide inventories. DOE monitoring guidance specifies that nuclides in use at a facility, as well as naturally occurring nuclides, should be monitored. In particular, the guidance states that "it is desirable to assess, document, and periodically reassess the distribution and fate of radionuclides in the environment, especially plutonium in soil samples" (DOE 1991).

The most significant pathway of soil contamination, barring direct contamination by dumping (which is prevented by LLNL administrative and management controls) is the deposition of materials from the air, whereas the pathway for sediment contamination is a combination of deposition from the air and from water. Consequently, the surveillance soils monitoring program addresses the surface of the soil on which materials can be deposited or from which materials can be resuspended. However, when air monitoring is carried out routinely, as at LLNL, soil sampling plays a supplementary role in the monitoring program (Hardy and Krey 1971).

9.2.3 Potential Sources and Contaminants

At the LLNL Livermore site, the major potential sources of radionuclides are the Building 332 Plutonium Facility; the Building 331 Tritium Facility; the southeast quadrant, from which low levels of plutonium can be resuspended; and waste management treatment and storage areas, from which materials can be emitted or resuspended. At Site 300, the primary radionuclide of concern for surveillance of ongoing activities is depleted uranium, which is currently used in explosive tests and which is a surface soil contaminant from tests in the past (Webster-Scholten 1994).

Soil contaminants can be solids, liquids, or gases. Plutonium, uranium, and nonradioactive metals are particulate contaminants. Tritium and organic contaminants of concern are generally liquids, but may be present in the environment as gases. All types of materials can settle out of the atmosphere or can be scoured from the atmosphere and transported by rainfall.

Annual emissions of nonradioactive toxic air contaminants have been estimated in the *Final Environmental Impact Statement and Environmental Impact Report* (EIS/EIR; DOE and UC 1992). Two tables from that document (Table 5.1.8-1 and Table 5.1.8-2) are reproduced here as **Table 9-1** and **Table 9-2**. If the materials listed in these tables are released and then deposited in sufficient quantities, they can be sources of soil contamination.

Table 9-1 Annual emissions estimates of toxic air contaminants that could cause soil contamination, Livermore site

Contaminant	Baseline condition annual amount (lb/year)	Assumed increase by tenth year (lb increase)
Chlorine	675	61
Ethylene glycol ethyl ether acetate	212	19
Fluorocarbons	28,770	2,589
Glycol ethers (other)	24	2
Hydrogen fluoride	<0.1	0.01
Methanol	1,230	111
Toluene	274	25
1,1,1-Trichloroethane	16,270	1,464
Xylenes	117	11
Benzene	196	18
Carbon tetrachloride	493	44
Chloroform	633	57
Dioxane (1,4-)	161	14
Ethylene dichloride	<1	0.1
Formaldehyde	35	3
Methylene chloride	738	66
Trichloroethene	728	66

Source: Table 5.1.8-1, DOE and UC 1992

Table 9-2. Annual emissions estimates of toxic air contaminants that could cause soil contamination, Site 300

Contaminant	Baseline condition annual amount (lb/year)	Assumed increase by tenth year (lb increase)
Boilers/diesel fuel		
Arsenic	0.43	0.039
Beryllium	0.026	0.002
Cadmium	0.11	0.010
Chromium	0.014	0.001
Copper	2.9	0.261
Formaldehyde	4.2	0.378
Lead	0.092	0.008
Magnesium	0.27	0.024
Mercury	0.031	0.003
Nickel	1.8	0.162
Polyaromatic hydrocarbons	0.23	0.021
Fuel dispensers, gasoline		
Dispensers	110.7	9.963
Tank loading	968.5	87.165
Spray booths		
Glycol ethers	117	10.530
Toluene	40	3.600
Xylene	11	0.990
High-explosive detonation, Buildings 801, 850, 851		
Ammonia	20.9	1.881
Benzene	0.18	0.016
HCl	7.3	0.657
HCN	3.9	0.351
HF	26.5	2.385
Polyaromatic hydrocarbons	0.000003	0
Toluene	0.3	0.027
High-explosive metals		
Beryllium	0.31	0.028
Nickel	0.42	0.038
Cooling tower		
Chloroform	0.12	0.011
Sodium hydroxide	13.3	1.197

(continued)

Table 9-2. Annual emissions estimates of toxic air contaminants that could cause soil contamination, Site 300 (concluded)

Contaminant	Baseline condition annual amount (lb/year)	Assumed increase by tenth year (lb increase)
Limited chemistry lab		
Ethylene dichloride	1	0.090
Fluorocarbons	3.9	0.351
Methylene chloride	55	4.950
Toluene	0.36	0.032
Drinking water chlorination		
Chlorine hydroxide	15	1.350
Cold cleaning		0
Freon 113	721	64.890
Vapor extraction system		
Trichloroethene	8	0.720
Refrigerants		
R12	145	13.050
R13	80	7.200
R22	375	33.750
R113	66	5.940
R502	100	9.000
R503	70	6.300
Automotive parts cleaning		
Cresol	1.8	0.162
Methylene chloride	4.8	0.432
Linear accelerator x-ray equipment		
R12	580	52.200

Source Table 5.1.8-2, DOE and UC 1992

9.2.4 Collection Methods

There are three generally accepted methods for collecting soils samples: coring, template, and trench. The coring method uses a coring tool to take samples of a standard volume and depth; it usually involves taking a number of samples to a depth of 5 cm to represent one sampling location. The template method is used in locations where the presence of rocks makes it impossible to collect samples using the coring method. The template method employs a square, cold-rolled steel template, 20 or 30 cm on the inner edge, to mark an area; the area is then excavated to the appropriate depth using chisels and scoops. The trench method is used to establish a depth profile. It requires digging a trench about 60 cm wide by 90 cm long by 60 cm deep and taking samples by pressing a flat-bottomed, three-sided pan with cutting edges on the open side into the face of the trench.

The coring method is preferred for collecting surface samples from soil. LLNL follows the coring method set out by the American Society for Testing and Materials, *Standard Practice for Sampling Surface Soils for Radionuclides* (ASTM 1990). The sampling technologist chooses two 1-m^2 areas from which to collect the sample. Surface vegetation is cleared away from the sampling area, and an LLNL-designed, stainless steel core sampler (8.25 cm in diameter) is driven into the ground to a depth of 5 cm for each subsample. The sample is a composite consisting of ten subsamples collected individually at the four corners and the center of each square (procedure EMP-S-S, *Soil and Arroyo Sediment Sampling*). As previously determined by soil profiles to 30 cm deep, a surface sample from a depth of 5 cm is sufficiently deep to obtain 90 to 95 percent of airborne material, and the results are reproducible (EML 1990).

The coring method is also used to collect sediment samples. As previously determined by a comparison of samples taken 30–45 cm deep and 0–5 cm deep, a sediment sample taken 0–5 cm deep is sufficient to obtain materials deposited in the sediment sampling locations (Gallegos et al. 1993). For particulate radionuclide analysis, the sediment coring samples are collected the same way as soil samples, except the ten subsamples are taken at 1-m intervals along a linear transect that approximates the center line of the arroyo or channel. The transect is plotted to get a sample that is representative of the flow of water and resultant deposition from what is known to be a spatially heterogeneous deposition process. For tritium analysis, a sample is taken 5–15 cm deep from one core of the transect. Because the concern being addressed by vadose zone soil sampling is the potential effect of sediment contamination on groundwater, these samples are collected at 30–45 cm deep for metals analysis and at 45–65 cm deep for volatile organic compound analysis.

9.3 Extent and Frequency of Monitoring and Measurements

9.3.1 Criteria for Selecting Sample Locations

9.3.1.1 Soils

Choices of soil sampling locations are based on the following criteria:

- Proximity to LLNL and the potential for being affected by LLNL operations from wind deposition of contaminants
- Background locations with geologically similar substrates as those near LLNL, but unlikely to be affected by LLNL operations
- Areas of known or suspected LLNL-induced contamination
- Proximity to an air sampling location to enable analysis of resuspension

Specific sampling locations should represent the geographical areas in which they are located. Some areas—such as frequently tilled or disturbed areas, locations near buildings or other obstructions, or areas with unusual wind or precipitation influences—are avoided because samples are intended to be representative of the geographical area. Practical considerations also influence the selection of sampling locations. The use of private property is discouraged because private ownership may change, and attitudes toward sampling may also change. Also, private property may be developed, rendering the location no longer useful. If a location on private property is chosen, a written access agreement is required. Government installations (federal, state, city, or regional) can be good sources of sampling locations as long as appropriate arrangements are made and development does not occur on the property. Other considerations for sampling locations include locations of underground utilities, access during inclement weather, and the safety of personnel in vehicle operation or sample collection.

Consistent sampling locations enable evaluation of long-term trends. The LLNL environmental monitoring program soil sampling locations are shown in **Figure 9-1** and **Figure 9-2**. Specific location descriptions are maintained in the Sampling Locations Database (EMP-QAS-LOC, *Locations Database SOP Supplement*).

Six sampling locations are positioned around the Livermore site perimeter; four sampling locations are offsite in generally downwind directions; and three sampling locations are offsite in generally upwind directions, representing background locations. In addition, samples are collected at the Livermore Water Reclamation Plant (LWRP); historic releases, including an estimated 32-mCi plutonium release to the sewer in 1967, resulted in local contamination of soils in the area around the LWRP. From 1988 to 2001, samples were collected from six locations per year at the LWRP. The data collected in the previous 14 years are sufficient for understanding the plutonium in the area. In addition, construction at the LWRP site in recent years has reduced the surface area of concern. Another 14 sampling locations are at Site 300 near active or historic experimental test sites and at background locations.

No set number of sampling locations is required. Sufficient sampling locations have been established so that long-term trends and differences between background and locations affected by LLNL operations can be identified. The two generally upwind perimeter locations, MET and MESQ (**Figure 9-1**), may not both be necessary, but both are air particulate monitoring locations, and both are near offsite areas that are being increasingly developed for residential use (Chapter 1).

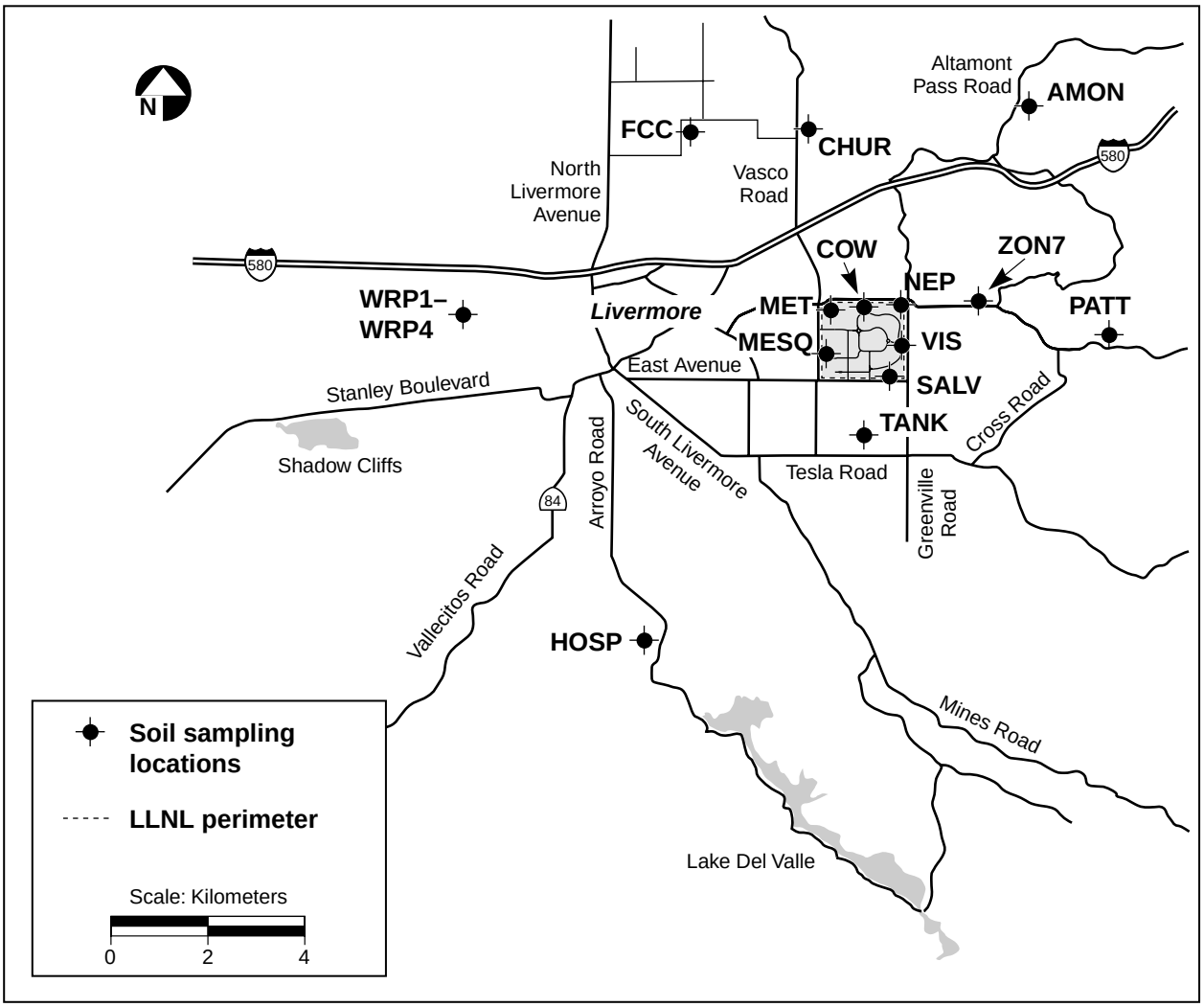

Figure 9-1. Soil sampling locations, Livermore Valley

9.3.1.2 Sediment

The selection of sediment sampling locations is based on the following criteria:

- An influent or effluent point of an arroyo or storm drainage channel to represent sediment conditions as water flows onto or away from the Livermore site
- A location where sediment collects in large volume
- A location that drains an area potentially affected by ongoing LLNL operations

Other considerations include access to the location, location of underground utilities, the use of the location as a storm water sampling point so that data comparisons can be made, and safety of personnel during vehicle operation or sample collection.

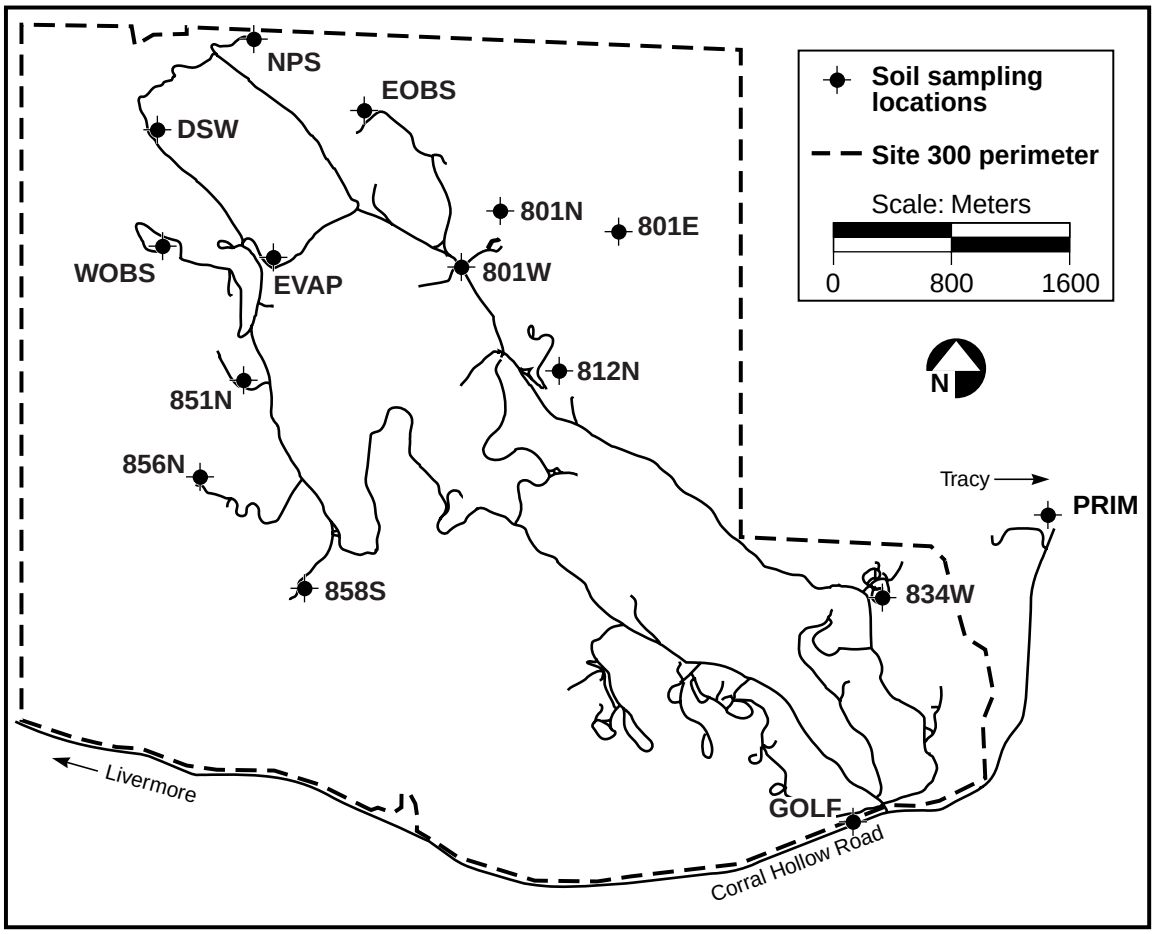

Figure 9-2. Site 300 soil sampling locations

Sediment samples are currently taken at six locations around the Livermore site: three locations are influent points, two are effluent points, and one is in a settling basin that precedes drainage into the Drainage Retention Basin (**Figure 9-3**). Sampling influent location ALPO was removed from the sampling schedule in calendar year 2000 because the location was consistently under-water and unsuitable for sampling. Sampling location CDB was physically removed when the settling basin for which the sampling location was established was replaced by storm water drainage pipe. (See **Figure 7-1** for the locations of ALPO and CDB.) Specific location descriptions are maintained in the Sampling Locations Database (EMP-QAS-LOC, *Locations Database SOP Supplement*).

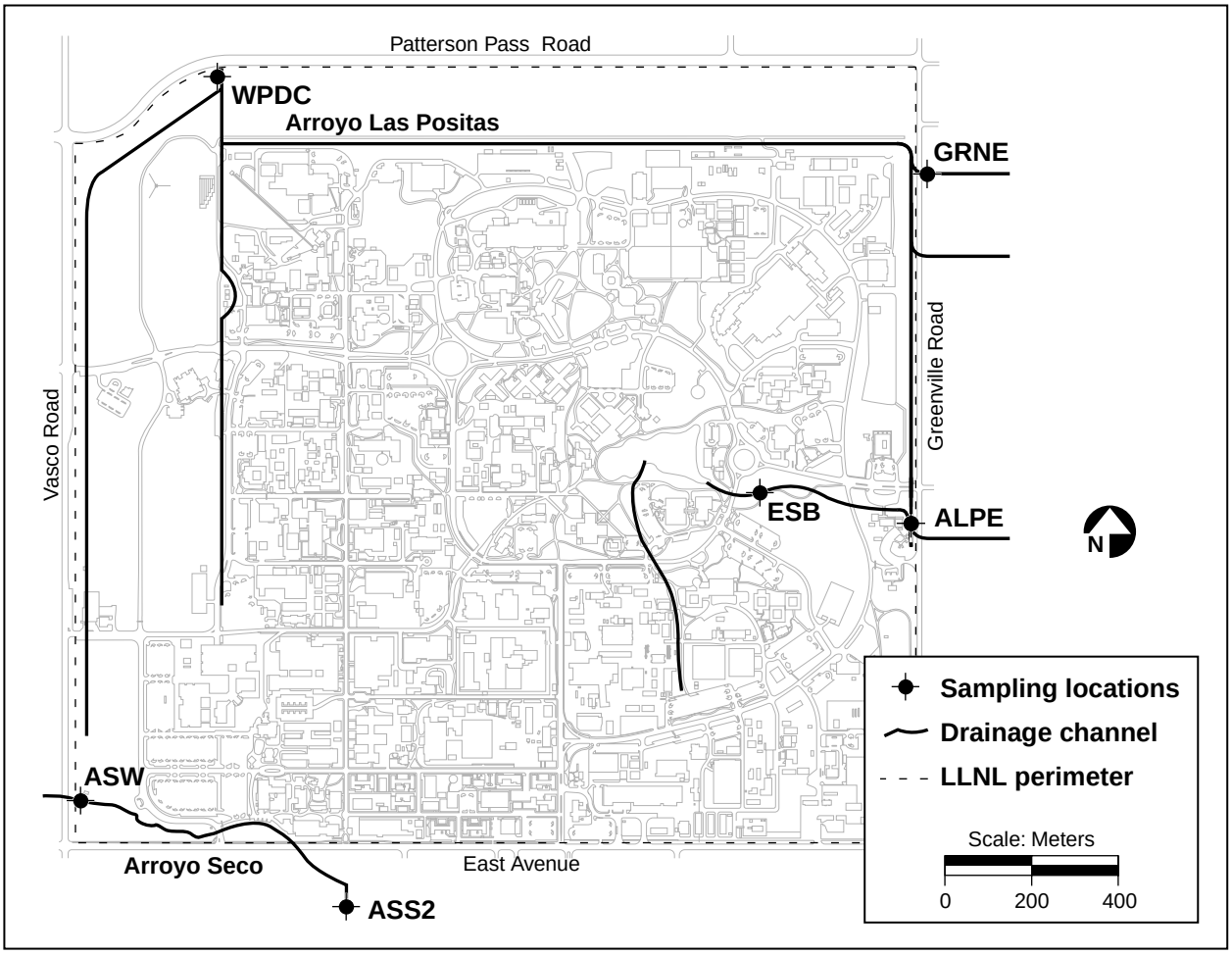

Figure 9-3. Arroyo and drainage basin sediment sampling locations

Sediment sampling locations have not been established at Site 300. The drainage courses at Site 300 are steep, causing the flowing water to scour the drainages, so that sediment is not deposited. Because of these conditions, sediment sampling at Site 300 is not warranted.

9.3.2 Sampling Frequency

Soil and sediment sampling is conducted annually, as recommended by DOE/EH-0173T (DOE 1991) for sampling that is conducted to determine trends. Soil and sediment sampling is generally conducted in the second quarter of each year. The second quarter is the time of year when soils and sediments are no longer extremely wet from the rainy season, new sediment has been deposited, and when the ambient air temperature is not so high that sampling technologists will suffer heat-related stress due the physically demanding effort required to collect soil and sediment samples.

9.3.3 Analytes

The radiological analytes of greatest interest for the Livermore site are plutonium and tritium. All soil and sediment samples are analyzed for plutonium and gamma-emitting nuclides; sediment samples are also analyzed for tritium because these samples are taken in locations that channel water on the site.

The radiological analytes of interest at Site 300 are the isotopes of uranium, especially uranium-238 and uranium-235, and the ratio of these values in a given sample. Depleted uranium (i.e., natural uranium depleted of much of the uranium-235) has historically been and is currently used in experimental tests at Site 300. The variation of the sample ratio of uranium-235/uranium-238 from the natural ratio of 0.726 percent gives an indication of the impact of LLNL operations on the site.

Nonradiological analytes include metals and organic compounds in sediments from operations at the Livermore site because of the possibility of transport of these materials from storm water channels to groundwater through the vadose zone at the site. Although the direct effects of nonradiological materials on sediments is negligible (Gallegos 1994), the continuing possibility that nonradiological contaminants may impact groundwater caused reinstatement of vadose zone sediment monitoring for nonradiological materials in 1996. The current Livermore site vadose zone sediment monitoring program is conducted as part of the groundwater protection management effort (discussed in Chapter 8).

The vadose zone sediments are analyzed for total and soluble concentrations of metals and soluble concentrations of organic compounds measured by the Toxicity Characteristic Leaching Procedure (TCLP). LLNL has developed background levels for total and soluble metals in soils and sediments and de minimis (or designated) concentration levels for soluble organics (Marshack 1991). This designated level methodology (DLM) determines the soluble levels of contaminants that would not adversely impact groundwater beyond its beneficial uses. The DLM is implemented by application of a simple attenuation factor and specific water quality objectives. The San Francisco Bay Regional Water Quality Control Board (SFBRWQCB) and LLNL have agreed upon an attenuation factor of 100. Any constituents with soluble concentrations above these de minimis levels may adversely impact the groundwater beneath. In addition, LLNL has developed, and the SFBRWQCB has approved, a site-specific DLM for beneficial reuse of soils at the Livermore site. If the constituent in soils is above its background level, the DLM can be used to determine if its concentration is protective of groundwater quality. U.S. EPA Region IX has recently published soil screening levels for evaluating migration of materials to groundwater, based on a method similar to the DLM. However, the soil screening levels have not been set for many materials and the soil screening levels are higher than those set by DLM. (See http://www.epa.gov/region09/waste/sfund/prg/s1_01.htm)

Beryllium is used in explosive tests at Site 300. Preliminary results of dispersion measurements and modeling of beryllium from high explosive tests at Site 300 during 1991 show that these tests have a very small "footprint" and that soils testing would only show elevated levels of beryllium if the soil samples are obtained in that footprint. In addition, not all beryllium in the test shot becomes part of the explosive cloud (Baskett 1994). However, in view of the fact that some samples at locations near firing tables show increased beryllium levels, samples representing background and soils near firing table operations at Site 300 continue to be analyzed for beryllium.

9.4 Procedures For Laboratory Analysis

Preservation is not required for soils and sediment samples that are analyzed for particulate radionuclides. Sediment samples that are analyzed for tritium are chilled in the field and frozen until analyzed. Sediment samples collected for metals and organic compound analysis are kept cool until analysis; they are kept on dry ice while in the field; samples for TTLC and STLC metals analyses are stored in a refrigerator and samples for TCLP organic analyses are kept in a freezer. The samples are still refrigerated or frozen when delivered to analytical laboratories.

Soil samples to be analyzed for plutonium and gamma-emitting radionuclides have defined sample preparation requirements. These samples are dried at 100°C for at least two days, pulverized in a grinding mill, sieved through a 32-mesh sieve, and blended. Samples for gamma analysis are packed in a tared, steel can and allowed to equilibrate for at least 30 days before counting.

Radiological analyses for soil and sediment samples are completed by LLNL's Chemistry and Materials Sciences Environmental Monitoring Radiological Laboratory (EMRL). EMRL follows verified analytical methods in its radiological analyses. The methods used include plutonium-238 and plutonium-239+240 by alpha spectroscopy, gamma scan by EPA Method 901.1 using a high purity germanium detector, and tritium by liquid scintillation. Plutonium is measured by alpha spectroscopy following acid leaching. Tritium is measured by liquid scintillation following freeze-dry extraction of the soil moisture.

Nonradiological analyses are performed by off-site laboratories. Standard EPA methods are used, including EPA Methods 200.7, 245.2, 7471A and 6010B for total metals. Soluble extraction and metals analyses are carried out by California's Waste Extraction Test, followed by the same analyses used for total metals on that extract. Analysis of polychlorinated biphenyls by EPA Method 8082 and soluble extraction of volatile organic compounds is performed by EPA's Toxicity Characteristic Leaching Procedure (EPA Method 1311), followed by EPA Method 8260 analysis. Beryllium content is determined by atomic emission spectrometry (EPA Method

200.7). Chain-of-custody procedures are followed throughout the sampling, delivery, and analytical processes.

9.5 Quality Assurance Requirements

9.5.1 Data Quality Objectives

9.5.1.1 Precision

The detection limits for radionuclides in soils are shown in **Table 9-3**.

Table 9-3. Detection limits for radionuclides in soil

Radionuclide	Detection Limit (Bq/g)
$^{239+240}Pu$	1.0×10^{-6}
^{137}Cs	1.0×10^{-4}
^{238}U	2.0×10^{-2}
^{235}U	2.0×10^{-4}
^{232}Th	1.0×10^{-3}
^{40}K	1.0×10^{-2}
^{3}H	1.7×10^{0} (Bq/L of extracted moisture)

A lower detection limit for uranium-238 would be advantageous because it would be useful to have well-characterized background values. However, the current detection limit is sufficient to determine impacts on areas affected by LLNL operations, and the expense of analytical methods with more sensitive detection limits is not justified.

The detection limit for beryllium in soils is 0.05 mg/kg.

The analytes, analytical methods, and reporting limits for total metals, soluble metals, and organic compounds are shown in **Table 9-4**.

Table 9-4. Analytes, analytical methods, and reporting limits for subsurface sediment samples

Analyte	Method	Reporting limit (mg/kg)
Total metals		
Antimony	EPA 6010 or 6020	1
Arsenic	EPA 6010 or 6020	0.5
Barium	EPA 6010 or 6020	5
Beryllium	EPA 6010 or 6020	0.5
Cadmium	EPA 6010 or 6020	0.1

(continued)

Table 9-4. Analytes, analytical methods, and reporting limits for subsurface sediment samples (continued)

Analyte	Method	Reporting limit (mg/kg)
Total metals (continued)		
Chromium	EPA 6010 or 6020	5
Cobalt	EPA 6010 or 6020	5
Copper	EPA 6010 or 6020	5
Lead	EPA 6010 or 6020	10
Mercury	EPA 7471	0.05
Molybdenum	EPA 6010 or 6020	5
Nickel	EPA 6010 or 6020	10
Potassium	EPA 6010 or 6020	100
Selenium	EPA 6010 or 6020	2.5
Silver	EPA 6010 or 6020	2.5
Thallium	EPA 6010 or 6020	1
Vanadium	EPA 6010 or 6020	5
Zinc	EPA 6010 or 6020	5
Soluble metals	CA WET followed by:	**Reporting limit (mg/L)**
Antimony	EPA 6010 or 7041	0.06
Arsenic	EPA 6010 or 7060	0.05
Barium	EPA 6010 or 7041	0.5
Beryllium	EPA 6010 or 7091	0.04
Boron	EPA 6010 or 6020	0.5
Cadmium	EPA 6010 or 7130	0.05
Chromium	EPA 6010 or 6020	0.5
Cobalt	EPA 6010 or 6020	0.5
Copper	EPA 6010 or 6020	0.5
Iron	EPA 6010 or 6020	0.5
Lead	EPA 6010 or 7420	0.5
Manganese	EPA 6010 or 6020	0.15
Mercury	EPA 245.2 or 7471	0.005
Molybdenum	EPA 6010 or 6020	0.5
Nickel	EPA 6010 or 6020	0.5
Potassium	EPA 6010 or 6020	10
Selenium	EPA 6010 or 7740	0.05
Silver	EPA 6010 or 7760	0.5
Thallium	EPA 6010 or 7841	0.02
Vanadium	EPA 6010 or 6020	0.5
Zinc	EPA 6010 or 6020	0.5

(continued)

Table 9-4. Analytes, analytical methods, and reporting limits for subsurface sediment samples (concluded)

Analyte	Method	Reporting limit ((µg/L)
Organic compounds		
1,1-Dichloroethylene	TCLP 8260	10
1,2-Dichloroethane	TCLP 8260	2.5
1,4-Dichlorobenzene	TCLP 8260	10
2-Butanone (MEK)	TCLP 8260	10
Benzene	TCLP 8260	5
Carbon tetrachloride	TCLP 8260	2.5
Chlorobenzene	TCLP 8260	10
Chloroform	TCLP 8260	20
Trichloroethylene (TCE)	TCLP 8260	10
Vinyl chloride	TCLP 8260	10

In accordance with LLNL procedure EMP-S-S, *Soil and Arroyo Sediment Sampling*, field duplicate samples are submitted with each batch of soil samples. At locations chosen for duplicate samples, two identical samples are collected. Adjacent cores are collected from the corners and the center of the sampling square. Separate composites of ten cores each are made, and the two samples are identified with unique sample identifier codes. Similarly, duplicate 10-g aliquots for beryllium analyses are produced. The sampling locations of field duplicate samples are not identified on the sample bags, the sample identification tags, or vial labels, so that the analytical laboratory does not know where the samples originated (procedure EMP-QA-DM, *Sample and Data Management*). However, this information is recorded on field tracking forms (FTFs), which are filled out in the field by the sampling technologist and which contain detailed information about actual sampling locations and other conditions affecting sampling. Approximately 10 percent of samples are field duplicates. After the results are obtained, the ratios of the individual sample pairs (of greater-than-detection-limit results) are averaged; the average ratio should be between 0.7 and 1.3. If the average is not within this range, the data are first examined for transcription errors; and then the analytical laboratory is contacted to discuss any problems that may have occurred during analysis. Continued ratios outside the range may indicate problems with the analytical method and require further investigation, including preparation of a nonconformance report (NCR) to document the actions taken.

The analytical laboratory creates laboratory duplicates (also called splits) in accordance with the laboratory standard operating procedures. Laboratory duplicates are introduced blind into the sample processing at a rate of about 10 percent of samples. Results from duplicate samples are compared according to CES procedure CES-SOP-P500, *CES Control Charts*.

9.5.1.2 Accuracy

Soil is not very amenable to the creation of field blank and spike samples. It is virtually impossible to create a blind field blank that would not be immediately obvious to the analytical staff. In addition, blank soil samples from the National Institute for Standards and Technology (NIST) are very expensive (on the order of $10 per gram). Because about 300 g per sample are needed, the use of blank soil samples gets very expensive and, furthermore, is of little value because the blank soil is physically different from the soils collected in the Livermore Valley and Site 300.

Field spikes are also very difficult to prepare due to the heterogeneity of soils and the difficulty of evenly dispersing any known amount of material in soil.

The radiological laboratory does run blank and standard reference NIST-traceable samples, as do the nonradiological laboratories. For example, NIST "Environmental Radioactivity River Sand" is used as a primary standard for gamma soils analysis.

The radiological laboratory also participates in the DOE Environmental Measurements Laboratory Quality Assurance Program. In these studies, the DOE sends samples with known amounts of radionuclides to the participating laboratories, compares the analytical results (thereby determining the accuracy of the various participating laboratories), and publishes reports of the results so that analytical laboratory personnel, and their customers, can evaluate the analytical laboratory's relative performance.

9.5.2 Audits and Self-Assessments

All analytical laboratories (both LLNL laboratories and offsite contract laboratories) that perform analyses for these sampling networks are scheduled for auditing periodically. These audits allow LLNL to assess the capabilities of the laboratories. The Environmental Protection Department Assurance Office performs audits and inspections of analytical laboratory operations. Triennial self-assessments of all monitoring networks are also performed (LLNL procedure ORAD-QA-SA, *Self Assessments*).

9.6 Program Implementation Procedures

The soil and sediment samples are collected by sampling technologists following the written LLNL procedure EMP-S-S, *Soil and Arroyo Sediment Sampling,* and EMP-QA-DM, *Sample and Data Management*. Locations are marked with permanent location markers to enable the technologists to readily locate the same sampling location from year to year. The written procedures include requirements for sample collection and submittal for chemical analysis, keeping a log, and filling out FTFs and chain-of-custody forms. The procedures also require the

sampling technologists to alert the environmental analyst about difficulties encountered during any sampling event.

Before handling any samples, sampling technologists put on clean, disposable vinyl gloves to avoid contaminating samples. New gloves are worn at each sampling location. Samples are double-bagged to avoid sample contamination, and sampling equipment is decontaminated between sampling events. After decontamination, the sampling equipment is kept in a clean plastic bag to avoid subsequent contamination.

In general, soil and sediment sampling follows one of three patterns. The first is used for collecting surface composite samples. To collect samples for radionuclide analysis, the sampling technologist selects two 1-m^2 areas near the permanent marker and then uses a stainless steel coring device, 8.25 cm in diameter, to take ten 5-cm-deep subsamples. The subsamples are taken at the center and the four corners of each 1-m^2 area. To enable replication if necessary, the technologist notes the direction and distance from the sampling marker in the log book.

The collection of arroyo and drainage channel samples for radiological analysis follows a second, different pattern. A transect is laid in the channel, and ten 5-cm-deep samples are collected along the transect.

The third pattern differs from the second in that single-point samples are collected at one of the transect sampling subsamples at 15-, 45-, and 60-cm deep for analysis for tritium, metals, and organic compounds. To deter analyte evaporation, tritium samples and samples for organic compounds are chilled in the field and kept cool until delivered to the analytical laboratory.

An environmental analyst is assigned the responsibility for the networks. The analyst designs and maintains the sampling networks; schedules the sampling; determines analytes, collection methods, and analytical methods; communicates and coordinates network activities with sampling technologists and analytical laboratory personnel; evaluates the accuracy, precision, technical validity, and overall quality of data; reviews and analyzes the data; and reports the results.

9.7 Action Levels

Sample results are compared to the running historic geometric means for the Livermore and Site 300 locations for lognormally distributed materials such as plutonium-239, cesium-137, uranium-235, thorium-232, and beryllium. The 5-year running mean and standard deviation for radionuclides in soils are shown in **Table 9-5**. (Results for naturally occurring and fallout materials are consistent from year to year and can be used as an indicator of sampling or analytical problems.)

Table 9-5. Mean and standard deviation for radionuclides

Radionuclide	Mean (Bq/g)[a]	Standard deviation
$^{239+240}Pu$	7.78×10^{-5}	3.8
$^{239+240}Pu$[b]	2.03×10^{-3}	3.3
^{137}Cs	1.28×10^{-3}	3.0
^{238}U	2.59×10^{-2}	1.8
^{238}U (Site 300)	3.95×10^{-1}	3.7
^{235}U	1.73×10^{-3}	1.5
^{235}U (Site 300)	7.41×10^{-3}	2.1
^{232}Th	2.85×10^{-2}	1.4
^{40}K	4.48×10^{-1}	0.078
^{3}H	7.80×10^{0} (Bq/L)	3.9

a The arithmetic mean is shown for ^{40}K; geometric mean is shown for other radionuclides.

b Livermore Water Reclamation Plant

The 5-year running historic geometric mean and standard deviation for beryllium at most Site 300 sampling locations are 0.78 and 1.9, respectively, and for the Building 812 area (an area of known contamination) are 4.38 and 4.5, respectively.

Any results for lognormally distributed analytes outside two geometric standard deviations of the mean (a warning level) are examined for data transcription errors, and the analytical lab is contacted to discuss any problems that may have occurred during analysis. Any results outside three geometric standard deviations (the action level) are also subject to examination for transcription errors and analytical problems. In addition, the location is resampled, perhaps in duplicate or triplicate, depending on the nature of the problem. For normally distributed materials, such as potassium-40, the results are compared to a running arithmetic mean and standard deviation, with the same warning and action levels. If no transcription, analytical, or other error is found to explain an out-of-limit value, the environmental analyst notifies EPD management in writing following procedure ORAD-QA-NCR (*Nonconformance Reporting and Tracking*), and further action, such as a special study in the area of the problematic sample, is taken with EPD management concurrence.

For metals, results for total concentrations in sediment samples are first compared to background values. If the results for total concentrations are less than background, then no further comparisons are necessary. If the results for total concentrations are greater than background, then the soluble results are compared to the soluble background value. Again, if the soluble result value is less than background, no further comparisons are necessary. If the

soluble result value is greater than background, then that soil is concluded to be not representative of background.

Similarly, for organic compounds, results are compared to DLM levels. Any locations having results higher than the DLM will be resampled to confirm the result. If the result for the second sample is also above the DLM, the analyst notifies EPD management of this in writing following procedure ORAD-QA-NCR. Further action, such as special study implemented in the area of the sample, is taken with EPD management concurrence. The current values representing total background, soluble background, and de minimis (or designated) levels for organics are shown in **Table 9-6** and **Table 9-7**.

Table 9-6. Background screening concentration values for total and soluble metals in soil, Livermore site

Metal	Background screening value
Total (mg/kg)	
Antimony	1.12
Arsenic	8.51
Barium	308
Beryllium	0.62
Cadmium	1.59
Chromium	72.4
Chromium VI	any detection
Cobalt	14.6
Copper	62.5
Lead	43.7
Mercury	0.14
Molybdenum	any detection
Nickel	82.8
Selenium	any detection
Silver	any detection
Thallium	any detection
Vanadium	65.2
Zinc	75.3

Metal	Background screening value
Soluble (mg/L)	
Antimony	any detection
Arsenic	0.237
Barium	16.7
Beryllium	any detection
Boron	to be determined
Cadmium	any detection
Chromium	0.727
Cobalt	0.985
Copper	2.6
Iron	to be determined
Lead	0.987
Manganese	to be determined
Mercury	0.0063
Molybdenum	any detection
Nickel	1.68
Selenium	any detection
Silver	any detection
Thallium	any detection
Vanadium	1.22
Zinc	4.52

Source: Jackson 1995

Table 9-7. De minimis (or designated) concentration levels for organic chemicals found in Livermore site soil

Constituent	Water quality objective (µg/L)	Reference	Attenuation factor	De minimis level (µg/L)
Organics				
1,1-Dichloroethylene	6	Cal Primary MCL[a]	100	30
1,2-Dichloroethane	0.5	Cal Primary MCL	100	2.5
1,4-Dichlorobenzene	5	Cal Primary MCL	100	25
2-Butanone (MEK)	8,400	Cal Taste & Odor Threshold	100	42,000
Benzene	1	Cal Primary MCL	100	5
Carbon tetrachloride	0.5	Cal Primary MCL	100	2.5
Chloroform	80	EPA Primary MCL[b]	100	400
Trichloroethylene (TCE)	5	Cal Primary MCL	100	25
Vinyl chloride	0.5	Cal Primary MCL	100	2.5

Source: Isherwood 1994

a Cal Primary MCL = California primary maximum contaminant levels

b EPA Primary MCL = U.S. Environmental Protection Agency primary maximum contaminant levels

9.8 Preparation and Disposition of Reports

The environmental analyst analyzes the monitoring results after all the results for the calendar year are obtained. The results are reported in the annual *Environmental Report* (e.g., Biermann et al. 2001; guidance document EMP-QA-AER, *Site Annual Environmental Report*). No other reporting for soil and sediment data is required.

9.9 Future Plans

The short-term plan for soil and sediment sampling is to determine background and DLM values for those materials for which they are required but which are not yet available, and to continue monitoring soil and sediment in the manner described in this chapter.

Long-term plans include following the development of federal and regional soil and sediment policies to assure that soil and sediment monitoring is conducted in an appropriate manner. An additional long-term plan is to keep up to date with changes in LLNL operations and to add and remove sampling locations as indicated by operational impacts or changes in sampling conditions.

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10 Vegetation and Foodstuff Monitoring

S. Ring Peterson

10.1 Introduction

Sampling and analysis of vegetation and foodstuff can provide information about the presence and movement of radionuclides released to the environment. At LLNL, vegetation and wine are sampled as terrestrial foodstuffs exposed to atmospheric releases of radionuclides. Concentrations of radionuclides in vegetation can be used to estimate concentrations in edible plant and animal products and dose to humans from ingestion of a normal diet. Although the ingestion of wine may be just a tiny fraction of the total diet, wine is the most important agricultural product in the Livermore Valley, representing an approximately $140-million annual industry. Since monitoring began, data have indicated that, although tritium concentrations in all wines are low, Livermore Valley wines contain statistically more tritium than do their California counterparts. Therefore, local wines are monitored to demonstrate the small but measurable effect of LLNL operations on wine.

Historically, milk and honey samples were collected directly from owners of local cows or goats and from beekeepers. Increasing development has reduced the number of dairy animals in the Livermore Valley so that now neither cow nor goat milk is available for sampling (Gallegos et al. 1994). Honey is also no longer sampled because of the difficulty obtaining samples from bees kept only in the Livermore Valley and because the calculated dose to people ingesting honey at the tritium values measured here would be extremely low (Gallegos et al. 1994).

10.2 Vegetation Monitoring Program

10.2.1 Rationale and Design Criteria for Vegetation Monitoring

10.2.1.1 Regulatory Drivers

The regulatory driver for vegetation and foodstuff monitoring is the applicable portions of Department of Energy (DOE) Order 5400.1 (see WSS B92 in Appendix B). Guidance in monitoring specific terrestrial foods appropriate for surveillance sampling and analysis is provided in the DOE's *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (DOE 1991). The DOE guidance calls for pathway analyses of important agricultural products grown within 16 km of the site. Although milk is considered the most important pathway-significant agricultural product, it is no longer included in the LLNL monitoring program because no dairy cows are found within 16 km of the Livermore

site. LLNL thus samples vegetation, the second most important agricultural product within 16 km. When locally grown vegetables, grains or fruit do not contribute significantly to diet, as is the case with LLNL, DOE guidance states that native (or, more correctly, non-cultivated) vegetation be used as an indicator species.

10.2.1.2 Monitoring Objectives for Vegetation

The primary purpose of vegetation monitoring is to evaluate the dose to people from radionuclides taken up by vegetation. Secondary purposes are to conduct pathway analyses, to evaluate long-term accumulation trends, and to estimate environmental radionuclide inventories.

LLNL vegetation monitoring does not include monitoring for nonradiological materials. Emissions levels of nonradiological materials at LLNL do not warrant routine monitoring. An evaluation of air deposition to vegetation for a variety of volatile organic compounds was conducted for the *Health Risk Assessment for Hazardous and Mixed Waste Management Units at Lawrence Livermore National Laboratory* (McDowell-Boyer et al. 1995) using the model CairTox. The evaluation showed that the ingestion pathway accounts for less than 1 percent of the overall risk calculated for these compounds. The evaluation was based on an assumed 1 mg/m^3 concentration in air; this concentration results in extremely low estimates of the levels of the compounds in plants, ranging from 7.4×10^{-6} to 9.4×10^{-4} mg/kg for chloroform and methyl ethyl ketone, respectively. These values are below any level of concern. Furthermore, the *AB2588 Air Toxics Risk Screening Document for Lawrence Livermore Laboratory, Plant 255* (LLNL 1991) indicates that concentrations of volatile organic chemicals in air would actually be much lower than 1 mg/m^3, ranging, at the point of maximum impact, from 7.5×10^{-4} $\mu g/m^3$ for ethylene dichloride to 2.4×10^{-2} $\mu g/m^3$ for trichloroethylene.

10.2.1.3 Sources and Analytes

At LLNL's Livermore site, the major contributors to airborne tritium emissions are routine emissions from the Tritium Facility (Building 331 and its associated operations) and the Building 612 Hazardous Waste Management yard. The major contributors of airborne particulate radionuclide emissions are operations associated with waste management operations at Building 514. At Site 300, the primary radionuclide of concern for surveillance of ongoing activities is uranium, which is used in tests at the site. Tritium is also present at Site 300.

Plutonium and uranium are not of concern in vegetation surveillance monitoring because they are only slightly soluble, leading to minimal plant uptake. Their low solubility also results in a low ingestion dose. Healy (1974) states: "Plutonium is only slightly absorbed from the GI tract

when ingested. In rats, chronic ingestion at low mass concentrations of [plutonium] nitrate resulted in an average uptake of 0.0003% of that fed, with 90% of the small fraction which was absorbed deposited in the skeleton." Inhalation of these radionuclides is a much more significant environmental pathway, and the air is monitored for these radionuclides. (See Chapters 3, 5, and 14.)

Tritium is the only nuclide released from LLNL that can be detected in vegetation. Most uptake is from tritium released to the atmosphere from LLNL's ongoing operations, but in a few locations uptake is from tritium-contaminated groundwater. Tritium moves through the environment as tritiated water (HTO). As such, it is easily assimilated into plant water. Through photosynthesis, tritium is incorporated into the organic matter of plants. Tritiated water and organically bound tritium (OBT) are readily transferred to animals that eat vegetation exposed to tritium in air or soil water. Radiation dose to human beings results from ingestion of contaminated plant or animal products.

Only the green, leafy material of grass and other vegetation is collected, since the vegetation must represent the normal diet of animals or humans. Leaves of different types of plants will exhibit similar tritium concentrations in their plant water, so the vegetation sampled does not have to be edible. Furthermore, the concentrations of HTO found in leaves are normally higher than those observed in fruits, fruit vegetables, root crops and grain for the same tritium concentration in air moisture (Peterson 2002). Thus, dose estimates based on HTO concentrations in leaves will be more health protective than those based on measured HTO in other edible plant parts.

Organically bound tritium in vegetation is not measured by LLNL. Although the dose per unit intake of OBT is about 2.3 times higher than dose per unit intake of HTO (ICRP 1996), the OBT contribution from the diet is unlikely to increase the tritium dose to the public by more than a factor of two (ATSDR 2002). Levels of tritium in the environment from LLNL operations are so low that "tritium doses to the communities surrounding LLNL, including potential contributions from OBT, HTO, and HT (tritiated gas) are below levels of public health concern" (ATSDR 2002).

10.2.1.4 Collection Methods

Since water is easily extracted from plants, it is the tritium in the free water of plants that is measured. Tritium concentrations in plant water rapidly reach equilibrium with tritium in air moisture. Therefore, collection methods used by the sampling technologists are designed to avoid contamination of the sample and ensure that the sample is sealed in a plastic bag so that no exchange can occur between the tritium in the plant water (at time of sampling) and air after leaving the sampling location. The sample is also placed on dry ice in the field to freeze it as

quickly as possible to prevent the loss of tritiated water to the sample container. All sampling performed is done in accordance with the LLNL *Environment, Safety, and Health Manual*. Any required training and/or special concerns associated with performing this sampling are identified in the Operations and Regulatory Affairs Division (ORAD) Integration Work Sheet (IWS) 2271, *Technical Support Group (TSG) Environmental Monitoring Activities.* Specific hazards associated with this activity and required environment, safety, and health (ES&H) controls are also identified in the IWS.

10.2.2 Extent and Frequency of Vegetation Monitoring and Measurement

To assess doses from ingestion of tritium in vegetation, LLNL primarily monitors annual grasses, the occasional forb, and a few leafy vegetables. Noxious plants (e.g., poison oak, stinging nettles) are not sampled to avoid injury to the sampling technologists. The potential for seasonal variability for vegetation is addressed through quarterly sampling. (Samples were collected monthly in the past, but the data were not sufficiently variable to justify continued monthly sampling.) Only plants that are green (i.e., living) are sampled. In dry summer months, mostly deep-rooted plants are sampled, since most grasses are dried. Duplicate samples are collected from each location. In addition, sets of QA duplicates are collected each quarter from one on-site, one Livermore Valley, and one Site 300 location. The vegetation locations for the area around the Livermore site comprise three groups (see **Figure 10-1**). The first group, "Near," includes locations at or within 1 km of the Livermore-site perimeter (AQUE, GARD, NPER, MESQ, MET, VIS, PIN1, and PIN2). PIN1 is a special case. It is a pine tree rooted in a location of known elevated tritium concentrations in soil and groundwater near Building 292 (see Chapter 5). PIN1 is considered a diffuse source of tritium, and miniscule doses at the perimeter fence are estimated based on potential ingestion of hypothetical foodstuffs contaminated by tritium released from PIN1. PIN2 is another pine tree in a location exposed only to atmospheric tritium.

The "Intermediate" group consists of locations in the Livermore Valley that are removed from the site (1 to 5 km from the Livermore-site perimeter), but close enough and often downwind so that they are still potentially under the influence of tritium releases at the site. The "Intermediate" locations are I580, TESW, ZON7, and PATT (**Figure 10-1**).

The third group, "Far," represents locations highly unlikely to be affected by LLNL operations. One background location (CAL) is more than 25 km away, while the other (FCC) is in the Livermore Valley but generally upwind and sufficiently distant from the Livermore site. Sampling at another "Far" location (PARK) was discontinued at the end of 2000 because, for several years, no tritium has been detected in samples from that location.

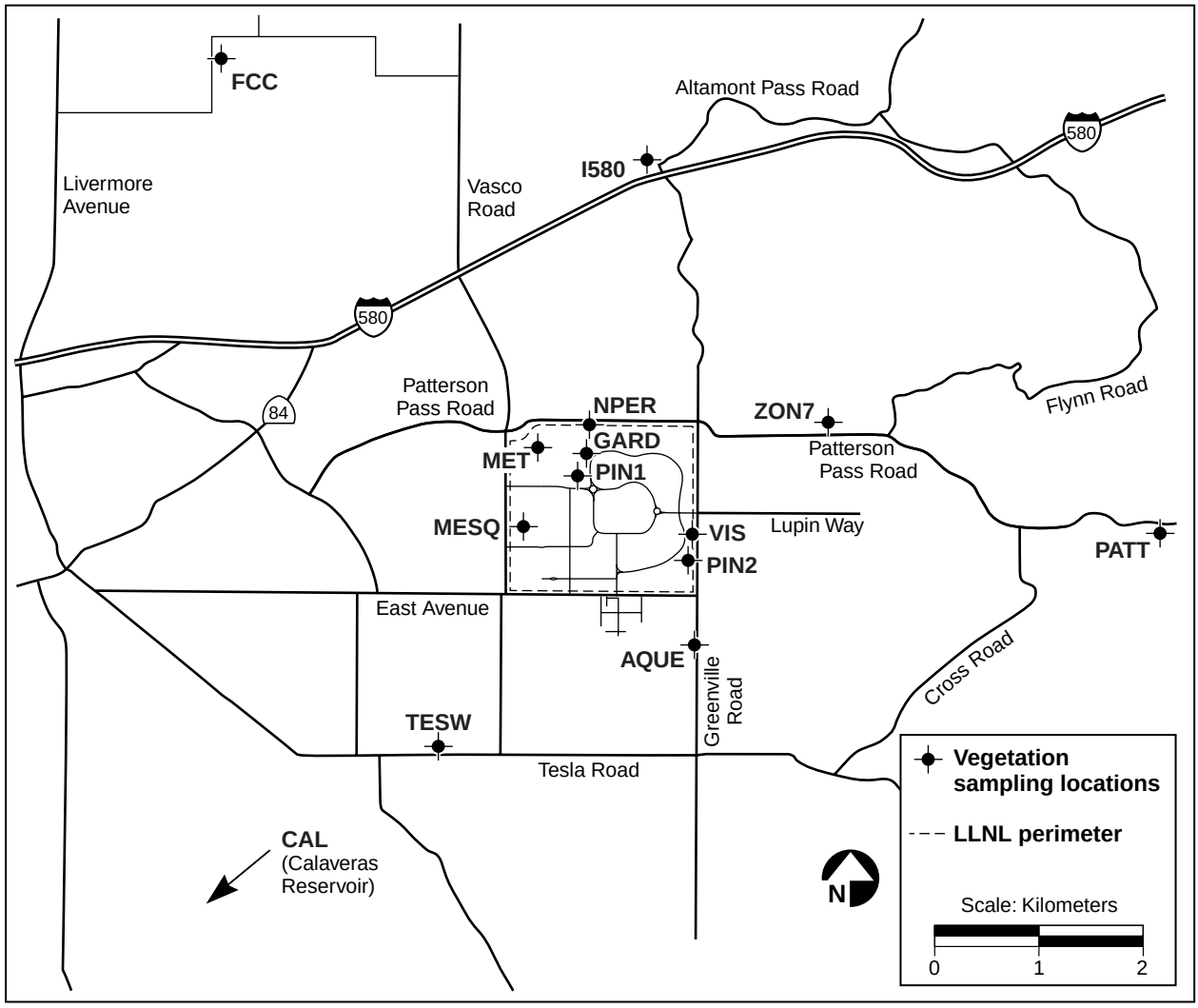

Figure 10-1. Vegetation sampling locations, Livermore Valley

Most sampling locations at Site 300 have historically exhibited natural background tritium levels in vegetation. Since 1992, no concentration from locations 801E, CARN, GOLF, GEO, and PRIM (the location replaced by COHO in the second quarter of 2000) has been significantly above the detection limit, and results amongst the locations have been indistinguishable. Because of this, at the end of 2000, sampling at locations GEO, CARN, and GOLF was discontinued (**Figure 11-2** in Tate et al. 1999). Locations 801E and COHO **(Figure 10-2**) will continue to be used to monitor background tritium or any changes in concentrations from new operations.

From 1971 until 1994, vegetation samples from location DSW (**Figure 10-2**) consistently exhibited much higher than background concentrations of tritium. DSW is adjacent to a landfill that contains debris contaminated with tritium from past experiments and is included in the investigation for contaminated groundwater under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (Biermann et al. 2001). More recently, vegetation samples from DSW have exhibited variable concentrations, ranging from relatively high to not detectable. Similarly, samples from the location EVAP (**Figure 10-2**) have shown both higher-than-background tritium values as well as non-detects since sampling began in 1993. The highest concentrations apparently occur when plants whose roots reach the water table are sampled randomly.

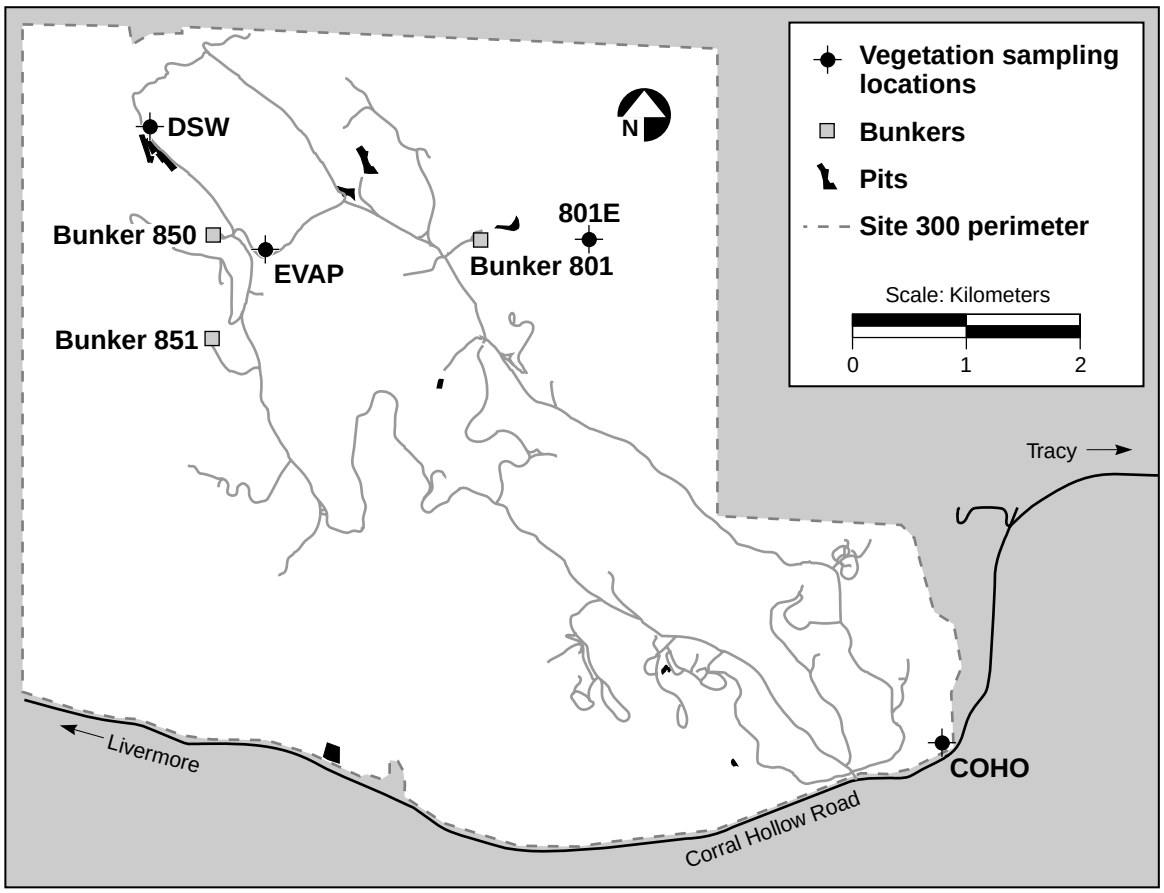

Figure 10-2. Site 300 vegetation sampling locations

Consistent use of the same sampling locations allows for better trending of data and closer monitoring of areas of concern. A detailed description of all sampling locations can be found in the Locations Database. The Locations Database is a Filemaker Pro database containing past and present sampling locations. It includes directions to the sampling location, the

environmental medium sampled at the location, safety concerns, and other pertinent information. The Locations Database SOP Supplement, EMP-QAS-LOC, describes the process to be used for defining, documenting, and approving sampling locations. In addition, a hardcopy of all current sampling locations is maintained by the TSG Coordinator in ORAD. All vegetation sampling locations are marked with permanent location markers. The requirements for a good sampling location are described in the LLNL procedure EMP-VG-S, *Vegetation and Foodstuff Sampling*. The primary requirement is that living vegetation be available for each sampling period at each location. All vegetation sampling, regardless of location, is conducted according to EMP-VG-S.

10.2.3 Procedures for Laboratory Analysis

Two bags of frozen, labeled samples of vegetation from each sampling location are delivered to the Chemistry and Materials Science Division. The vegetation is stored frozen until analysis. One bag of vegetation will be analyzed, and the other will be archived by the analytical laboratory. Vegetation samples are weighed on properly maintained and calibrated balances (SOP-CES-P542, *CES Balances*). Tritiated water is extracted from the samples by freeze-drying samples (CES-EM-P542, *Low Level Tritium Analysis – Freeze Dry*) in the Chemistry and Materials Science Environmental Monitoring Radiological Laboratory EMRL). The samples are then analyzed for tritium by liquid scintillation counting (SOP-EM-P552, *Operation of Packard Tri-Carb LSC for Environmental Sample*s). Concentrations are reported in pCi/L extracted plant water and in pCi/g dry weight vegetation.

10.2.4 Quality Assurance Procedures

10.2.4.1 Data Quality Objectives

Data quality objectives comprise the set of constraints on a given study. They include a specification of the level of uncertainty that the data user is willing to accept (Keith 1994).

10.2.4.1.1 Precision: The detection limits for tritium in vegetation are about 2.0 Bq/L.

In accordance with LLNL procedure EMP-VG-S, *Vegetation and Foodstuff Sampling,* field duplicate samples are submitted with each batch of vegetation samples. Approximately 10 percent of samples are field duplicates. Two "identical" samples are collected at locations chosen for duplicate samples. The sampling locations of field duplicate samples are not identified so the analytical laboratory does not know where the samples originated (procedure EMP-QA-DM, *Sample and Data Management*). However, this information is recorded on field tracking forms (FTFs), which are filled out in the field by the sampling technologist and which contain detailed information about actual sampling locations and other conditions affecting

sampling. After the results are obtained by the analyst, the concentrations of duplicates are compared. Different concentrations can be explained by analytical error and natural variability. When the source of the tritium is atmospheric, the difference in duplicates usually can be explained exclusively by analytical error. This is invariably true when concentrations are near the detection limits, which occurs much of the time in the vegetation network. When one of the results in a pair is a nondetection, the other result should be less than two times the detection limit (Chapter 14, Biermann et al. 2001). When the source of the tritium is soil water, as at locations DSW and EVAP, natural variability will be the cause of any large differences in the concentrations of the duplicates (up to a factor of three, historically, although usually less than a factor of two). These differences are to be expected because even plants growing adjacent to one another may have different root structures reaching water of different concentrations. Given the variability in the field from a groundwater source and the rapid exchange of HTO between air and vegetation when the tritium source is atmospheric, re-sampling cannot resolve any differences. If the magnitude of the differences cannot be explained, the analytical laboratory is contacted to discuss any problems that may have occurred during analysis. If there has been a mistake at the laboratory, a nonconformance report (NCR; procedure ORAD-QA-NCR, *Nonconformance Reporting and Tracking*) to document the actions taken must be prepared.

The analytical laboratory creates laboratory duplicates (also called splits) in accordance with technical implementing procedures (Hall and Edwards 1994). Laboratory duplicates are introduced blind into sample processing at a rate of about 10 percent of samples. The relative error ratio is calculated and reported for each split sample. If the control limit of 3.0 for the Relative Error Ratio is exceeded, the source of the problem is investigated and corrected (CES procedures, SOP-CES-P810, *Data Validation* and SOP-CES-P811, *Data Verification*).

10.2.4.1.2 Accuracy: The radiological laboratory runs blank and control samples traceable to standards of the National Institute of Standards and Technology (NIST). For vegetation it is virtually impossible to create a field blank that would not be immediately obvious to the analytical staff. To compensate for the lack of a field blank for vegetation, air monitoring samples are analyzed concurrently with vegetation samples, and an air silica gel blank is run as a field blank. Currently, no field spikes are prepared due to the difficulty of evenly dispersing any known amount of tritium in vegetation, but laboratory spikes made from blanks with standards added are counted.

The radiological laboratory also participates twice yearly in the DOE Environmental Measurements Laboratory Quality Assurance Program (SOP-CES-P820, *CES Performance Evaluation Program*). For tritium, the DOE sends water samples with known concentrations to the participating laboratories, compares the analytical results (thereby determining the accuracy

of the various participating laboratories), and publishes reports of the results so that analytical laboratory personnel and their customers can evaluate their analytical laboratory's relative performance. The results of the study are published on the EML web site http://www.eml.doe.gov/QAP/.

10.2.4.2 Audits and Self-Assessments

Internal analytical laboratories that perform analyses for the vegetation network are subject to the Environmental Protection Department (EPD*) Quality Assurance Management Plan* (Merrigan 2001), under which EPD performs assessments of the quality-affecting activities of organizations contributing supportive work to EPD. Such assessments are performed periodically as part of the EPD Quality Assurance Program. Triennial self-assessments of all monitoring networks are also performed (LLNL procedure ORAD-QA-SA, *Self Assessments*).

10.2.5 Program Implementation Procedures

The primary responsibility for activities related to vegetation monitoring is assigned to a Terrestrial & Atmospheric Monitoring & Modeling (TAMM) environmental analyst of ORAD. The analyst designs, implements, and maintains the sampling network; determines analytes, collection methods, and analytical methods; coordinates network activities with sampling technicians and analytical laboratory personnel; reviews and analyzes the data; performs dose assessments; follows trends in data; and reports results.

Vegetation is collected according to LLNL procedure EMP-VG-S, *Vegetation and Foodstuff Sampling,* and is submitted for analyses using sample control, chain-of-custody, and documentation procedures (EMP-QA-DM, *Sample and Data Management*). The written procedures include requirements for sample collection and submittal for chemical analysis, keeping a log, and filling out FTFs and chain-of-custody (CoC) forms. The procedures also require the sampling technologist to alert the environmental analyst about difficulties encountered during any sampling event.

10.2.6 Action Levels

Sample results are compared to the 5-year running historic geometric mean for each sampling group in the vegetation monitoring networks ("Near," PIN1, "Intermediate," or "Far" for Livermore site vegetation; "General," EVAP, or DSW for Site 300 vegetation). As discussed in **Section 10.2.2**, plants at PIN1, DSW, and EVAP are growing in locations of known groundwater contamination. However, their sometimes elevated concentrations of tritium are not a hazard, either because the type of vegetation is inedible (e.g., the pine tree) or because no

potential foodstuffs can be harvested from the location. Geometric means and standard deviations for 1996 through 2001 are provided in **Table 10-1.**

Table 10-1. Geometric means, geometric standard deviations, and upper warning and action limits for vegetation sampling groups (1998–2002)

Group	Geometric Mean (Bq/L)	Geometric Standard Deviation	Warning Limit (upper)	Action Limit (upper)
LLNL vegetation				
Near	3.2	3.1	32	10
PIN1	63	2.7	480	1,300
Intermediate	1.7	3.0	17	52
Far	0.67	3.2	7.2	24
Site 300 vegetation				
General	0.76	2.6	5.3	14
DSW	27	20	13,000	290,000
EVAP	16	13	3,000	42,000

Any results outside two geometric standard deviations (a warning level) are examined for data transcription errors, and the analytical lab is contacted to discuss any problems that may have occurred during analysis. In addition, an attempt is made to determine if the result is real due to an unusual release and wind patterns. If the release is real, other locations will probably have been affected to some degree, or the release may have been detected by another sampling network (e.g., air tritium). Any results outside three geometric standard deviations (the action level) are also subject to examination for transcription errors and analytical problems. In addition, the location is resampled, perhaps in duplicate or triplicate depending on the nature of the problem. If no transcription, analytical, or other error is found to explain an out-of-limit value, the environmental analyst notifies EPD management of this in writing following the NCR procedure (ORAD-QA-NCR, *Nonconformance Reporting and Tracking*), and further action, such as a special sampling study, is taken with EPD management concurrence.

10.2.7 Preparation and Disposition of Reports

The environmental analyst conducts dose assessments, based on the monitoring data and using methods detailed in guidance document ORAD-R-DA, *Radiological Dose Assessment Guidance Document*, for vegetation once all data for a calendar year are obtained. Data are analyzed based on ORAD-QA-D, *Data Analysis*. The monitoring and dose assessment results are reported in the annual *Environmental Report* (e.g., Biermann et al. 2001. No other reporting is required for vegetation.

10.2.8 Future Plans

The short-term plan for vegetation sampling is to continue monitoring in the manner described in this chapter. Sampling may be initiated at the location of the site-wide maximally exposed individual at Site 300.

The long-term plan for vegetation sampling may be to sample more frequently from locations DSW and EVAP to better understand the soil water/vegetation dynamics in those locations.

10.3 Wine Monitoring Program

10.3.1 Rationale and Design Criteria

10.3.1.1 Regulatory Drivers

The regulatory driver for foodstuff monitoring is the applicable portions of DOE Order 5400.1 (see WSS B92 in Appendix B). Guidance in monitoring specific terrestrial foods appropriate for surveillance sampling and analysis is provided in the DOE's *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (DOE 1991).

Although wine is made from grapes, a fruit, no specific regulatory requirement for routine wine monitoring has been identified. Explicit regulatory requirements are not the sole basis for monitoring, however. Monitoring is also carried out when there is a high level of public interest or concern, or where best management practices indicate monitoring is appropriate. In the past, tritium concentrations in Livermore Valley wines have attracted much public interest, as evidenced by newspaper and television coverage. Because of that interest, and because wines can contribute to radiological doses, however small, LLNL has analyzed more wine samples at more sensitive detection levels than might otherwise be required.

10.3.1.2 Monitoring Objectives for Wine

The primary purpose of wine monitoring is to evaluate the dose to the public from radionuclides found in wines purchased during the reporting (calendar) year. Secondarily, the impact of LLNL operations on tritium concentrations in Livermore Valley wines can be tracked based on concentrations decay-corrected to vintage year. Furthermore, long-term trends may be compared with those of wines grown in other areas.

10.3.1.3 Sources and Analytes

Tritium is the only nuclide released from LLNL that can be detected in wine. At LLNL's Livermore site, the major contributors to airborne tritium emissions are routine emissions from the Tritium Facility (Building 331 and its associated operations) and the Hazardous Waste

Management Yard of Building 612. Tritium is released from the Building 331 stacks as either tritiated gas (HT) or as tritiated water vapor (HTO). Tritium moves through the environment as tritiated water. As such, it is easily assimilated into plant water and incorporated into developing grapes. Through photosynthesis, tritium also is incorporated into the organic matter of grapes. The HTO and OBT in grapes made into wine can contribute to a radiation dose to human beings from drinking wine.

10.3.1.4 Collection Methods

Wine for annual analysis is purchased at local retail stores in 750 mL or 1 L bottles. The purchased wine represents what a customer might purchase and take home to drink during the calendar year. It represents more than one vintage year.

10.3.2 Extent and Frequency of Wine Monitoring and Measurements

Wine is sampled annually at the end of the calendar year. The annual wine sampling is an extremely sensitive issue because of the potential economic, political, and public relations impacts of the data, and because it involves the purchase of alcoholic beverages and their possession onsite at LLNL. As a controlled item, the purchase of wine samples requires special approval by DOE and both the LLNL Business Services Department and Safeguards and Security Department (see procedure EMP-VG-S, *Vegetation and Foodstuff Sampling*).

Wines of three types are sampled and analyzed annually for tritium concentrations. Each year since 1993, the following estate-bottled wines have been sampled: twelve bottles (plus two duplicates) from the Livermore Valley, six bottles (plus one duplicate) from California (outside the Livermore Valley), and four bottles from Europe (France, Germany, and Italy). LLNL has chosen to divide California into eight wine-producing regions (excluding Livermore) and Europe into thirteen wine-producing regions. Wine sampling regions are listed in the locations computer database (EMP-QAS-LOC, Locations Database SOP Supplement) and hardcopies of all current sampling locations are maintained by Technical Support Group and the environmental analyst. The selection of bottles that represent a viticultural area is random. Any wine from a designated area is considered representative of that area. Since 1996, an equal number of red and white wines from each geographic area has been sampled. In addition, in years up to and including 2000, other Livermore Valley wines not previously analyzed were purchased and archived for possible future analysis.

European wines were initially chosen for evaluation because Europe is a significant wine-growing region with historically high tritium content in wine from locations near nuclear power plants. California wines from regions other than the Livermore Valley serve as natural background samples for comparative purposes. Because geographic variability of the wines is

addressed, wines selected from a number of regions roughly represent the tritium exposure received by the wine-drinking public.

10.3.3 Procedures for Laboratory Analysis

To avoid airborne tritium contamination, wine samples are submitted unopened for analysis to the Noble Gas Spectrometry Laboratory (NGSL) in Chemistry and Materials Science. Chain-of-custody procedures are followed when delivering samples (see procedure EMP-QA-DM, *Sample and Data Management*). Samples are analyzed for tritium content (both HTO and OBT) by ^{3}He mass spectrometry (Surano et al. 1992).

10.3.4 Quality Assurance Requirements

10.3.4.1 Data Quality Objectives

Data quality objectives comprise the set of constraints on a given study. They include a specification of the level of uncertainty that the data user is willing to accept (Keith, 1994).

10.3.4.1.1 Precision: The detection limit for wine using ^{3}He mass spectrometry is 5.6×10^{-2} Bq/L. In accordance with LLNL procedure EMP-VG-S (*Vegetation and Foodstuff Sampling*), three QA duplicates are purchased each year, two from the Livermore Valley and one from elsewhere in California. The identity of each wine is listed on the FTF, but, on the CoC, each is referred to only as a QA sample. The labels are removed from the bottles before submission to the laboratory to disguise the identities of the vineyards. The bottles are relabeled as QA samples. Once the identity of the QA duplicates has been revealed, the likelihood that the samples are identical is calculated.

Twelve laboratory duplicates (also called splits) are analyzed each year. Results are expected to be very close because wines are well-mixed. Paired duplicates are compared, and the magnitude and distribution of deviations relative to stated errors are examined. In general, the duplicate analyses agree slightly better than those predicted by their stated uncertainties.

10.3.4.1.2 Accuracy: For wine, an empty sample bottle serves as a blank. A controlled 18 L cask of wine, purchased in 1990, serves as a secondary standard. Samples of this cask wine have been measured yearly, and the measurements serve as a good test of long-term reproducibility. The primary standard is produced by mixing a low-level NIST standard with either "dead" water or the cask wine. Once the identity of the QA duplicates has been revealed, the likelihood that the samples are identical is calculated.

A number of years ago, there was a laboratory intercomparison for low-level tritium concentrations in water. Five laboratories participated, analyzing 45 blind samples over a two-

year period. All laboratories measured the samples accurately. Based on these results, the NGSL adopted an uncertainty relation of 10% + 5 pCi/L (quadratic sum).

10.3.4.2 Audits and Self-Assessments

Formal audits and self-assessments are not done on the analysis of wine samples using ^{3}He mass spectrometry. Each year a formal report is issued by the laboratory to the environmental analyst. In each report, QA/QC activities, general procedures, etc. are carefully documented. The goal is to demonstrate the performance of the laboratory in the report and have a discussion with the EPD representative each year about the data.

10.3.5 Program Implementation Procedures

The primary responsibility for activities related to wine monitoring is assigned to an environmental analyst in the TAMM Group of ORAD. The analyst designs, implements, and maintains the sampling network; determines analytes, collection methods, and analytical methods; coordinates network activities with analytical laboratory personnel; reviews and analyzes the data; performs dose assessments; follows trends in data; and reports results.

Wine samples are collected according to LLNL procedure EMP-VG-S, *Vegetation and Foodstuff Sampling,* and are submitted for analyses using sample control and documentation procedures (EMP-QA-DM, *Sample and Data Management*). The written procedures include requirements for sample collection and submittal for chemical analysis, keeping a log, and filling out FTFs and COC forms.

10.3.6 Action Levels

Sample results are compared to the 5-year running historic geometric mean for each sampling group in the wine monitoring networks (Livermore, California, or Europe). These geometric means and standard deviations are provided in **Table 10-2**.

Table 10-2. Geometric means, geometric standard deviations, and upper warning and action limits for wine sampling groups (1998-2002).

Group	Geometric Mean (Bq/L)	Geometric Standard Deviation	Warning Limit (upper)	Action Limit (upper)
Livermore	1.8	1.7	5.4	9.5
California	0.44	1.2	0.67	0.83
Europe	1.4	1.6	3.5	5.5

Any results outside two geometric standard deviations (a warning level) are examined for data transcription errors, and the analytical lab is contacted to discuss any problems that may have occurred during analysis. Any results outside three geometric standard deviations (the action level) are also subject to examination for transcription errors and analytical problems. In addition, an attempt will be made to purchase the same wine, perhaps in duplicate or triplicate, for reanalysis. If no transcription, analytical, or other error is found to explain an out-of-limit value, the environmental analyst notifies EPD management of this in writing following the NCR procedure (ORAD-QA-NCR, *Nonconformance Reporting and Tracking*), and further action, such as a special study, is taken with EPD management concurrence.

10.3.7 Preparation and Disposition of Reports

The environmental analyst conducts dose assessments, based on the monitoring data and using methods detailed in guidance document ORAD-R-DA, *Radiological Dose Assessment Guidance Document*, for wine once all data for a calendar year are obtained. The monitoring and dose assessment results are reported in the annual *Environmental Report* (e.g., Biermann et al. 2001). In addition, tritium concentrations in wine decay-corrected to the harvest year are reported for all wines sampled. No other reporting is required for wine.

10.3.8 Future Plans

The short-term plan for wine sampling is to continue monitoring in the manner described in this chapter. In the longer term, the size of the wine sampling effort may be reduced. Levels of tritium in the Livermore Valley do not warrant the current expenditures of time and costs of analysis. Furthermore, all Californian wines consistently have very similar concentrations, so the numbers of these wines analyzed could be reduced.

A special study might be carried out using the archived wines. The original intent behind archiving wines each year was that, if old measurements were questioned, a similar wine could be re-sampled to prove or disprove the original measurement. In actual fact, there is some evidence that a small amount of exchange of tritium can occur through the cork (Roether 1967). Whether or not this exchange is of a magnitude to have changed the tritium concentrations in the wine beyond the normal level of uncertainty is a question that might be answered by a special study using the very sensitive analytical method, ^{3}He mass spectrometry.

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11 Direct Radiation Monitoring

Nicholas A. Bertoldo

11.1 Introduction

At a facility such as LLNL, where a wide variety of radiological operations take place, the potential exists for radiological impacts to the public and environment. Environmental surveillance and effluent monitoring (Chapters 3-10) for radionuclides, followed by pathway and dose assessments (Chapter 14), is one method to determine LLNL-induced radiological impacts, but for completeness, direct radiation impacts must also be evaluated. At LLNL this means evaluating direct gamma radiation doses. In order to effectively evaluate the contribution of dose to the public as a result of LLNL operations, the natural background radiation environment must be assessed. This is done to establish the benchmark level from which any contributory level may be determined.

11.2 Rationale and Design Criteria

11.2.1 Regulatory Drivers

In accordance with applicable portions of DOE Orders 5400.1 and 5400.5 (see WSS B93 and B94 in Appendix B), as well as the California Code of Regulations Title 17 (CCR 1997), LLNL must monitor direct radiation to establish background levels and to determine public doses resulting from its operations. To measure potential doses from DOE operations, the *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (DOE 1991) recommends using thermoluminescent dosimeters (TLDs) to monitor direct gamma radiation at the site perimeter. Furthermore, DOE Order 5400.1 requires that specific TLD-related activities (e.g., annealing, calibration, readout, storage, and exposure periods) be consistent with the recommendations of the American National Standards Institute (ANSI 1975). LLNL's use of TLDs meets the specifications of the above-mentioned orders, regulations, and guidance.

11.2.1.1 Work Smart Standards Applicable to Current Regulatory Drivers

Subsections of the regulatory drivers DOE Orders 5400.1 and 5400.5 Chg. 2 pertaining to the TLD surveillance monitoring network are referenced in LLNL Work Smart Standards (WSS) B93 and B94. These LLNL WSS, in addition to California Code of Regulations Title 17 *Standards for Protection Against Radiation* (CCR 1997), compose the regulatory drivers followed in the direct radiation monitoring network. The specific WSS citations are:

- DOE Order 5400.1, Chapter IV, paragraphs 1.a, 4, 5.b, and 10.c
- DOE Order 5400.5, Chg. 2, Chapter II, paragraphs 1 and 2

Public dose as defined in DOE 5400.5, does not include dose received from occupational exposures, naturally occurring "background" radiation, doses received as a patient from medical practices, or doses received from consumer products.

TLDs are deployed at locations around the Laboratory and off-site to ensure that any measurable direct radiation dose from LLNL operations would be detected by the monitoring network. This network serves to both characterize the ambient average level from terrestrial and cosmic background radiation and ensure detection of elevated dose imparted by LLNL operations.

11.2.2 Best Management Practices

To assess potential LLNL-induced doses directly in areas where members of the public reside, TLDs are also deployed and used to measure radiation exposures throughout the Livermore Valley. This off-site monitoring, which historically has measured natural, background radiation levels, augments the required site perimeter monitoring and meets public expectations of the Laboratory.

11.2.3 Monitoring Objectives

The primary purpose of direct radiation monitoring is to measure radiation doses and evaluate the dose received by the public, if any, from direct gamma radiation originating at LLNL. This is accomplished by deploying a sufficient number of TLDs around the Laboratory to ensure that any measurable direct radiation dose from LLNL operations would be detected by the monitoring network and to make direct measurements in areas where members of the public may potentially be exposed.

11.2.4 Potential Sources and Contaminants

There are many radiological operations throughout LLNL in a variety of research and development programs that employ direct gamma radiation sources. For example, Radioactive and Hazardous Waste Management (RHWM) manages direct gamma radiation sources as waste in the southeast corner of the Laboratory. Laser research uses direct gamma radiation sources in the northwest quadrant of the Laboratory. Biomedical Research, near the center of the Laboratory, has low-level direct gamma radiation sources.

Documentation and notification of changes in LLNL operations affecting the storage and use of gamma and neutron radiation sources is obtained through the following actions:

- participation in Environmental Support Teams by the Terrestrial & Atmospheric Monitoring & Modeling (TAMM) Group (see Chapter 1)
- consultation with the Hazards Control Department about classification of radioactive materials management areas, new operational safety procedures and facility safety procedures
- notification when new operations or facilities are planned through the review process of National Environmental Policy Act documentation for all new and modified operations (see Chapter 3)
- review of radioactive materials usage inventory forms collected as part of the National Emissions Standards for Hazardous Air Pollutants (NESHAPs) dose evaluation process (see Chapter 14)

11.2.5 Collection Methods and Devices

Penetrating radiation, which cannot be measured by collection of material on filters nor chemically trapped, is collected by trapping the penetrating gamma radiation in the crystal lattice of solid state devices known as TLDs. These dosimeters absorb the direct gamma radiation energy that is imparted to the dosimeter as a result of its exposure to the natural background radiation environment and anthropogenic radiation sources at the deployed location.

When certain crystals in the physical matrix of the TLD are exposed to gamma radiation, impurities in the crystals form low temperature trapping sites for electrons excited to higher energy states. The electrons remain in a high energy state at normal ambient temperatures. In the analytical laboratory, the TLD is processed in a three-phase process. First, the TLD is heated, causing the electrons to be released from the trapping sites; when they drop to a lower energy state, photons are emitted. Second, the photons are measured with a photomultiplier tube with the light intensity being proportional to the original absorbed dose of radiation; the light intensity measurement is recorded. Third, after the TLD is read, it is heated and read again. The second reading should be near zero, indicating that all of the gamma-radiation-induced stored energy has been released (and therefore measured). This second heat treatment is referred to as annealing and verifies that the TLD is ready for reuse in the field.

TLDs measure exposure as absorbed dose (in milliroentgen; mR). The absorbed dose is the quantity of energy deposited by radiation in a given amount of material. This is converted to radiation dose (mrem or mSv) by calibrating the dosimeter reader to read the absorbed dose

and then applying a quality factor for a beta/gamma radiation field (Graham and Trombino 1997). The accuracy of radiation measurements made with TLDs is evaluated by charting the performance of dosimeters exposed to known radiation exposures. These quality-control TLDs are irradiated for TAMM by the LLNL Hazards Control Calibration and Standards Laboratory with National Institute of Standards and Technology (NIST)-traceable cesium-137 standards.

LLNL uses the Panasonic Model UD-814AS1 TLD, which contains three components of activated calcium sulfate ($CaSO_4$) and one element of lithium borate ($Li_2B_4O_7$). Only the $CaSO_4$ components are used to measure LLNL direct environmental gamma radiation because of the crystal's sensitivity to environmental radiation levels. The luminescence of the $CaSO_4$ element is 30 times greater than other TLD crystals considered for use. This makes the UD-814AS1 TLD an obvious choice for measurements in the milliroentgen absorbed dose range (converted to the single-digit millirem range). Monitoring devices that have been rejected in favor of the UD-814AS1 TLD include CaF_2 TLDs, $CaSO_4$ dysprosium-activated TLDs, LiF TLDs, $Li_2B_4O_7$ TLDs, and Li_6Li_7 gamma neutron detectors.

LLNL used the CaF_2 TLD between 1980 and 1984 and experienced a 25% drop in the environmental gamma radiation measurements. After an investigation, it was determined that CaF_2 TLD faded and was more sensitive to sunlight. (Fading is the loss of signal due to trapped electrons returning to their normal state at ambient temperatures and thereby releasing the gamma energy prior to measurement. Detailed information on fading can be found in the *Argonne National Laboratory Operation Health Physics Training Manual* [Moe 1992]). The $Li_2B_4O_7$ TLD is also known to fade (Cameron et al. 1967). The LiF TLD does not yield the sensitivity that is required to measure the low dose levels seen at LLNL. The Li_6Li_7 TLD measures both gamma and neutrons simultaneously, but the background must be subtracted from both the neutron and gamma readings, leaving a high degree of uncertainty with regard to the low environmental exposures measured at LLNL.

11.3 Extent and Frequency of Monitoring and Measurements

Radiation monitoring locations are strategically selected to determine background and perimeter radiation exposures. The Livermore site perimeter locations have been chosen based on proximity to LLNL gamma emitting operations, potential public exposure, and accessibility of the monitoring location. The off-site dosimeters are located to provide information about background radiation and LLNL impact on radiation levels in nearby residential areas. All radiation monitoring locations are chosen to ensure that the exposures measured will be representative of those that could potentially result from LLNL operations.

In addition, the following network design criteria were considered before deciding on permanent TLD sampling locations:

- The assurance that the TLDs are placed as far as possible from large or dense objects and that proximity of a structure will not alter the measurement
- The assurance that sampling areas will not be temporarily obstructed to minimize distortion of the radiation field
- Suitable TLD hanging location including consistency in TLD height from the ground (approximately one meter)
- Population distributions
- Representative local geology

Sampling is done quarterly as directed in the guidance document DOE/EH-0173T (DOE 1991) producing a detectable background dose.

TLD sampling locations have undergone recent adjustments as a result of geographical changes, safety concerns, and overall reduction in sampling locations. Current sampling locations are listed in the Locations Database as described in EMP-QAS-LOC, Locations Database SOP Supplement.

11.3.1 Livermore Site and Livermore Valley

External exposures from gamma radiation are measured quarterly, using TLDs, at 14 Livermore-site perimeter locations and 23 off-site locations in the Livermore Valley (**Figures 11-1** and **11-2**). Quarterly sampling periods produce a readily detectable dose, following guidance in DOE/EH-0173T (DOE 1991). For TLDs in the LLNL vicinity, this nominally represents a quarterly background direct radiation dose on the order of 0.1 to 0.2 mSv (10 to 20 mrem). Furthermore, quarterly sampling allows evaluation of seasonal variation and increases the probability that data are obtained from all locations for at least a portion of the year. That is, if a TLD is lost or damaged at a given location, data from only a single quarter are lost, thus allowing an estimate of annual exposure to be made from data acquired during the other three quarters.

Contributions to direct radiation doses from LLNL operations have neither been historically above the natural background radiation environment levels at or beyond the Livermore-site perimeter, nor have they changed significantly over the last twenty years. Exposures measured at the LLNL perimeter typically are statistically identical to the off-site doses, which are considered to be natural direct radiation background levels. This indicates that LLNL operations do not contribute to the external dose at or beyond the Livermore-site perimeter.

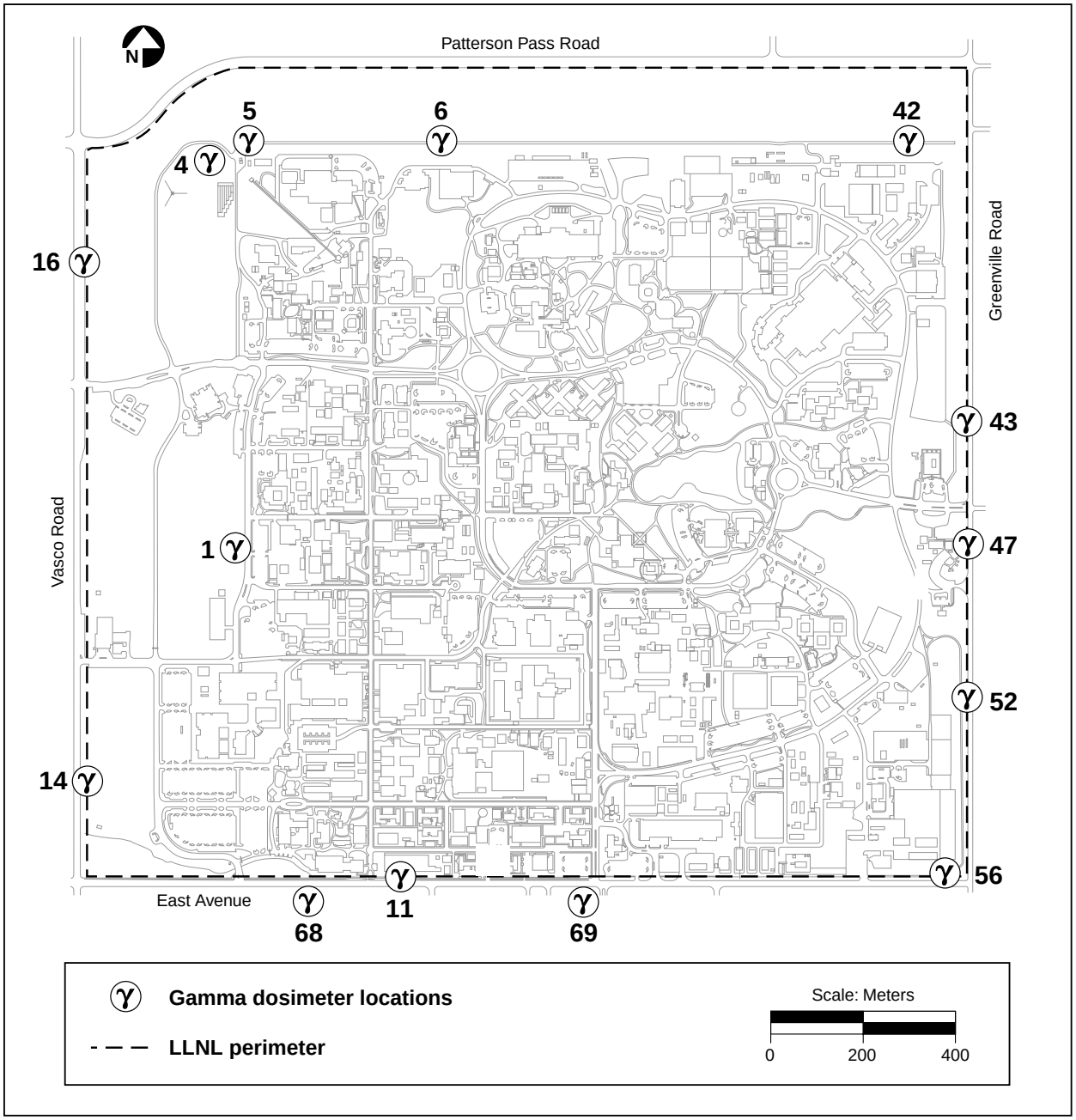

Figure 11-1. Gamma dosimeter locations, Livermore site

11.3.2 Site 300

There are nine on-site perimeter, four on-site interior, and four off-site TLD monitoring locations at Site 300 plus two locations in Tracy, CA. These locations are illustrated in **Figure 11-3**. Off-site dosimeters are located in areas accessible to the public, including locations at adjacent ranches, on Corral Hollow Road, at the Tracy Airport, and in the City of Tracy.

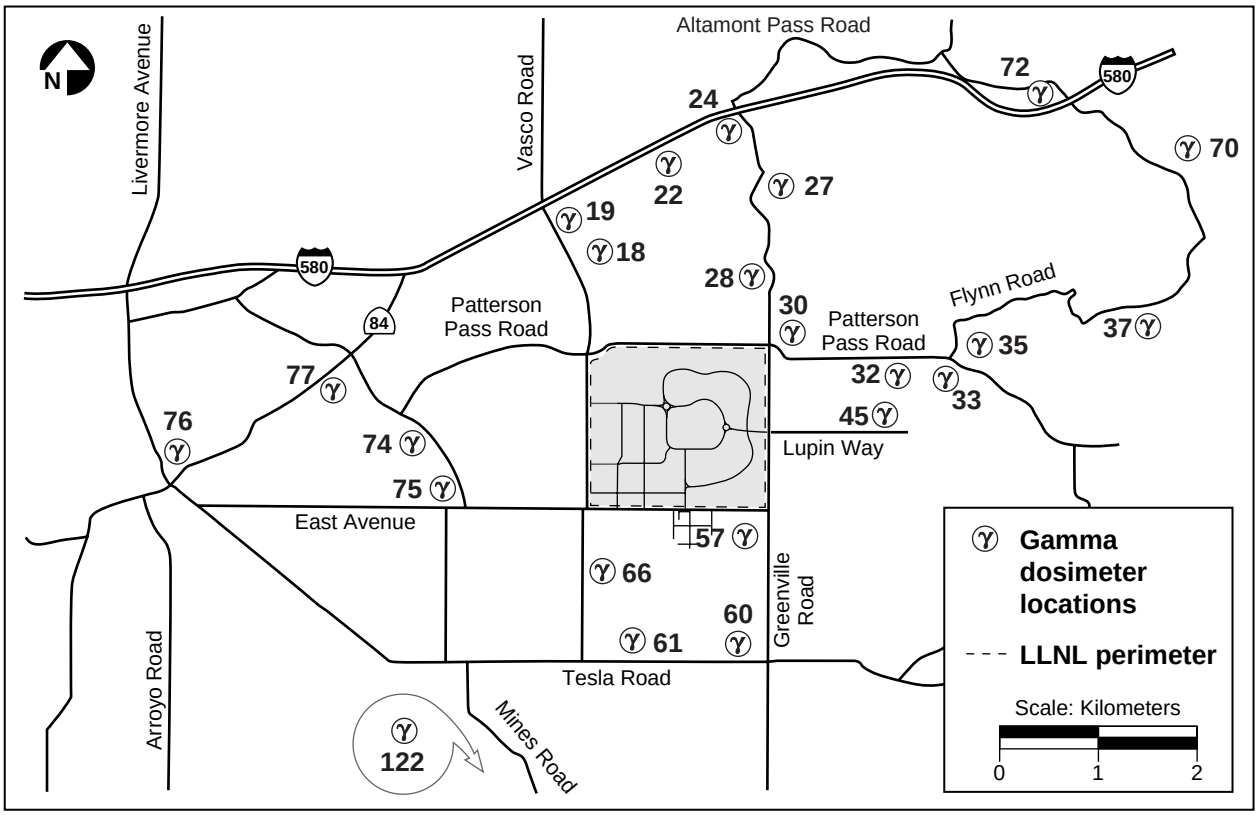

Figure 11-2. Gamma dosimeter locations, Livermore Valley

The initial TLD network design for Site 300 limited monitoring to the site perimeter and three locations in the San Joaquin Valley near the City of Tracy. These original off-site locations were chosen to provide exposure information about nearby population centers, as well as background radiation levels, and they continue to serve those purposes. However, the terrain and geological composition of Site 300 is different from that of the City of Tracy and the surrounding San Joaquin Valley; Site 300 has outcroppings of igneous rocks, whereas the City of Tracy and the surrounding area is located on sedimentary soils. The region around Site 300 has elevated levels of naturally occurring uranium, and this accounts for the difference between historically measured external gamma radiation between Site 300 and the City of Tracy. The more recently selected off-site monitoring locations, found on a geological substrate more comparable to that at Site 300, are used to evaluate the potential for local, LLNL-induced exposures.

11.3.3 State of California Co-Monitoring

Currently, the California Department of Health Services (DHS), Radiological Health Branch, co-monitors direct gamma radiation using their own TLDs at nine LLNL monitoring locations;

this co-monitoring effort began in 1987. These radiation dosimeters are also collected and read on a quarterly basis. Historically, data from the State dosimeters have been in good agreement with data from LLNL TLDs.

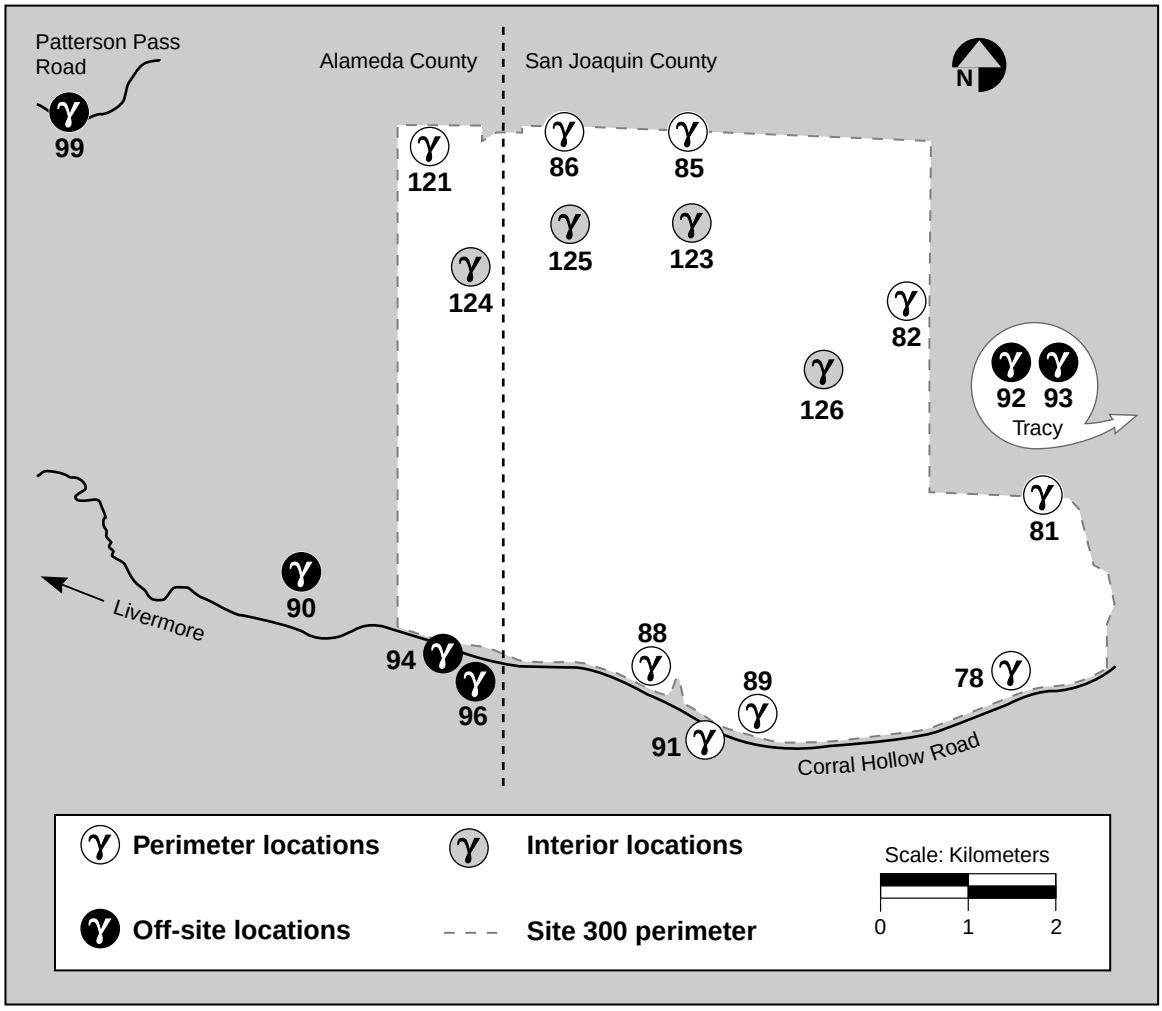

Figure 11-3. Gamma dosimeter locations, Site 300 and vicinity

11.4 Procedures for Laboratory Analysis

TLDs are read and annealed by the LLNL Hazards Control Department, Personnel Dosimetry Group. Calibration of the TLD reader is performed by the Hazards Control Standards and Calibration Laboratory using standards traceable to National Institute of Standards and Technology (NIST). Data are electronically reported to the TAMM environmental analyst. The environmental analyst is responsible for calculating the gamma exposure on the TLDs, ensuring that the data are corrected to a 90-day standard quarter, performing quality control checks, and

reporting the data in the annual Environmental Report. See procedure EMP-TLD-CALC, *TLD Calculation*, for details on analytical laboratory and calculation methods.

11.4.1 Calibration

Each quarter, when environmental TLDs are read, the Panasonic TLD reader used by the Personnel Dosimetry Group is calibrated. A batch of annealed TLDs slated for calibration usage is stored for the first half of the quarter in a zip-locked plastic bag in a lead container, on-site and outdoors. The lead container protects the calibration TLDs from natural terrestrial and cosmic background radiation while allowing them to be subjected to the same environmental conditions as those being used for monitoring. At mid-quarter, of the 12 calibration TLDs, 6 are irradiated to 100 mR exposures while 6 of the "zero" or "background" TLDs are exposed only to "natural" dose. The calibration TLDs are then returned to the lead container until the quarter's end when all TLDs recovered from the field plus the calibration TLDs in the lead shielded container are returned to LLNL's Personnel Dosimetry group for reading. See procedure EMP-R-SCA, *External Environmental Radiation Monitoring and Calibration*, for details on the calibration of the Panasonic reader and the reading of the TLDs.

11.4.2 TLD Data Analysis

The TLDs measure environmental gamma radiation exposure in milliroentgens. The measured exposure is converted to dose by using a correction factor to determine the absorbed dose and by applying a quality factor to determine the dose equivalent. A quality factor of one (1) is applied for gamma radiation, and the dose equivalent in rem (or mrem) is obtained from the absorbed dose in rads.

All measured doses at the Livermore-site boundary are compared to both recent and historical background measurements to determine the contribution, if any, from LLNL operations. All data are reported as total doses (EDE in mrem), including those from both background and LLNL sources.

When a TLD is missing, the annual dose is calculated as four times the average quarterly dose determined from available data. TLDs that are wet, damaged, or found on the ground are not accepted for use in monitoring. The analyst indicates which TLDs were reported as missing or damaged in the data tables for the annual *Environmental Report* (e.g., Biermann et al. 2001).

Summary statistics, accuracy and precision of analytical results are reported using means, range, variance, standard deviation and/or confidence intervals as stated in guidance document ORAD-QA-D, *Data Analysis* (see Chapter 12).

11.5 Quality Assurance Requirements

To ensure that appropriate analytical methods and TLD holding times are being used, the TAMM analyst examines results from blanks and spikes of known exposures by comparing the reported data to the known exposures. Each quarter, a set of quality control (QC) TLDs are irradiated with known exposures ("spikes"); some of the QC TLDs remain unexposed and therefore serve as "blanks." Although handled in a similar manner, these QC TLDs should not be confused with the calibration TLDs described in **Section 11.4.1**. Like the calibration TLDs, the QC TLDs are stored in a lead container, subjected at mid-quarter to known exposures, returned to the lead container, and submitted for analysis at the end of quarter along with the environmental monitoring and calibration TLDs. However, unlike the calibration TLDs, members of the Personnel Dosimetry Group do not know which of the submitted TLDs are the QC TLDs nor do they know the exposures. The average value of the QC TLD readings must fall within ±20% of the "true" TLD exposure value (Graham and Trombino 1997).

The Personnel Dosimetry Group participates in the DOE Laboratory Accreditation Program (DOELAP) every two years and must meet specified interlaboratory comparison performance goals and pass a two-day on-site audit. TAMM participates in the DOE Environmental Measurements Laboratory (EML) Intercomparison Study Program whenever intercomparison tests are offered; TLDs with known exposures are sent to TAMM and are then forwarded on to the Personnel Dosimetry Group for analysis. The analytical results are published, allowing TAMM to evaluate the performance of the Personnel Dosimetry Group in an independent quality check.

Evaluations of the monitoring network are continually performed by the TAMM environmental analyst to ensure that monitoring locations are suitable and comply with applicable regulations. New construction near the direct gamma radiation network may require that a monitoring location be abandoned or moved to a more suitable location.

When deviations from procedures occur, nonconformance reports are completed in accordance with ORAD-QA-NCR, *Nonconformance Reporting and Tracking*. Sampling and analysis procedures are reviewed annually to determine whether the procedures are up-to-date and being performed correctly.

As stated in **Section 11.3.3**, the California Department of Health Services (DHS) co-monitors at 9 of the LLNL monitoring locations. According to the DHS personnel, the DHS dosimeters consist of four individual elements of calcium sulfate dysprosium-doped powder, wrapped with a cadmium foil to provide linear energy response, and assembled into a single package. The material is annealed together and subsequently read simultaneously. Control packets are used to determine transit exposure. Selected packages are exposed within the NIST calibration range in Sacramento, CA, for quality control purposes. The gross exposures received by the

dosimeters are determined by the Radiation Detection Company, Sunnyvale, CA, and are reported to DHS Radiological Health Branch. LLNL is in contact with DHS regarding the co-monitoring program and its data.

11.6 Program Implementation Procedures

The procedure EMP-R-L, *Radiation Monitoring Locations*, has been replaced with the Locations Database. The Locations Database is a Filemaker Pro database containing information about past and present sampling locations. It includes directions to the sampling location, the environmental medium sampled at the location, safety concerns, and other pertinent information. EMP-QAS-LOC, Locations Database SOP Supplement, describes the process to be used for defining, documenting, and approving sampling locations.

11.7 Action Levels

Action levels for environmental TLDs are now derived by calculating a four-year average with the error limited to plus or minus three standard deviations of all combined locations on a quarterly basis. Measurements that fall outside the action level range are investigated. LLNL management is notified if the unusual measurement cannot be attributed to sampling variability or errors in analytical methodology. The quarterly action level for all TLD locations is set to the quarterly 4-yr mean $\pm 3\ \sigma$. These calculated quarterly ranges are as follows:

- 1st Quarter: 0.145 ± 0.061 (mSv)
- 2nd Quarter: 0.152 ± 0.070 (mSv)
- 3rd Quarter: 0.155 ± 0.070 (mSv)
- 4th Quarter: 0.154 ± 0.077 (mSv)

Due to seasonal effects, the measured data tends to be higher in dry quarters. The annual mean of the Livermore Valley is approximately 0.60 mSv. Although the data may be seen to vary terrestrially by soil moisture content and geological constituents that produce higher natural background at some locations, the mean + 3 sigma upper bound tends to account for both terrestrial and cosmic variability. As the overall mean background is represented by the Livermore Valley data at a dose level of 0.60 mSv annual average, a reasonable investigative action level set to 0.23 mSv/quarter/location would remain conservative based upon the public dose limit of 1 mSv/yr above background. The lower bound of 0.08 mSv addresses measurement attributable errors and missing data.

11.8 Preparation and Disposition of Reports

The data from the environmental gamma radiation network are processed, reduced, and reported in the annual *Environmental Report* (e.g., Biermann et al. 2001). No other reporting is required for the direct radiation data. Sampling location maps, descriptions of collection and analytical methods, all data from all monitoring locations, summary statistics, statistical evaluations, comparisons with background radiation levels, trending of data, and discussion of overall environmental impacts are included in the SAER.

11.9 Future Plans

The direct radiation monitoring network is presently being augmented to include the use of active sensors deployed near the perimeter. Ionizing radiation measurements in air will be conducted utilizing a network of Geiger-Mueller counters whereby the processing of data will be done in real-time. It is our aim to utilize this capability as an early warning system in the event of accidental airborne releases that may have deleterious effects to the public and the environment.

11.10 References

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12 Procedures for Laboratory Analysis, Data Management, and Data Analysis

Lucinda M. Clark • James R. Merrigan

12.1 Laboratory Analysis

12.1.1 Regulatory Drivers

Portions of U.S. Department of Energy (DOE) O 414.1A (see WSS B89 in Appendix B) define the requirements for quality assurance (QA). Analytical laboratories that analyze environmental monitoring samples are required to meet the requirements of the *Environmental Protection Department Quality Assurance Management Plan* (QAMP) (Merrigan 2001), which meets the intent of DOE O 414.1A. In addition, laboratories are contractually required to participate in laboratory inter-comparison programs as specified in DOE Order 5400.1, Chapter IV, Paragraph 10c.

12.1.2 Analytical Capabilities

The Lawrence Livermore National Laboratory (LLNL) Environmental Protection Department (EPD) uses both onsite and offsite laboratories to analyze environmental monitoring samples. The majority of samples are analyzed by offsite laboratories operating under blanket service agreements (BSAs) with LLNL. A small percentage of samples are analyzed onsite. This usually occurs when the onsite laboratory is able to provide rapid turnaround times, nonstandard analyses, or lower reporting limits than are available from offsite laboratories.

12.1.2.1 Offsite Analytical Laboratories

The LLNL Procurement and Materiel Department initiates and administers BSAs with offsite analytical laboratories. LLNL technical experts work with a representative of the Procurement Department to develop a statement of work (SOW) that defines the requirements a laboratory must meet in order to be awarded a BSA. Candidate laboratories must demonstrate their ability to meet these requirements both before the award and during the tenure of the BSA. LLNL currently has BSAs with two laboratories that perform non-radiological analyses and three laboratories that perform radiological analyses of environmental monitoring samples.

12.1.2.2 LLNL Onsite Laboratories

LLNL environmental monitoring samples are also analyzed by two onsite organizations: the Environmental Monitoring Radiation Laboratory (EMRL) and the Hazards Control Department (HCD) Safety Programs Division Laboratories.

12.1.2.2.1 Environmental Monitoring Radiation Laboratory. The EMRL consists of personnel matrixed to EPD from the LLNL Chemistry and Materials Science Environmental Services (CES) organization. CES is an integrated sample management and analytical program within the Chemistry and Materials Science (C&MS) Directorate whose mission is to provide high-quality analytical data in support of the environmental monitoring, hazardous waste management, and environmental restoration programs at LLNL. An inter-directorate memorandum of understanding (MOU) defines the responsibilities of CES and EPD and the scope of work for the EMRL. EMRL operates under the CES quality assurance plan and Integrated Safety Management System. EMRL analyzes sewage, groundwater, air filters, silica gel, soil, and vegetation samples for various radioactive isotopes of interest at trace levels.

12.1.2.2.2. Hazards Control Department Safety Programs Division. Three laboratories within the Hazards Control Department (HCD) Safety Programs Division analyze EPD environmental monitoring samples. These laboratories include the Hazards Control Analytical Laboratory (HCAL), the Radiation Measurements Laboratory (RML), and the Personnel Dosimetry Laboratory (PDL). The HCAL analyzes sewer effluent and sludge samples for metals and processes molecular sieves for the air effluent monitoring program. The RML analyzes air filter and sewage samples for gross alpha, gross beta, and tritium, and filters used to collect radionuclides in air effluent as part of the National Emission Standards for Hazardous Air Pollutants (NESHAPs) monitoring program. The PDL issues and analyzes the thermo-luminescent dosimeters (TLDs) for the environmental monitoring radiation program.

12.1.3 Quality Assurance

Laboratories that analyze environmental monitoring samples must maintain a written and implemented quality assurance plan (QAP) that, at a minimum, meets the requirements of DOE O 414.1A, Chg. 1, Attachment 1. In addition, the analytical laboratory must document laboratory processes in approved standard operating procedures (SOPs). The EPD Assurance Manager reserves the right to review and approve each analytical laboratory's QAP and SOPs (including all revisions).

12.1.4 Certification

Analytical laboratories must maintain California Department of Health Services Environmental Laboratory Accreditation Program (CA ELAP) certification for all methods used to analyze EPD environmental samples for which such certification is available. Offsite laboratories that analyze environmental samples for radioactivity must also maintain a certification from the Nuclear Regulatory Commission (NRC) or the appropriate state agency to accept and analyze radio-active samples. Copies of all required certifications must be provided to the EPD Assurance Manager upon request.

The fields of testing for which the primary laboratories used to analyze environmental monitoring samples are certified are shown in **Table 12-1**. The Hazards Control Personnel Dosimetry Laboratory has Department of Energy Laboratory Accreditation Program (DOELAP) accreditation.

Table 12-1. Certified fields of testing for analytical laboratories.

Laboratory	Fields of Testing
Non-radiological offsite analysis	Microbiology of drinking water and wastewater Inorganic chemistry and physical properties of drinking water Analysis of toxic chemical elements in drinking water Organic chemistry of drinking water (GC/MS) Organic chemistry of drinking water (non-GC/MS) Physical properties testing of hazardous waste Inorganic chemistry and toxic chemical elements of hazardous waste Extraction tests of hazardous waste Organic chemistry of hazardous waste (GC/MS) Organic chemistry of hazardous waste (non-GC/MS) Wastewater inorganic chemistry, nutrients and demand Toxic chemical elements in wastewater Organic chemistry of wastewater (GC/MS) Organic chemistry of wastewater (non-GC/MS)
Radiological offsite analysis	Radiochemistry
LLNL Hazards Control	Analysis of toxic chemical elements in drinking water Radiochemistry Toxic chemical elements in wastewater
LLNL EMRL	Radiochemistry

Reference: http://www.dhs.cahwnet.gov/org/ps/ls/elap/elapindex.htm

12.1.5 Performance Requirements

12.1.5.1 Inter-Laboratory Comparison

Analytical laboratories must maintain participation, as applicable, in California- or DOE-approved inter-laboratory comparison programs (or studies) such as the DOE Environmental Measurement Laboratory Quality Assessment Program (QAP), the Mixed Analyte Performance Evaluation Program (MAPEP), or the recently privatized Water Pollution/Water Supply (WP/WS) studies.

12.1.5.2 Internal Quality Control

Analytical laboratories must perform the quality control (QC) analyses listed in **Table 12-2**. If an analytical laboratory desires to use a method for which the QC sample analyses listed in **Table 12-2** are not appropriate, laboratory personnel must notify the EPD Assurance Manager in advance so that appropriate QC sample analyses and reporting requirements can be determined.

Table 12-2. Minimum QC requirements per batch of 20 samples or less

QC Sample Type	QC Failure Corrective Action
Organic Analysis	
Method Blanks	If analytes are detected in the method blank, follow method-specified actions.
Matrix Spikes	If % recovery is outside of control limits, perform method-specific corrective actions.
Matrix Spike Duplicate	If % relative percent difference is outside of control limits perform method-specific corrective actions.
Laboratory Control Samples	If % recovery is outside control limits, reanalyze sample batch.
Surrogates	If % recovery is less than lower acceptance limit, reanalyze sample.
Inorganic Analysis	
Method Blanks	If analytes are detected in the method blank, no analyte detections are acceptable; redigest/reanalyze samples.
Matrix Spikes	If % recovery <30%, perform a post-digestion spike on LLNL samples to check for matrix interferences.
Matrix Spike Duplicate	If % relative percent difference is outside of control limits perform method specific corrective actions.
Laboratory Control Samples	If % recovery is outside control limits, reanalyze sample batch.
Radiological Analysis	
Method Blanks	If analytes are detected above sample minimum detectable activity (MDA) in the method blank, follow method-specified corrective actions.
Matrix Spikes	If % recovery is outside of control limits, perform method specific corrective actions.
Sample Duplicate	If relative percent difference is outside of control limits, perform method-specific corrective actions.
Laboratory Control Samples	If % recovery is outside control limits, reanalyze sample batch.
Tracer Yields	If % recovery is less than lower acceptance limit, reanalyze sample.

12.1.5.3 Analytical Control Limits

Each analytical laboratory must set acceptance or control limits for the applicable QC sample analyses listed in **Table 12-2**. The control limits must be approved by the EPD Assurance Manager. When results from the QC sample analyses specified in **Table 12-2** fall outside of these control limits, the analytical laboratory must perform the applicable corrective actions listed in **Table 12-2**.

12.1.5.4 Method Detection Limit Studies

Each analytical laboratory must perform method detection limit (MDL) studies for each analytical instrument and matrix. MDLs must be updated as required by the approved methodology.

12.1.5.5 Calibration

Each analytical laboratory must perform all calibrations and calibration verifications required by the approved methodology. If the calibrations and calibration verifications do not meet all specified performance requirements, the associated analytical data may be rejected.

12.1.5.6 Performance Evaluation

Periodically, at the discretion of the LLNL Performance Evaluation (PE) Committee, LLNL will provide PE samples to analytical laboratories. Laboratories are required to provide a written explanation addressing any unacceptable PE sample results to the EPD Assurance Manager. The written explanation must include a determination of the root cause, proposed corrective actions, and a corrective action implementation schedule to resolve the problem and prevent its recurrence.

12.1.5.7 Audits and Assessments

Each analytical laboratory must be available for audits by LLNL to verify past performance and current capabilities. The frequency of audits is determined by the EPD Assurance Manager. A minimum of a 24-hour notice will be given before any facility audit. The audit scope will include, but not be limited to QA/QC program, analytical instrumentation (including calibration), sample control (i.e., receipt, storage, tracking, etc.), operating procedures, analytical methods (including QC compliance), document and record management, training, waste management, data validation, and reporting.

12.1.6 Deliverables

12.1.6.1 Quality Assurance Documents

Each analytical laboratory must provide the following documentation to the EPD Assurance Manager upon request:

- Laboratory quality assurance plan (QAP)
- Laboratory standard operating procedures (SOPs)
- Laboratory facility and equipment listings
- Organization chart updates
- Resumes for all relevant personnel shown on the organization chart who are involved with EPD sample analyses
- Copies of Nuclear Regulatory Commission/state license and California certifications as applicable
- Unique laboratory identification codes for each inter-laboratory comparison program in which the analytical laboratory participate
- Hardcopy report of the results of each inter-laboratory comparison study in which the analytical laboratory participates
- Written explanation for any unacceptable results identified by the inter-laboratory comparison study within 30 calendar days of the publication of the results. The explanation must include a determination of the root cause and a schedule of corrective action to be taken to resolve the problem and prevent its recurrence

- Names and telephone numbers of agency contacts for all inter-laboratory comparison program studies, so that EPD can contact them for verification of report accuracy, when required
- Copies of any correspondence sent to a State or Federal inter-laboratory comparison program related to unsatisfactory performance
- Analytical control limits for each analyses performed for EPD
- MDL studies for each analyses performed for EPD
- Previous audit reports and documented corrective actions

12.1.6.2 Analytical Data Deliverables

In order to reduce data entry error, all analytical data deliverables must, to the greatest extent possible, be generated directly from the analytical laboratory's Laboratory Information Management System (LIMS). When hand entry of analytical results or other information is necessary, it must be performed only once, into the analytical laboratory's LIMS.

12.1.6.2.1 Hardcopy Reports. The hardcopy report consists of the original data report mailed or delivered to the Technical Support Group (TSG) Data Management Team within EPD. The hardcopy report includes:

- Case narrative (not provided by Hazards Control laboratories)
- Chain of custody form
- Summary of analytical results
- Summary of QC sample results (not provided by Hazards Control laboratories)
- Invoice (offsite analytical laboratories only)

Case Narrative. The case narrative must include:

- EPD sample identifier(s) from the chain of custody form
- Analytical laboratory sample ID(s) (e.g., log number)
- Analysis requested by EPD for each sample on the chain of custody form and the methodology used
- Indication of whether holding times were exceeded
- Description of any occurrence that may have adversely affected sample integrity or data quality
- Detailed description of all problems encountered during sample handling and analysis and how they could affect the sample results

- Statement that all calibration acceptance criteria were met or explanation of any that were not
- Date of report
- Authorization by lab director or designee for release of data

If the hardcopy report is revised, the case narrative accompanying the revised report must clearly indicate which data were revised, why, and under whose direction.

Chain of Custody Form. A completed chain of custody form is included with all hardcopy reports. The analytical laboratory must supply appropriate and accurate receiving and relinquishing signatures and dates.

Summary of Analytical Results. The summary of analytical results for each sample must include the following.

- Chain of custody form number
- EPD sample identifier(s) from the chain of custody form
- Analytical laboratory sample ID(s) (e.g., log number)
- Sample QC batch number
- Sample collection date as indicated on the chain of custody form
- Date the analytical laboratory received the sample
- Sample matrix
- Date and time of sample extraction, if applicable
- Sample extraction method, if applicable
- Requested analysis code as indicated on the chain of custody form
- Analysis method
- Date and time of analysis
- Analyte name
- Analyte parameter code for each analyte
- Reporting limit flag, a symbol used to indicate whether the analytically determined value is less than the reporting limit
- Analytical uncertainty (error) at two sigma deviation, where applicable
- Calculated value (analytically determined value), where applicable (calculated and negative values should always be reported for radiological analyses)

- Units
- Reporting limit
- ID of the instrument used for analysis
- Analytical chemist's ID
- Data qualifier flags, if any, and their definitions
- California State Certification Number, where applicable
- Any applicable notes or comments
- Dilution or concentration factor of the samples

  When dilutions are performed on EPD samples, the analytical laboratory must report the results from the lowest dilution possible for each analyte. The summary report for each sample may contain the results from different dilutions for different analytes, but only one dilution for each analyte. Results are to be reported to reflect the undiluted sample. EPD reserves the right to request the analysis of samples at specific dilution factors; when this is desired it will be indicated on the chain of custody form.

Summary of QC Sample Results. A summary of QC sample results must be provided for each analysis and must include the following.

- Method blank results and reporting limits
- Surrogate or tracer yield recoveries, when applicable, and corresponding control limits
- Sample duplicate results, when applicable, precision expressed as relative percent difference (RPD), and corresponding control limits
- Matrix spike (MS) and matrix spike duplicate (MSD) results, sample result before spike, spike amount, percent recoveries, RPD, laboratory sample ID for sample used for matrix spikes, and corresponding control limits
- Laboratory control samples (LCS) and when applicable, laboratory control samples duplicate (LCSD) or standards results, percent recovery, and control limits
- QC batch number
- Date and time of analysis
- Instrument ID
- Analyst ID
- Analysis request code

- Analysis method
- Analyte name
- Analyte parameter code
- Units
- Matrix
- Error, where applicable
- Data qualifier flags, if any, and their definitions
- QC sample ID
- Associated EPD samples

12.1.6.2.2. Official Facsimile (Fax) Report. Official fax reports are a copy of the hardcopy report sent via fax to EPD upon request. Official fax reports include all the data elements described in **Section 12.1.6.2.1**. Official fax reports do not replace hardcopy reports.

12.1.6.2.3. Preliminary Results. Preliminary results are available upon request and may be sent by facsimile or by electronic mail. Preliminary results must include chain of custody form documentation and the summary of sample results.

12.1.6.2.4. Electronic Data Deliverables (EDD). Analytical laboratories (with the exception of the Hazards Control laboratories) must deliver electronic versions of hardcopy report to EPD. Data and information in the EDD must exactly match the data and information in the hardcopy report. The format for EDDs is described in documented specifications for transmitting analytical and QA/QC data. Certain specialty analyses whose results do not lend themselves to the specified format may be excluded from the EDD when mutually agreed upon by EPD and the analytical laboratory before analysis is performed. EPD requires weekly EDD transmissions from offsite analytical laboratories.

12.1.6.3 Subcontracting by Offsite Analytical Laboratories

Offsite analytical laboratories may subcontract a limited amount of work to other qualified analytical laboratories. Analyses to be subcontracted must be identified and approved in advance by the EPD Assurance Manager. The following conditions apply to all subcontracted work:

- The analytical laboratory subcontracting the work retains all responsibilities and liabilities defined in the EPD Statement of Work.
- No requirements of the EPD Statement of Work may be waived without prior written permission from EPD.
- The analytical laboratory must pre-qualify any subcontractors at its own expense.

- The analytical laboratory must perform ongoing assessments of the subcontractor at its own expense to assure the quality of the work being performed. These assessments should include at minimum an evaluation of the subcontractor's facility, QAP and SOPs, intercomparison studies, and internal assessments. EPD retains the right to require the analytical laboratory to perform ongoing formal, on-site assessments in certain cases.
- If changes in subcontractor operations are sufficient to possibly alter data quality for EPD samples, the analytical laboratory must notify EPD of the deficiency within 30 days and provide a corrective action plan, schedule, and documented verification that the deficiency is being corrected.
- All final data and associated QC information must be reviewed and verified by the analytical laboratory that subcontracted the work.
- The analytical laboratory that subcontracts the work is responsible for transmitting all deliverables, including the electronic data deliverable.
- All subcontractors must possess current State of California certifications and NRC radioactive material handling certifications, if applicable, for the analyses they perform.
- Subcontractor's facilities must show openness and cooperation during investigations of data anomalies.

12.1.7 Management of Samples and Waste

12.1.7.1 Environmental Sample Activity

The radioactivity level of all environmental samples is below the U.S. Department of Transportation (DOT) level of 2 nCi/g. Radiological analysis of environmental samples must be completed in a low level radiological laboratory with appropriate temporal and spatial segregation of samples, equipment, lab space, and lab glassware to assure the integrity of low level samples.

12.1.7.2 Sample Receipt and Storage

The analytical laboratory must maintain EPD samples in an appropriate storage facility in accordance with Federal and State regulations for sample storage, segregation, and preparation. The analytical laboratory must have a tracking procedure for the receipt, segregation, storage, distribution, and disposal of samples.

12.1.7.3 Sample Retention

The analytical laboratory must retain samples for a minimum of 90 days following receipt, unless the samples are returned to EPD.

12.1.7.4 Disposal of Environmental Sample

The analytical laboratory must properly dispose of all unused portions of environmental samples.

12.1.7.5 Disposal of Generated Waste from Environmental, Hazardous, and Radioactive Sample Analysis

The analytical laboratory is responsible for disposing of waste generated from sample analysis in accordance with appropriate Federal and State guidelines governing the disposal of hazardous and radioactive waste.

12.1.8 Customer Service/Point of Contact (POC)

The LLNL Analytical Contract Management Team (ACMT), chaired by the EPD Assurance Manager, serves as the decision- and policy-making body concerning EPD's interactions with analytical laboratories. Analytical laboratories must submit formal concerns, requests, and queries to the ACMT for consideration and resolution.

EPD also maintains an Analytical Contract Forum that serves as a communication vehicle for the analytical laboratories and EPD users to address logistical and operational concerns, requests, and queries.

EPD has designated analytical points of contact (POCs) to address day-to-day issues with analytical laboratories. Each analytical laboratory assigns and maintains a single individual to be the POC for environmental monitoring samples. The POC is knowledgeable of the analytical needs and requirements of the EPD organization that performs environmental monitoring.

Additionally, the analytical laboratory is expected to:

- Provide amended reports in a timely manner when necessary.
- Notify the EPD POC immediately when internal problems that may have affected previously-reported data are identified.
- Participate cooperatively with EPD in the development of ongoing improvements in sample preservation and survivability during transport to the analytical laboratory.
- Provide ready access to laboratory technical personnel for discussion and resolution of difficulties. Technical personnel should be prepared to disclose fully the analytical details needed to resolve the problem.
- Cooperate in an investigation of potential laboratory problems when warranted.

12.1.9 Sample Transportation

12.1.9.1 Onsite Laboratories

The technologists who collect the samples deliver them directly to onsite laboratory personnel. Each onsite laboratory has protocols and procedures for accepting custody and logging in samples. Laboratories must follow the chain of custody procedure described in EMP-QA-DM, *Sample and Data Management*.

12.1.9.2 Offsite Laboratories Used for Nonradiological Analysis

Offsite laboratories used for nonradiological analysis provide courier service for pickup of samples at LLNL's Livermore main site and Site 300. The courier service picks up samples every LLNL workday at a regularly scheduled time set by EPD. Sample pickup on weekends and holidays is made available upon EPD's request. The analytical laboratory courier service must deliver samples to the analytical laboratory's facility within 4 hours of taking receipt. Laboratories follow the chain of custody form procedure described in EMP-QA-DM, *Sample and Data Management*.

12.1.9.3 Offsite Laboratories Used for Radiological Analyses

EPD ships samples to offsite laboratories used for radiological analyses using a commercial carrier (e.g., Federal Express). The analytical laboratory provides personnel to receive samples on weekends and holidays when notified in advance by EPD. Laboratories follow the chain of custody procedure described in EMP-QA-DM, *Sample and Data Management*.

12.1.9.4 Shipping Containers

Offsite analytical laboratories provide shipping containers including coolers, boxes, and DOT-approved shipping containers to EPD upon request. The analytical laboratory is responsible for cleaning and decontaminating the coolers. All coolers are returned to EPD in a clean, dry, usable condition, free from any visible residue or trash.

12.1.9.5 Packaging Materials

Offsite analytical laboratories provide sample packaging and shipping material upon request. Such materials include custody seals, Ziplock style bags (various sizes), packing material (i.e., bubble wrap, foam rubber, adsorbent materials), and reusable cooling material (i.e., blue ice packs). Shipping materials are provided to EPD in a clean, dry, usable condition.

12.1.9.6 Sample Containers, Labels, and Blank Water

Each analytical laboratory provides EPD with a list of sample containers and sample quantities required to perform each type of laboratory analysis (including applicable quality control samples).

EPD typically orders sample containers, labels, trip blanks, and field blank water from offsite analytical laboratories. Sample containers must be certified Level 1, clean, sterilized, and

processed to meet EPD protocols. Chain of custody documentation must be available for all sample containers. EPD orders bottles with or without acid/base preservatives and with or without waterproof labels affixed. The analytical laboratory provides deionized, analyte-free water for field blanks and trip blanks. Additionally, the analytical laboratory tracks lot numbers of acid/bases used for preservation, sample container lot numbers, as well as the quality of deionized water used for blanks. This information is made available to EPD upon request.

12.1.9.7 Temperature Verification

Analytical laboratories verify sample temperature immediately upon receipt using a certified thermometer that is National Institute of Standards and Technology (NIST)-traceable and checked for accuracy on a regular basis.

12.1.9.8 Sample Condition

Each analytical laboratory reviews and documents the condition of the samples and chain of custody documentation upon receipt. The analytical laboratory notifies the applicable EPD POC immediately of any discrepancies. Discrepancies include but are not limited to sample breakage/leakage, insufficient sample volume, exceeding temperature required for preservation, headspace or bubbles in the samples, documentation inconsistencies, illegible documentation, incomplete documentation, and inappropriate requested analyses. Analysis of samples that exceed preservation or hold time requirements must be authorized by EPD.

12.1.10 Records Retention

All sample and QC hardcopy data are considered QA records and are maintained indefinitely. Offsite laboratories are required by contract to retain all related project information for a minimum of 3 years. After 3 years, the information is turned over to EPD for storage if requested.

12.2 Data Management

Environmental monitoring data are a critical component of the LLNL environmental protection effort. Scientific validity, acceptability, and legal defensibility of the environmental monitoring data depend on careful record keeping and tracking of environmental samples and the corresponding data.

Data management begins with the creation of specific sampling plans for each environmental medium, continues through actual sampling activities to data receipt and review, and concludes with final storage of data and associated documentation.

12.2.1 Sampling Plans

The responsible EPD environmental analyst determines the sampling strategy for each environmental medium. The resultant sampling plan is documented in analyte request sheets, which are updated at least quarterly. Each analyte request sheet lists sample locations, sampling

frequency, analytes, requested analysis codes, laboratories to be used, and QC sample identifiers and locations required for the current quarter. It is prepared by TSG Data Management Team personnel, in cooperation with the environmental analysts, sampling technologists, and the Operations and Regulatory Affairs Division (ORAD) QA Coordinator.

12.2.2 Sample Tracking Documentation

Field sampling technologists collect samples identified in the analyte request sheet. Sampling technologists complete documentation to ensure sample validity and corresponding data acceptability.

12.2.2.1 Sample Identifiers

Each sample has a unique sample identifier. Quality control samples (duplicates and blanks) are given temporary, nonspecific, blind identifiers when they are submitted to analytical laboratories. When data are received from a laboratory, the blind identifiers are decoded to reveal the actual sample locations and/or the QC sample type.

12.2.2.2 Field Tracking Forms

EPD uses field tracking forms (FTFs) to document sample collection information in the field. FTFs contain sample identifiers, sampling locations, requested analyses, QC sample identifiers, the sampling date, the initials of the person who took the sample, the numbers of all associated chain of custody forms, and special instructions. All field notes are entered on FTFs, including flow information, equipment used, field analytical measurements, distance from the permanent marker at the sampling site where applicable, and comments regarding unusual, questionable, or noteworthy events that occurred during sampling.

12.2.2.3 Chain of Custody Forms

At the end of each sampling event, the sampling technologist uses information from the FTF to initiate a chain of custody form. The chain of custody is a five-part, color-coded form used to track samples and data as they progress through the sampling, analysis, and data management process. In addition to information about the samples and the analytical laboratory, it contains the signatures documenting who is responsible for the samples and/or data at each step in the process. The chain of custody form remains with the sample at all times until analyses are complete, and then it accompanies the data through the review and approval process. It is ultimately archived with the hardcopy data.

12.2.4 Sample Custody Tracking

After samples are collected and documentation is generated, the technologist either delivers the samples to an onsite laboratory or arranges to transport them to an offsite laboratory via courier or common carrier. The technologist signs the chain of custody form to relinquish the samples upon delivery.

Analytical laboratory personnel sign the chain of custody form to acknowledge receipt and accept custody of the samples. The laboratory is responsible for tracking the samples in its custody using a system acceptable to EPD. When analysis is completed, laboratory personnel sign the chain of custody form to relinquish custody and return it to EPD with the data.

The TSG Data Management Team receives and date stamps the hardcopy report of the analytical data, decodes any QC identifiers, and distributes copies to the responsible environmental analyst. The analyst reviews the data to determine whether the required analyses have been performed, identifies any unusual values, and flags items requiring immediate response and reporting. If necessary, the analyst requests revised reports or reanalysis. After determining that the data and analytical results are acceptable, the analyst signs the original chain of custody form and returns it to TSG Data Management. TSG Data Management personnel compile a data package consisting of the FTF, the chain of custody form, the original hardcopy report of the analytical data, and any other pertinent information. The completed data package is archived in the TSG Document Retention Center.

12.2.5 Data Storage

12.2.5.1 Hardcopy

A data package is a QA record and is the hardcopy version of all the environmental monitoring data associated with a sampling event. Data packages are filed by sampling quarter and medium and archived indefinitely.

12.2.5.2 Electronic Data Storage

Electronic storage of environmental monitoring data allows immediate comparative evaluations of data as well as easy generation of report tables, graphs, and charts for data review and regulatory compliance reporting.

All routine environmental monitoring, wastewater, and air effluent monitoring data are stored in electronic form within the EPDDATA database using Ingres, a commercially available relational database software package running on a Sun UNIX mainframe computer. Ingres recognizes the Standard Query Language (SQL) for data manipulation but also contains its own forms and reporting tools, allowing efficient, yet secure electronic access to the data. EPD computations support personnel provide system and network support as well as software maintenance and application development related to this database.

Protective controls are built within the Ingres applications to prevent users from making unauthorized changes and access is password-controlled. All environmental analysts have read-only access to the database; TSG Data Management Team personnel are able to update and add records. Automatic verifications and checks are built into the database applications to prevent changes from being made by unauthorized users.

Ingres cleanup routines are run on the database every weeknight, and an optimization/checkpoint routine is run three times weekly. These procedures help ensure the integrity and performance of the database. For security against data loss, *new* information kept on the Sun mainframe is copied or archived daily and weekly (that is, incremental backups); all in information is copied or archived monthly (that is, a full backup). In addition, when needed on a table by table basis, Ingres logs each data entry transaction in a journal providing a tool for tracing problems and recreating data. As a backup, a read-only copy of the database is created twice weekly and stored on a separate computer.

12.2.5.3 Data Retrieval

Data reports can be generated quickly and accurately from the EPDDATA database. Several procedures have been written within Ingres to produce standard formatted reports. The TSG Data Management Team also creates customized reports using front-end software, such as BrioQuery, Ingres Report-Writer, and Excel spreadsheet applications, often providing data files in special formats for direct input into statistical and graphical packages. Other software systems, such as SAS (a statistical analysis tool), are also used to access database records.

12.3 Data Analysis

Data analysis is the act of seeking patterns, trends, and relationships within a set of data in order to gain an understanding of the real-world processes the data represent. Data analysis supports the objectives of the LLNL environmental monitoring effort through:

- Characterization—measuring the environment
- Detection—discovering contamination
- Decision—choosing actions in response to either of the above

12.3.1. Characterization

Examples of characterization include measuring the impact of LLNL operations on the environment, surrounding population, and employees; establishing background concentrations of specific analytes; establishing a well-defined history of the physical, biological and chemical condition of the local environment; quantifying contaminant releases and predicting their distribution; predicting trends; and measuring the performance of emission control systems.

Data analysis methods used for characterization include identifying a statistical distribution to model the data (e.g., normal, lognormal), graphing data as a function of time and location, modeling trends, calculating summary statistics (measures of central tendency and variation, cumulative totals, annual maxima), and using geostatistical methods to assess spatial variation (contour plots, kriging, declustering methods).

12.3.2 Detection

It is essential that any unexpected releases of contaminants to the environment be identified and characterized in a timely manner. In addition, it is important to identify previously undiscovered historical contamination and monitor areas of known contamination for any significant changes.

Data analysis methods used for detection include plotting data as a function of time and performing statistical tests for trends, comparing individual sample results with historical data or established standards, and comparing mean concentrations between different locations (such as upgradient and downgradient).

12.3.3 Decision

Some environmental monitoring data are used to make specific decisions, for example, determining whether a tank of wastewater may be released to the sewer, whether LLNL complies with a permit, and whether there has been a contaminant release. LLNL's environmental monitoring program uses formal statistical tests (such as t-tests and analysis of variance) and comparisons of individual sample results with regulatory, permitted, or internal standards for making such decisions.

Groundwater monitoring at some Site 300 facilities uses a retest procedure in which an initial result exceeding a permit limit is either confirmed or refuted based on the analysis of two confirmation samples. The permit limit, also called a statistical limit, is calculated from historical or upgradient data. Any of several statistical methods is employed, depending on the nature of the available data. Such limits are updated periodically, as new data become available.

When appropriate, environmental analysts base decisions on an evaluation of whether sample results exceed expected natural variation. The use of formal statistical methods in decision-making assures a quantitative, reproducible basis for the decision.

12.3.4 Implementation of Data Analysis

Various factors contribute to the variability of environmental data. These include natural variation with time and location, sample collection, sample handling, sample processing, sample measurement, cross-contamination, and recording. Environmental analysts are expected to be cognizant of these and to consider them when interpreting data.

Environmental analysts use methods that fairly and accurately convey the information present in the data. Timely and appropriate analysis and proper presentation are essential to achieving this goal. Much of the environmental data analysis uses basic methods such as plotting concentration versus time, or the calculation of means, medians, and standard deviations. Analysts use appropriate measures of central tendency and dispersion (e.g., the geometric mean for lognormal data and the arithmetic mean for normally distributed data), or medians instead

of means when nondetections are present. Guidance that is more detailed is given in EMP-QA-D, *Data Analysis*.

Environmental analysts use probability plots and formal statistical tests to examine the distribution of their data. Environmental data are often positively skewed, in which case an asymmetric distribution, such as the lognormal, is a better model than the normal distribution. Some environmental data present special problems for which standard methods of analysis do not exist.

12.3.4.1 Extent and Frequency of Data Analysis

For some monitoring networks, the extent and frequency of data analysis are specified by permit, regulation, or DOE order. When not specified by regulation or permit, the extent and frequency of data analysis are at the analyst's discretion and based on professional judgment, including an assessment of factors such as the potential threat to the environment or the rate of change in contaminant concentration.

12.3.4.2 Data Presentation

Data analyses provide appropriate data summaries, validate and quantify data interpretation, and draw conclusions from complex data sets in environmental monitoring reports.

Nonradiological data that are reported by an analytical laboratory as being below the detection limit are identified in reports with a less-than (<) sign. Radiological data that are reported as being below the minimum detectable activity (MDA) are also presented with a less-than sign. Other radiological data are presented with their associated 2σ counting error. EPD's environmental monitoring standards require that analytical laboratories report an estimate of the radiological activity, even when the estimated value is less than the MDA or less than zero. Such estimates are generally used in the calculation of statistical tests and summary statistics.

12.3.4.3 Outliers

Outliers are unusually extreme (large or small) values within a set of data. Because the environment can have substantial natural variation, data analyses in the environmental monitoring program do not routinely omit outliers. When a suspected outlier is determined to be due to an error, the result is either corrected or omitted. Additional details are given in guidance document EMP-QA-D, *Data Analysis*.

12.3.4.4 Nondetections

Data sets with a small proportion of values reported as being below the limit of detection can generally be analyzed with standard methods without greatly affecting the conclusions. When the number of nondetections is large, standard methods do not produce meaningful results. Environmental monitoring staff have researched the environmental statistics literature and found a variety of methods for analyzing data with nondetections. For example, the method of

maximum likelihood takes into account the percentage of nondetections when estimating the mean and standard deviation. Additional details and references are given in guidance document EMP-QA-D, *Data Analysis*.

12.3.5 Data Analysis Quality Assurance

All environmental monitoring reports, including any data analyses they contain, are reviewed prior to release by individuals other than the author. In reports containing substantial data analysis, the staff statistician is available for the review.

Data analysis software is purchased or licensed from reputable vendors that perform their own internal testing. Comparisons of results from different software packages, using the same data, help verify the software quality. Although not a rigorous check, analysts continually review results for reasonableness using professional judgment. This provides an opportunity to catch gross errors. In addition, software results are from time to time compared with hand calculations and against published solutions to example data sets in statistical textbooks.

12.3.6 Resources for Data Analysis

EPD has provided its environmental analysts with substantial resources for data analysis. The environmental monitoring staff includes a full-time statistician to provide the environmental analysts with a source of data analysis advice and the potential to use specialized or advanced data analysis methods. A variety of software for data analysis and graphics is also available.

12.4 Future Plans

12.4.1 Laboratory Analysis

EPD has been an active participant in DOE's efforts to standardize and consolidate the individual analytical laboratory auditing programs across the DOE Complex. DOE has established three main efforts geared toward meeting this goal; the National Analytical Management Program (NAMP); the NAMP Environmental Management Consolidated Auditing Program (EMCAP); and the Integrated Contractor Purchasing Team (ICPT) effort.

NAMP is a DOE Complex-wide effort to standardize the generation and management of DOE environmental analytical data. EPD has been actively involved in the development NAMP.

The EPD Assurance Manager is a member of the steering committee for the NAMP EMCAP which provides a means for evaluating and qualifying the capabilities and performance of commercial analytical laboratories. EPD will continue to participate in EMCAP audits by providing certified audit personnel, both lead auditors and auditors who are subject matter experts. EPD has used the results of the EMCAP audits of commercial analytical laboratories to verify the quality of their data.

EPD continues to be an active participant in the DOE ICPT effort for developing DOE Complex-wide standardized procurement contractual documentation (e.g., blanket order agreement [BOA]) for environmental analytical services. Currently, EPD is still managing its commercial analytical laboratories through the use of individual procurement contracts but is evaluating the potential use of the ICPT BOAs for the future.

12.4.2 Data Management

EPD plans to investigate the use of sample bar-coding and small field computers for simplified sample tracking. This system could help eliminate data entry errors by automating transfers of sample tracking documentation into the database.

In an effort to continue use of the most cost-effective and appropriate tools, EPD is in the process of migrating the environmental monitoring database from Ingres to Oracle.

12.4.3 Data Analysis

EPD's environmental monitoring program continues to adapt and improve its data analysis capabilities in response to changes in the Laboratory's mission as well as associated regulatory requirements and best management practices.

In cases where permits specify that decisions be made based on single samples, an evaluation of whether this is causing too many incorrect decisions will be made. The outcome of this evaluation will be shared with permitting agencies to provide them with a better understanding of the data LLNL reports.

12.5 References

Merrigan, J. R. (2001) *Environmental Protection Department Quality Assurance Management Plan*, Revision 4, Lawrence Livermore National Laboratory, Livermore, CA (UCRL-AR-146357-Rev. 4).

13 Quality Assurance

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13.1 Regulatory Drivers

U.S. Department of Energy (DOE) Order O 414.1A (see WSS B89 in Appendix B) defines the requirements for quality assurance (QA). Lawrence Livermore National Laboratory (LLNL) conducts environmental monitoring activities in accordance with the *Environmental Protection Department Quality Assurance Management Plan* (QAMP) (Merrigan 2001), which meets the intent of DOE O 414.1A. DOE O 414.1A prescribes a risk-based, graded approach to QA. This process promotes the selective application of QA and management controls based on the risk associated with each activity, maximizing effectiveness and efficiency in resource use.

13.2 Quality Assurance Program

The Operations and Regulatory Affairs Division (ORAD) of the LLNL Environmental Protection Department (EPD) is responsible for environmental monitoring and surveillance, as required by DOE Order 5400.1 (see WSS B93 in Appendix B). The EPD Assurance Manager, who is responsible for managing the department's QA program, reports directly to the Department Head. The ORAD QA Coordinator, who is responsible for ensuring that the EPD QA program is implemented within ORAD, reports directly to the ORAD Division Leader and serves as the ORAD liaison to the EPD Assurance Office, participating in regular meetings with QA staff from the EPD Assurance Office and the other EPD divisions. The QA Coordinator is responsible for identifying and facilitating the correction of quality-related problems within the division and is authorized to bring these problems as far up the QA and management chains as necessary to ensure adequate resolution.

Although the overall responsibility for quality within EPD belongs to the Department Head, the achievement of quality is the responsibility of every person who performs work for the department. EPD management provides tools, training, information, and support; determines quality requirements; and ensures that activities are regularly assessed and continuously improved. EPD personnel are required to meet established quality requirements and encouraged to make recommendations and participate in solutions that lead to continuous quality improvement within the department.

The EPD QA program is defined in the EPD QAMP (Merrigan 2001). The QAMP consists of 10 sections covering the 10 criteria of DOE O 414.1A, Chg 1, Attachment 1. As a part of EPD,

ORAD must carry out its activities in a way that meets the requirements of the QAMP and any subsequent revisions.

13.3 Training and Qualification

The EPD Training Management Plan, which is based on performance-based training principles, governs the EPD Training Program. This plan addresses EPD's training requirements and processes associated with the qualification and requalification of EPD personnel, including documentation and record keeping, self-assessment of the training program, and interfaces between the EPD Training Group and personnel performing work for EPD.

EPD personnel are qualified to perform their assigned job responsibilities. Qualifications are based on knowledge, skills, and experience relevant to the technical; environment, safety, and health (ES&H); and managerial aspects of the assignment. EPD uses position description forms to define position-specific duties and responsibilities. Each position description form describes the prerequisite skill, knowledge, and ability requirements for a given position. These forms are updated annually.

Individual training plans are developed and maintained for all EPD personnel using the Livermore Training Records and Information Network (LTRAIN) database. The training plans address the technical, ES&H and, when appropriate, management training requirements specific to each job assignment.

Ongoing review of EPD personnel's training, skills, knowledge, and abilities is performed as part of the annual EPD performance appraisal process and is documented in employee performance appraisal reports.-

13.4 Quality Improvement

13.4.1 Nonconformance Reporting and Tracking

Nonconformances related to environmental monitoring are managed in a graded manner, depending on their type and severity. When samples are planned but not collected, the sampling technologist notifies the ORAD QA Coordinator and the responsible environmental analyst in writing. Minor problems with analytical laboratories are documented on Analytical Lab Problem Reporting forms, which are delivered to the ORAD QA Coordinator. More serious problems, including repeated laboratory deficiencies that seem to indicate a trend, equipment breakdown, calibration failure, or sampler errors are documented and tracked in a formal nonconformance management system. The ORAD QA Coordinator prepares an annual report for management and the EPD Assurance Manager summarizing all types of nonconformances that occurred during the year.

13.4.2 Self-Assessments

Environmental monitoring activities are subject to ORAD self-assessments at least once every three years. Self-assessments are performed by QA staff, environmental analysts, or sampling technologists. These assessments include reviews of procedures, safety documents, data packages, nonconformance reports, and other documents as well as field visits to determine how closely procedure and safety document requirements are being followed. Observations made during self-assessments are documented in self-assessment reports and tracked to closure.

13.4.3 Employee Participation and Feedback

EPD uses feedback documents and processes to ensure that employee input is integrated into EPD decisions and processes. Feedback documents, such as safety suggestion forms, surveys, and training evaluation forms, are used to communicate employee input to EPD line management. Feedback processes include activity "tailgate" meetings, procedure reviews and read-throughs, Department Head safety breakfasts, performance appraisals, and focus area meetings. Such feedback processes provide mechanisms for employee input to be incorporated into EPD activities.

13.5 Documents and Records

13.5.1 Document Preparation and Change Control

13.5.1.1 Standard Operating Procedures and Instructions

Standard operating procedures (SOPs), SOP supplements, and instructions for environmental monitoring activities are prepared by personnel familiar with the activity, usually the responsible environmental analyst or sampling technologist. Draft documents that impact environmental monitoring activities are subject to peer review by sampling technologists, the sampling technologists' supervisor, and other EPD personnel as appropriate. Following peer review, these documents are reviewed by the QA Coordinator to ensure applicable QA requirements have been included then submitted to the appropriate line manager for approval. Substantive revisions to these documents are subject to the same level of review and concurrence or approval as new documents. Editorial changes can be made with approval from the QA Coordinator.

13.5.1.2 Integration Work Sheets

All integration work sheets (IWSs) that define environmental monitoring activities are entered into the LLNL institutional electronic IWS system. IWSs are approved by the ES&H team

leader(s), the facility point(s) of contact, and the responsible individual, and are authorized by the authorizing individual before work can begin. The IWS review and authorization process is defined in Document 2.2, "Managing ES&H for LLNL Work, of the LLNL *ES&H Manual* (LLNL 2001).

13.5.1.3 Analyte Request Sheets and Field Tracking Forms

Analyte request sheets and field tracking forms that document sampling plans and provide areas for recording field data and observations are prepared and revised as described in EMP-QA-DM, *Sample and Data Management*. Changes to these documents are approved by the responsible environmental analyst. Quarterly Analyte Request Sheets must also be approved by the responsible line manager and the ORAD resource manager to authorize the expenditure of funds for laboratory analysis.

13.5.1.4 Environmental Monitoring Reports

All reports prepared by EPD are subject to review and approval before they are issued. The review is conducted in a graded manner dependent on the type of report and its intended audience. Reviewers can include line management (Group, Division, Department, and/or Directorate), the LLNL Legal Department, facility representatives, and LLNL program representatives. All reports that are distributed off-site must be reviewed and released by the LLNL Technical Information Department (TID).

13.5.2 Document Distribution

13.5.2.1 Standard Operating Procedures and Instructions

Standard operating procedures (SOPs), SOP supplements, and instructions that describe environmental monitoring activities are maintained as electronic portable document format (pdf) files and made available to all EPD staff via a web-based application. The QA Coordinator and the technical coordinator for the sampling technologists also maintain controlled hard copy versions for use by EPD staff. Each time one of these documents is created or updated, the ORAD QA Coordinator sends an electronic mail message to all potential users informing them of the new or revised document and providing instructions for accessing it. The Technical Support Group Leader, who supervises the sampling technologists, is responsible for ensuring that technologists perform read-throughs of applicable sections of new or revised documents before they perform affected work. Personnel are responsible for ensuring that they use the current version of an SOP, SOP supplement, or instruction when performing work.

13.5.2.2 Integration Work Sheets

Electronic IWSs are available to EPD personnel on-line through a direct link that appears on the LLNL ES&H web page. The responsible individual is responsible for ensuring that personnel performing the work defined in an IWS are familiar with the contents of the IWS and are implementing all controls defined in the IWS. For new or significantly revised activities, the responsible individual must conduct a prestart review with personnel who will perform the work.

13.5.2.3 Analyte Request Sheets and Field Tracking Forms

Technical Support Group (TSG) data management personnel prepare and maintain the quarterly analyte request sheets and field tracking forms. Current hardcopy versions of these documents are available from TSG data management personnel and from the technical coordinator for the sampling technologists.

13.5.3 Records Management

13.5.3.1 Environmental Monitoring Data

Environmental monitoring data is compiled into data packages and retained indefinitely in the Technical Support Group Document Retention Center. Data packages are described in more detail in **Section 12.2**.

13.5.3.2 Environmental Monitoring Reports

Environmental monitoring reports are retained as records as specified in LLNL Records Retention Schedules. These schedules were developed by the LLNL Records and Archives Management Group and are based on record schedules approved by the Archivist of the United States and the University of California.

13.5.3.3 Standard Operating Procedures and Instructions

The ORAD QA Coordinator retains original, signed copies of current, superseded, and cancelled SOPs, SOP supplements, and instructions for environmental monitoring activities. These records are maintained indefinitely.

13.5.3.4 Integration Work Sheets

Integration work sheets are retained indefinitely in an electronic database. The LLNL Administrative Information Systems (AIS) Department is responsible for maintenance of the LLNL IWS database.

13.6 Work Processes

13.6.1 Safety Documents, Procedures, and Instructions

ORAD uses SOPs, SOP supplements, and instructions to define environmental monitoring and associated QA activities. Work is authorized using IWSs, which summarize hazards and controls associated with each activity. More detailed descriptions of hazards and controls are provided in operational safety plans (OSPs) for activities that meet the criteria specified in Appendix 2-E of Document 2.2 of the LLNL *ES&H Manua*l. ORAD also uses internal guidance documents to provide general guidance or reference information. Current SOPs, SOP supplements, instructions, IWSs, OSPs, and guidance documents related to environmental monitoring are given in **Tables 13-1** through **13-4**.

13.6.2 Work Authorization

EPD uses the IWS process to ensure that all work activities have been reviewed and authorized. Activities not commonly performed by the public must be formally authorized before work begins. As part of the IWS development process, LLNL ES&H Team workplace evaluations and hazards assessments may be used to determine the appropriate level of safety documentation and identify the need for permits or other documentation. Once hazards have been identified and controls verified to be in place, the IWS is used to document authorization of the work.

13.6.3 Identification and Control of Samples and Data

Samples and data are identified and controlled as described in EMP-QA-DM, *Sample and Data Management*. All sampling events are documented on field tracking forms (FTFs). Samples that are submitted to analytical laboratories for analysis are accompanied by chain of custody forms that are use to track custody of the samples as they move from the sampler to the analytical lab and the data as it moves from the lab to the analytical laboratory and finally to TSG data management personnel for archival. More detailed information regarding sample and data tracking is provided in Chapter 12.

13.6.4 Identification and Control of Procured/Fabricated Items

Procured items, including commercially available or off-the-shelf procured items, are identified by manufacturer's markings. Examples include catalog numbers, batch numbers, heat numbers, lot numbers, serial numbers, and purchase order numbers. Such identifiers are affixed to the item and/or are contained in supporting documentation (i.e., records traceable to the item).

Table 13-1. ORAD SOPs related to environmental monitoring

Code	Title	IWS	OSP
EMP-AE-DAM	Air Effluent Data Analysis and Data Management	n/a	n/a
EMP-AE-MFC	Air Effluent Stack Mass Flow Probe Calibration	588, 731	n/a
EMP-AE-PCM	Air Effluent Periodic Confirmatory Measurements	777	n/a
EMP-AE-SF	Air Effluent Stack Flow Measurement	571, 588, 731	n/a
EMP-AE-SFDR	Air Effluent Stack Flow Data Retrieval	591, 731	n/a
EMP-AE-SFRM	Sampler Air Flow Rate Measurement	571, 588, 731	n/a
EMP-AP-CA	Air Particulate Sampler Calibration	2271	O-252
EMP-AP-LV	Low Volume Radiological Air Particulate Sampling	2271	O-252
EMP-AP-S	Air Particulate Sampling	2271	O-252
EMP-AT-FMC	Air Tritium Electronic Flow Meter Calibration	n/a	n/a
EMP-AT-S	Air Tritium Sampling	2271, 305, 540, 573	O-252
EMP-M-D	Meteorological Data Management and Analysis	n/a	n/a
EMP-M-MCA	Meteorological System Maintenance and Sensor Calibration	562	n/a
EMP-QA-DM	Sample and Data Management	n/a	n/a
EMP-R-SCA	External Environmental Radiation Monitoring and Calibration	2271	O-252
EMP-S-S	Soil and Arroyo Sediment Sampling	2271	O-252
EMP-SW-B196	Sewage Sampling at B196	546	L-92
EMP-SW-C196	Sewage Sampling at C196	546	L-92
EMP-SW-CA	Sewer Equipment Calibrations	546	L-92
EMP-SW-DS	Diversion Facility Tank Sampling	546	L-92
EMP-SW-HCAR	Hazards Control Off-Shift Sewer Alarm Response	546	L-92
EMP-SW-M	Sewer Equipment Maintenance	546	L-92
EMP-TLD-CALC	TLD Calculation	n/a	n/a
EMP-VG-S	Vegetation and Foodstuff Sampling	2271	O-252
EMP-W-S	Water Sampling	2271	O-252
ORAD-QA-IWS	Preparation and Maintenance of ORAD IWSs	n/a	n/a
ORAD-QA-NCR	Nonconformance Reporting and Tracking	n/a	n/a
ORAD-QA-SA	Self Assessments	n/a	n/a
ORAD-QA-SOP	Preparation and Revision of Documents that Define ORAD Operations	n/a	n/a
WGMG-PT-S	Pretreatment Sampling of Rinsewater	567	n/a
WGMG-SW-LWRP	Sewage Sampling at LWRP	546	L-92
WGMG-UT-M	UB193A pH Monitoring Station Maintenance	546	L-92
WGMG-WD-AR	Wastewater Discharge Authorization	n/a	n/a

Table 13-2. ORAD SOP Supplements related to environmental monitoring

Code	Title	IWS	OSP
EMP-HAZ-SUP	Hazards and Controls for Environmental Sampling	Various (see supplement)	Various (see supplement)
EMP-QA-BOT	Aqueous Sample Bottle Requirements	674	n/a
EMP-QAS-COC	Completing Chain of Custody Forms	n/a	n/a
EMP-QAS-FTF	Completing Field Tracking Forms	n/a	n/a
EMP-QAS-LOC	Locations Database SOP Supplement	n/a	n/a
EMP-QAS-SS	Special Sampling	Evaluate each project for need	Evaluate each project for need
EMP-WSS-CT	Cooling Tower Sampling	2271	O-252
EMP-WSS-DRB	LLNL Main Site Drainage Retention Basin Sampling	2271	O-252
EMP-WSS-HEP	Site 300 HE Process Wastewater Discharge Sampling	2271	O-252
EMP-WSS-PPT	Site 300 Photo Process Retention Tank Sampling	2271	O-252
EMP-WSS-RO	Storm Water Runoff Sampling	2271	O-252
EMP-WSS-SWEP	Site 300 Sewage Pond Sampling	546	L-92
EMP-WSS-WSD	Site 300 Water System Discharges Monitoring and Sampling	2271	O-252
ORAD-QAS-RC	Completing ORAD Procedure Review Checklist	n/a	n/a

Specially engineered and fabricated items are assigned unique identification numbers. Unique identifiers are affixed to the item, and/or contained in supporting documentation (i.e., records traceable to the item).

Some EPD procured items are identified and controlled using the LLNL property management process, which assigns unique identifiers (called property numbers) to EPD items with a property value greater than $5000. The LLNL property management process tracks both the item custodian and the item storage location.

13.6.5 Suspect/Counterfeit or Indeterminate Item Identification

EPD has processes in place to ensure that suspect/counterfeit, or indeterminate (SC/I) items are not introduced into EPD activities. As part of the LLNL procurement process, EPD technical release representatives (TRRs) screen EPD procurement documents to ensure that items are not procured from identified SC/I vendors. SC/I management assessments of workplaces are conducted to identify potential SC/I items in the work environment.

Table 13-3. ORAD instructions related to environmental monitoring

Code	Title	IWS	OSP
B193_Inst_01	Routine Inspection and Maintenance Activities	546	L-92
B193_Inst_02	pH Probe Calibration and Servicing	546	L-92
B193_Inst_03	163A and 125C pH Probe Calibration and Sampler Servicing	546	L-92
B193_Inst_04	Weekly Sample Collection, Archiving, and Disposal	546	L-92
B193_Inst_05	ISCO Rapid Transfer Device (RTD) Download to Flowlink	546	L-92
B193_Inst_06	Computer Backup and Monitoring Data Archival	546	L-92
B193_Inst_07	Strip Chart Recorder Maintenance	546	L-92
B193_Inst_08	Sigma Flow Meter Maintenance and Calibration	546	L-92
B193_Inst_09	Oxidation/Reduction Potential (ORP) Probe Calibration and Servicing	546	L-92
B193_Inst_10	Channel Grinder Maintenance	546	L-92
B193_Inst_11	Electroconductivity (EC) Probe Calibration and Servicing	546	L-92
B193_Inst_12	Biennial System Operational Test	546	L-92
B193_Inst_13	Use of Caution and Repair Tags at UB193	546	L-92
B196-AFS-INS	Instructions for Maintenance of the Sewer Analytical Flow System	546	L-92
B196-CAL-FLOW	Enterra Flow Meter Calibration	546	L-92
B196-CAL-GAMX	Gamma-X Energy and Efficiency Calibration	546	L-92
B196-CAL-PH	pH Probe Calibration	546	L-92
B196-CAL-XRFA	X-Ray Fluorescence Calibration	546	L-92
B196-CM-INS	Instruction for Chart Maintenance	546	L-92
B196-GRI-INS	Instruction for Replacing the Sewage Grinder Cutter Cartridge	546	L-92
B196-LND-INS	Instruction for Liquid Nitrogen Level and Detector Maintenance	546	L-92
B196-MAC-INS	Instruction for Servicing the Macerator	546	L-92
B196-MAR-INS	Instruction for Marinelli Beaker Replacement and Servicing	546	L-92
B196-pH-INS	Instruction for pH Probe Servicing	546	L-92
B196-PUMP-INS	Instructions for Booster Pump Maintenance	546	L-92
B196-REFR-INS	Instructions for Cleaning the Composite Sample Refrigerator	546	L-92
B196-SHS-INS	Instruction for Maintaining the Sodium Hypochlorite System	546	L-92
B196-SWM-INS	Instruction for Stilling Well Maintenance	546	L-92
B196-TUBE-INS	Instructions for Replacing the Peristaltic Pump Tubing B196 Composite Sampler/Refrigerator	546	L-92
B196-XRFA-INS	Instruction for Replacement and Servicing of the XRFA Flow Cells	546	L-92
EMP-AP-S, Instruction 1	Weekly Filter Preparation and Documentation	2271	O-252
EMP-AP-S, Instruction 2	Air Filter Exchange	2271	O-252
EMP-AP-S, Instruction 3	Post-Sampling Activities	2271	O-252

(continued)

Table 13-3. ORAD Instructions related to environmental monitoring (continued)

Code	Title	IWS	OSP
EMP-AP-CA Inst 1	Office Setup for Calibration	2271	O-252
EMP-AP-CA Inst 2	Field Temperature Measurement for Hi-Vol Calibration	2271	O-252
EMP-AP-CA Inst 3	Flowrate Calibration	2271	O-252
EMP-AT-S_Inst_1	Air Tritium Pre-Sampling Activities	2271, 305, 540, 573	O-252
EMP-AT-S_Inst_2	Air Tritium Sampling Activities	2271, 305, 540, 573	O-252
EMP-AT-S_Inst_3	Annual Rotameter Calibration Check	2271, 305, 540, 573	O-252
EMP-M-D, Inst. 1	Preparation of Monthly Records of Meteorological Observations for LLNL and Site 300	n/a	n/a
EMP-M-D, Inst. 2	Preparation of Annual Records of Meteorological Observations for LLNL and Site 300	n/a	n/a
EMP-M-D, Inst. 3	Preparation of Graphical Wind Rose	n/a	n/a
EMP-S-S-Inst1	Soil and Sediment Sample Processing Instruction	n/a	n/a

Table 13-4. ORAD guidance documents related to environmental monitoring

Code	Title	IWS	OSP
EMP-NS-S	NESHAPs Report Guidance Document	n/a	n/a
EMP-QA-AER	Site Annual Environmental Report	n/a	n/a
EMP-R-DA	Radiological Dose Assessment Guidance Document	n/a	n/a
ORAD-QA-D	Data Analysis	n/a	n/a

13.6.6 Handling, Storage, and Shipping

Processes used to ensure that environmental monitoring samples are handled, stored, and shipped to prevent damage, loss, or deterioration are defined in EMP-QA-DM, *Sample and Data Management*. Samples are shipped in sealed coolers using either a laboratory courier or a common carrier such as Federal Express. Couriers are prohibited from opening ice chests until they arrive at the analytical laboratories. Samples are preserved according to the requirements of the analytical methodology. Samples waiting for shipment are kept with the sampling technologist or stored in a locked, refrigerated storage space. Chain of custody forms accompany samples at all times and are used to document transfer of custody.

13.6.7 Maintenance and Calibration of Environmental Monitoring Equipment

When identifying and procuring environmental monitoring equipment, EPD line managers must ensure that it is of the proper type, range, accuracy, and tolerance to conform to established performance requirements.

Environmental monitoring equipment used to obtain quantitative data is physically marked with a unique identifier and an LLNL Calibration Program sticker to identify it as part of the Safety, Security, & Environmental Protection Directorate Calibration Program. Environmental monitoring equipment is calibrated, adjusted, and maintained at pre-established intervals, or immediately before and after use. The calibration status of environmental monitoring equipment is identified and tracked in a database. In addition, certificates of conformance, calibration basis documents, calibration results, and the range, precision, and accuracy of each piece of environmental monitoring equipment are kept on file.

Environmental monitoring equipment must be calibrated using equipment and/or standards that are traceable to nationally recognized standards, such as those of the National Institute of Standards and Technology (NIST). If nationally recognized standards are not available, the basis for calibration must be documented and approved by line management.

Before using environmental monitoring equipment, environmental monitoring personnel verify that the calibration status of the equipment is current. If the equipment's calibration has lapsed, it is tagged "not to be used" and segregated pending recalibration.

If equipment is found to be outside of acceptable tolerances during the recalibration process, a documented verification and validation evaluation of data generated from the suspect equipment during the out-of-calibration period is performed to determine the level of effect and significance. Equipment identified as being out of calibration and associated suspect data are documented in nonconformance reports.

EPD line managers ensure that environmental monitoring equipment is handled and stored in such a way as to protect it from adverse conditions that could potentially compromise its calibration status.

13.7 Design Control

EPD items and processes are designed using sound engineering and scientific principles and appropriate standards. Design work, including changes, incorporate appropriate requirements such as general design criteria and design bases.

EPD personnel or groups other than those involved in the original design verify EPD designs for adequacy. Designs are verified, validated, and approval prior to being implemented.

13.8 Procurement

13.8.1 Commercial-Grade Items

EPD personnel select commercial-grade items based on end-user application needs, key performance parameters or specifications, and traceability or certification to standards. Commercial-grade items are identified in procurement documentation by the manufacturer's published product description or identifier. Upon receipt of a commercial-grade item, EPD TRRs use LLNL procurement processes to ensure that damage was not sustained during shipment, the item received was the item ordered, and associated documentation was received and acceptable. EPD end users then inspect or test the item to ensure that it complies with the manufacturer's published safety and performance requirements.

13.8.2 Noncommercial-Grade Items

Procurements of noncommercial-grade items or services are planned as early in the procurement process as possible. The planning process is documented to identify the procurement method to be used and the sequence of procurement actions and their associated milestones.

13.8.2.1 Selection of Suppliers

EPD selects suppliers based on the supplier's capability to provide items or services in accord with the requirements established in procurement documents. Potential suppliers are evaluated by reviewing their history of providing a similar product or service; reviewing their QA documentation and/or other quantitative/qualitative documented information; and/or assessing their facilities, personnel and QA program implementation.

13.8.2.2 Monitoring of Supplier Performance

EPD monitors supplier performance periodically to ensure the ongoing acceptability of services or items they provide. The formality and frequency of supplier monitoring are based on the relative importance, complexity, quantity, and safety function of the procured item or service. Monitoring is accomplished through surveillances, inspections, and document and nonconformance reviews.

13.8.2.3 Acceptance of Procured Items and Services

Noncommercial-grade procured items are inspected upon receipt and evaluated to ensure that they conform to the requirements of the procurement documentation, that required documentation is included, and that the item was not damaged in shipment.

13.8.2.4 Procurement Documents

Supplier-generated noncommercial-grade procurement documents are reviewed and accepted by EPD TRRs, LLNL Procurement Department personnel matrixed to EPD, or subject matter experts in a manner consistent with the requirements of the LLNL Procurement Department.

13.9 Inspection and Acceptance Testing

After receiving the hard copy data from the analytical laboratory, TSG data management personnel verify that all data for samples listed on the chain of custody form are included and decode QC sample identifiers. TSG data management personnel then deliver a copy of the hard copy report to the responsible environmental analyst. The environmental analyst verifies that all necessary information is included and performs an initial review of the data. If the data are unacceptable, the environmental analyst contacts the analytical laboratory and arranges for a reanalysis. If the data are acceptable, the environmental analyst signs and dates the chain of custody form and returns it to TSG data management personnel. TSG data management personnel perform extensive validation testing of the electronic data deliverables that accompany the hard copy reports to ensure that data formatting is correct and that the data in the electronic send matches the hardcopy report. When both electronic and hardcopy data are acceptable, TSG data management personnel sign the chain of custody form to indicate acceptance of the associated data.

13.10 Management Assessment

13.10.1 Walkabouts

EPD line managers perform walkabouts to determine the effectiveness of processes and controls, observe work conditions and the work environment, identify workplace issues that could potentially have a negative impact on a deliverable, and obtain feedback from activity personnel concerning potential improvements to an activity or its product. All issues requiring response or resolution that are identified during walkabouts are documented, agreed upon by personnel involved in the walkabout, and tracked to closure.

13.10.2 Self-Assessments

Line manager involvement in self-assessments ensures that activities and operations performed according to EPD documents are being done properly and safely. Self-assessments include a review of the adequacy of hazards and controls.

13.10.3 Prestart Reviews

As part of the IWS process, prestart reviews are conducted for activities not commonly performed by the public before to beginning work. Prestart reviews are conducted in accordance with the requirements of Appendix 2-J in Document 2.2 of the *ES&H Manual*.

13.11 Independent Assessment

13.11.1 Assessments by the EPD Assurance Office

The EPD Assurance Office develops and maintains a schedule for independent assessments of EPD activities. The schedule is flexible and coordinated with ongoing EPD operations. EPD Assurance Office independent assessments are performed in accordance with established procedures, checklists, or assessment templates. Activities are evaluated against specific requirements, criteria, and objectives. Objective evidence is reviewed to ensure that results reflect the goals of the planned activities.

Assessors identify conditions adverse to quality and report conditions requiring corrective action to the responsible line manager. Actions taken to correct the immediate situation and similar conditions, and to prevent a recurrence, are determined by the organization being assessed and initiated as soon as practical. Independent assessment reports are written and corrective actions are reported and tracked in accordance with EPD Assurance Office implementing procedures.

13.11.2 Assessments by Outside Organizations

Many outside organizations conduct independent assessments of environmental monitoring activities. These include:

- LLNL Assurance Review Office (ARO)
- LLNL Office of Audit and Oversight
- Safety, Security, & Environmental Protection Directorate
- Representatives of regulatory agencies

13.12 Future Plans

EPD Assurance Office staff and other EPD quality assurance personnel will perform assessments to determine the current degree of implementation of the *EPD Quality Assurance Management Plan*. The resultant gap analysis will be used to determine and prioritize areas for improvement. The scope of the *EPD Quality Assurance Management Plan* will be expanded to

incorporate management controls from other programs (e.g., Integrated Safety Management System and Conduct of Operations).

13.13 References

Merrigan, J. M. (2001), *Environmental Protection Department Quality Assurance Management Plan*, Lawrence Livermore National Laboratory, Livermore, CA (UCRL-AR-146357-Rev. 4).

LLNL (2001) "Managing ES&H for LLNL Work," Document 2.2, *Environment, Safety, and Health Manual,* Lawrence Livermore National Laboratory, Livermore, CA (UCRL-MA-119618) http://www.llnl.gov/es_and_h/hsm/doc_2.02/doc2-02/html

14 Dose and Risk Assessment

Robert J. Harrach

14.1 Introduction

This chapter describes the methods used to determine potential radiological doses to individuals and populations caused by releases of radionuclides to the environment from Lawrence Livermore National Laboratory (LLNL), and cites the federal regulations and standards that govern these emissions. LLNL determines the degree of public exposure from a combination of computer modeling and physical measurements, including the environmental surveillance and effluent monitoring efforts described in Chapters 3 through 11.

14.2 Radiation Protection Standards

The release of radionuclides and the resultant radiological impact to the public from operations at LLNL are regulated by both the U.S. Department of Energy (DOE) and the U.S. Environmental Protection Agency (EPA).

14.2.1 DOE Radiation Protection Standards

DOE environmental radiation protection standards are defined in DOE Order 5400.5, Chg. 2, Chapter II, Paragraph 1 (except 1.a.3.c and 1.c.), and Paragraph 6 (see WSS B94 in Appendix B). The standards for controlling exposures to the public from operations at DOE facilities are based on recommendations by the International Commission on Radiation Protection and Measurements (ICRP 1977, 1980).

The primary DOE radiation standards[1] for protection of the public are:

- 1 mSv/y (100 mrem/y) effective dose equivalent (EDE) for prolonged exposure of a maximally exposed individual (MEI) in an uncontrolled area.
- 5 mSv/y (500 mrem/y) EDE for occasional exposure of this individual.

These dose limits include consideration of releases of radiation to all media (air, surface water, groundwater, soil, etc.) and include all exposure modes for members of the public. EDEs take

[1] Doses are commonly expressed in units of millirem per year (mrem/y), millisievert per year (mSv/y), or microsievert per year (μSv/y), where 1 mrem = 0.01 mSv = 10 μSv. A glossary of radiological terms, such as EDE and MEI, and units is provided in Section 14.10.

into account nonuniform irradiation of the body via different pathways of exposure, as well as varying sensitivity of different organs to different kinds of radiation. These limits pertain to the sum of the EDE from external radiation and the committed 50-year EDE from radioactive materials ingested or inhaled during a particular year that may remain in the body for many years.

The concentrations of radionuclides that can be inhaled or ingested annually without exceeding the DOE primary radiation protection standard for the public are specified in DOE Order 5400.5 Chg. 2, Chapter III, (see WSS B95 in Appendix B). DOE Order 5400.5 stipulates that DOE facilities should have the capabilities, consistent with the types of operations conducted, to monitor routine and non-routine releases and to assess doses to members of the public.

14.2.2 EPA Radiation Protection Standards

EPA regulates radionuclide emissions to the atmosphere from DOE facilities under the authority of Section 112 of the Clean Air Act. Standards for public exposure to airborne radioisotopes (other than radon) released by DOE facilities are set by Subpart H of the *National Emission Standards for Hazardous Air Pollutants (NESHAPs),* under Code of Federal Regulations (CFR), Title 40, Part 61.90-61.97 (see WSS A12 in Appendix B). (Radon is regulated by Subparts Q and T of CFR, Title 40, Part 61.) NESHAPs implements the dosimetry method recommended by the ICRP in its Publication 26 (ICRP 1977).

EPA's radiation dose standard stipulates that radiological releases to air from DOE activities shall not cause members of the public to receive an EDE greater than 100 μSv (10 mrem) in a year, taking into account all exposure pathways (inhalation, ingestion, dermal absorption, etc.) from these air releases. In addition, EPA regulates the potential emissions (calculated without taking credit for emission-abatement devices that may be present) from any single release point. If the potential emissions would produce an annual dose to the public MEI exceeding 1 μSv (0.1 mrem), then continuous monitoring of the release point is required. EPA regulations not only specify the allowed levels but also define the approved methods by which airborne emissions and their impacts must be evaluated and controlled.

14.3 Preparation and Disposition of Reports

All DOE facilities are required by DOE O 231.1, Paragraph 5.d.2, (see WSS B92 in Appendix B) to prepare an annual environmental report for the site. The report covers activities of the previous calendar year involving releases to all media via all pathways. LLNL presents its annual report, called the site annual environmental report (SAER), to the DOE Operations Office in Oakland, California (DOE-OAK), from which it is distributed to appropriate program senior officials, the Office of Scientific and Technical Information, EPA, and other agencies and organizations, as

appropriate. LLNL SAERs are available for the years 1971 through 2000; the most recent, Biermann et al. (2001), covers activities in 2000. In addition to hardcopy availability, the present and six previous SAERs are accessible on the Internet at http://www.llnl.gov/saer.

Because DOE facilities are subject to EPA's regulatory requirements, in particular 40 CFR Part 61, Subpart H, they also must submit an annual report to EPA to demonstrate compliance with radiological-NESHAPs requirements (addressing radiological releases to air). LLNL NESHAPs annual reports are available for the years 1991 through 2000, along with seven quarterly NESHAPs reports covering the last quarter of 1991 through the second quarter of 1993. The most recent is the *LLNL NESHAPs 2000 Annual Report* (Gallegos et al. 2001); the content and character of these reports is described in EMP-NS-S, *NESHAPs Report Guidance Document* (Gallegos 2000).

Notification of "environmental occurrences" that resulted in releases of hazardous materials, including but not limited to radionuclides, from both routine operations and unplanned releases, is required under a number of environmental laws, regulations, and several DOE orders. Documentation of unplanned releases, for example, is required by the "unusual occurrence" reporting requirements of DOE O 232.1A, Attachment 1 (see WSS B183 in Appendix B). Each SAER documents that year's environmental occurrences in its "Compliance Summary" chapter (for example, see Chapter 2 in Biermann et al. 2001). Unplanned releases of radioactive material are described annually in both the SAER and the NESHAPs Annual Report.

Beyond these periodic reporting requirements, DOE O 414.1, Attachment 1, (see WSS B89 in Appendix B), requires that comprehensive and detailed information on LLNL's dose and risk assessment activities be documented as part of a quality assurance (QA) program. The document EMP-R-DA, *Radiological Dose Assessment Guidance Document* (Harrach 1998), meets this requirement and provides a level of detail and emphasis that complements the annual reports.

14.4 Responsibility for Compliance Demonstrations

The Environmental Protection Department (EPD) is the lead organization for environmental support to Laboratory programs. EPD's Operations and Regulatory Affairs Division (ORAD) is responsible for assessing and reporting on the compliance of LLNL operations with environmental laws and regulations through environmental data acquisition and analyses necessary to assess LLNL's releases of radioactivity and public dose impacts.

Ultimate responsibility for conducting operations in a manner that complies with all environmental laws and regulations lies with the Laboratory programs.

14.5 Evaluation of Doses

Physical measurements and computer modeling calculations are both important in the determination of the radiation exposure of the public resulting from LLNL activities. As described in Chapters 3 through 11, the measurements include surveillance monitoring of airborne gases and particles; monitoring of stack air and sewer water effluent; sampling of soil, surface water, groundwater, storm water, vegetation, and food products; and monitoring of direct penetrating radiation.

Public doses from LLNL operations almost exclusively arise from releases of radionuclides to air during routine operations and as a result of accidents. Radionuclides that leave LLNL via the water pathway are not directly consumed (ingested or inhaled) by any public individual, and, therefore, do not represent a direct pathway for radiation exposure of the public. All of the principal exposure pathways are taken into account in analyses of air releases:

- Internal exposures via inhalation of air, dermal absorption, and ingestion of foodstuffs and drinking water
- External exposures by irradiation from contaminated ground and immersion in contaminated air

It is difficult to ascertain, by physical measurements alone, the public exposure to radiation caused by LLNL operations, because the amounts of LLNL-generated radioactive material dispersed into the atmosphere cause very small levels of exposure compared to those due to sources in the natural environment. Furthermore, DOE and EPA want to assure that data developed to demonstrate compliance with applicable standards and requirements are correct and representative. DOE and EPA therefore sanction the use of computer codes that implement the agencies' approved dispersion and dosimetry models and mandate that these codes be used to calculate potential doses to the public from both routine and unplanned releases.

LLNL's primary calculational tool for estimating dose and risk from routine operations is the computer code CAP88-PC, developed by EPA's Office of Radiation Programs under an interagency agreement between DOE and EPA. CAP88-PC is briefly described in **Section 14.7** and more thoroughly in the *User's Guide for CAP88-PC* (Parks 1992) and in the guidance document EMP-R-DA (Harrach 1998). The code computes dose and risk to both individuals and collective populations from chronic or long-term radiological emissions to air. Other air-dispersion modeling codes are used at LLNL as needed to address unplanned releases or short-term releases from experiments or operations.

A complementary approach to deriving EDEs using the built-in dosimetry model in CAP88-PC or other EPA-mandated code is to explicitly calculate doses using mathematical formulas from, for example, the U.S. Nuclear Regulatory Commission's Regulatory Guide 1.109 (NRC 1977). This mathematical approach has been used historically at LLNL (preceding the availability of CAP88-PC), and it continues to be used to evaluate annual doses to the public inferred from sampling of local environmental media (air, water, vegetation, and wine). Details are given in Chapter 12 and Appendix A of the 2000 SAER (Biermann et al. 2001) and in EMP-R-DA, *Radiological Dose Assessment Guidance Document* (Harrach 1998).

When probable off-site impacts are assessed, three categories of potential doses are emphasized, as defined below and in **Section 14.10**.

(1) The dose to the "site-wide maximally exposed individual member of the public" (SW-MEI), which combines the effects of all emission points for evaluation under the 100-µSv/y (10-mrem/y) EPA standard.

(2) The maximum dose to any member of the public in any direction due to each emission point on the site, assessed both by taking no credit and full credit for emission abatement devices, such as filters, that may be present in exhaust pathways. The no-credit evaluation determines the need to conduct continuous monitoring of that emission point under the 1-µSv/y (0.1-mrem/y) standard; the full-credit scenario determines the need to obtain EPA approval to start the project.

(3) The collective EDE or population dose to the people residing within 80 km of each of the two LLNL sites, computed by adding the products of individual doses received and the number of people receiving them.

The site-wide maximally exposed individual (SW-MEI) is defined as the hypothetical member of the public at a single, publicly accessible location (where members of the public reside or abide) who receives the greatest LLNL-operations-attributed EDE from all sources. Such public facilities include schools, churches, businesses, and residences. The location of the SW-MEI is sensitive to the frequency distribution of wind speeds and directions in a given year and can change from year to year. At the Livermore site, the SW-MEI has for the past decade been located at the UNCLE Credit Union, about 10 m outside the controlled eastern perimeter of the site. This location lies 948 m from the Tritium Facility (Building 331), in an east-northeast direction (the typical prevailing wind direction). At Site 300, the SW-MEI occupied a new location in 2000 compared to previous years: on the south-central boundary of the site bordering the Carnegie State Vehicular Recreation Area, approximately 3.2 km south-southeast of the firing table at Building 851.

When new projects or proposed changes to existing projects are reviewed for joint compliance with NESHAPs and the National Environmental Policy Act (NEPA), doses in the second category above are a primary concern. The possible environmental issues raised by each proposed activity or project are examined from several different points of view in a process coordinated by LLNL's Environmental Protection Department, including a review and evaluation of potential emissions of radionuclides and air toxics. These requirements are spelled out in Document 31.1, "Air Quality Compliance," of the *Environment, Safety, and Health (ES&H) Manual*, which can be found at the following Internet address:
http://www.llnl.gov/es_and_h/hsm/doc_31.01/doc31-01.html

14.6 Specification of Source Terms in Model Runs

Accurate characterization of emission sources is crucial to credible air-dispersion and dose-assessment modeling and for accurately gauging the impacts of LLNL operations on workers, the public, and the environment. The source term(s) for each emission point or area in the computer modeling calculations is determined by one of three methods: (1) direct monitoring of releases from key exhaust stacks (Chapter 3), (2) a radionuclide usage inventory process, or (3) air surveillance monitoring at selected locations (Chapter 5). Dose assessment modeling runs are then conducted using meteorological data for the year concerned (Chapter 4).

For monitored sources, the continuous sampling data on curies released per unit time for each radionuclide are used directly as model inputs. The number of effluent sampling systems in operation and the facilities containing them vary over time. Typical numbers are 70 to 100 sampling systems distributed over 5 to 10 facilities. The latter generally include the Tritium, Plutonium, and Heavy Elements Facilities (see Chapter 3).

For unmonitored sources, the emission rate is calculated from radiological usage inventories by applying EPA-specified fractions for potential release to air of materials in different physical states. All facilities having a potential to discharge radionuclides to the atmosphere report their radionuclide usage inventories to the Terrestrial and Atmospheric Monitoring and Modeling (TAMM) Group in ORAD, giving the quantity (in curies) and the physical state (solid, liquid, powder, gas) for each radioisotope as well as stack data and information on the type of operation. The facilities update these inventories periodically. Facilities that contribute most significantly to the off-site dose are inventoried annually, while facilities with a potential for only minor radiological releases may reinventory only once every 3 years. For modeling purposes, the inventory quantity (in curies) is multiplied by a state-dependent release fraction to give the potential annual release to air (i.e., the effective emission rate) in accordance with 40 CFR Part 61, Appendix D (CFR 1998). If the material is an unconfined gas, the fraction 1.0 is used; for liquids and powders, 1.0×10^{-3} is used; and for solids, 1.0×10^{-6}. For materials that were encapsulated or sealed for part of the year, or that resided in different facilities over the

course of the year, time weighting factors are introduced to properly account for the release potential. Similarly, new data of the usage-inventory type are obtained each year for all Site 300 explosive experiments as well as for diffuse (extended area, non-stack) sources at both sites, such as open-air waste storage and waste accumulation areas. Data on inventories and descriptions of the diffuse sources can be found in the NESHAPs Annual Reports for 1993 through 2000 (Harrach et al. 1994; Surano et al. 1995; Gallegos et al. 1996; Gallegos and Biermann, 1997; Gallegos et al. 1998; Biermann et al. 1999; Gallegos et al. 2000; Gallegos et al. 2001).

Finally, the emissions from certain difficult-to-characterize sources, such as diffuse sources, sometimes can be inferred from data obtained by continuously monitoring the ambient air for radioactive particles and tritiated water vapor at selected field points in and around the site. This routine air surveillance monitoring program has been particularly useful in registering the magnitude of unplanned releases (e.g., see the section on "Unplanned Releases" in Chapter 12 of Harrach et al. [1998]).

14.7 Modeling Air Dispersion and Doses with the CAP88-PC Code

CAP88-PC uses a modified Gaussian plume equation to estimate the average dispersion of radionuclides released from up to six co-located sources (elevated stacks or uniform area sources). Plume rise can be driven either by momentum or buoyancy, or set to a predetermined level. Flat terrain is assumed; variation in radionuclide concentrations due to complex terrain cannot be modeled by CAP88-PC. Assessments are done for a circular grid with a radius of 80 km or less around a facility, allowing up to 20 user-selected radial distances. Concentrations and doses are sector-averaged for each selected radius. For specifying populations, each element of area in sixteen 22.5-degree compass sectors is bounded above and below by arcs with radii from the set of user-selected distances, and on its sides by radial line segments separating the sectors. Up to 36 radionuclides can be included in a single run, chosen from a total library of 265 radionuclides. CAP88-PC computes results for each of seven different (Pasquill-Gifford) atmospheric stability categories, specified as part of the wind file. The code thus computes, in a single run, dose rates in sixteen 22.5-degree compass sectors for up to 20 radial distances extending as far as 80 km from the radionuclide release point, for a steady emission comprised by up to 36 different radionuclides, for the distribution of wind speeds, directions, and atmospheric stabilities appropriate to the site for the year concerned.

The mathematical models and explicit equations used in CAP88-PC are described in Chapter 8 of Parks (1992) under the major headings of "Environmental Transport" and "Dose and Risk Estimates." The differences between CAP88-PC and earlier similar codes are discussed in Appendix E of Parks (1992).

A modified version of CAP88-PC that incorporates an improved treatment of doses from releases of tritium was developed at LLNL (Peterson and Duckworth 2001). The standard CAP88-PC model treats only the dispersion and dose consequences of the tritiated water vapor form of tritium (HTO). The new model distinguishes between releases to air of molecular tritium gas (e.g., HT) and takes into account the effects on dose of conversion of HT to HTO and the conversion of some HTO to organically bound tritium (OBT) in the environment. This new model, called NEWTRIT, was programmed into CAP88-PC and used to generate dose results for comparison with default CAP88-PC model runs. NEWTRIT uses the latest dose coefficients for HT, HTO, and OBT of the International Commission on Radiological Protection (ICRP 1995; 1996). The NEWTRIT model was published in the journal *Health Physics* (Peterson and Davis 2002), and was presented in June 2001 to the EPA and DOE for consideration of its use in regulatory compliance modeling.

14.7.1 Inputs to CAP88-PC

In order to model atmospheric dispersion and estimate public radiation dose with CAP88-PC, site-specific data for a variety of parameters are required. These data define the emission sources (discussed in **Section 14.6**), meteorological conditions (see Chapter 4), local agricultural characteristics and land use, and distribution of population surrounding the site, with separate data required for the Livermore site and Site 300. Agricultural characterizations of the LLNL sites and discussions of the population-data input files are given in NESHAPs Annual Reports (e.g., Gallegos et al. 2001).

14.7.2 CAP88-PC Output

The CAP88-PC code calculates radionuclide dose rates, concentrations in air, rates of deposition on ground surfaces, concentrations in food, and intake rates to people from ingestion of food produced in the assessment area (using the terrestrial food chain models in the NRC Regulatory Guide 1.109 [NRC 1977]). Summaries of calculated exposures and risks are broken down by organ, pathway, and radionuclide.

14.8 Radiological Doses from LLNL Operations

The calculated EDE to the site-wide maximally exposed individual member of the public is reported annually to DOE in the SAER (e.g., Biermann et al. 2001) and to EPA and DOE in the LLNL NESHAPs Annual Reports (e.g., Gallegos et al. 2001), treating the Livermore site and Site 300 separately. For both sites, these doses, calculated using primarily the EPA's CAP88-PC code, typically are found to be less than 1 percent of EPA's standard of 100 μSv/y (10 mrem/y) and to be several thousand times smaller than doses received from natural background radiation.

Population doses, or collective EDEs, are also presented in these reports, incorporating the population data mentioned in **Section 14.7.1**. Annual population dose levels attributed to operations at the two LLNL sites typically fall in the range 10–100 person-mSv (1–10 person-rem), more than 200,000 times lower than the collective EDE these same populations receive from natural background sources.

14.9 Quality Assurance and Quality Control Programs

Quality assurance (QA) and quality control (QC) efforts associated with LLNL's radiological dose assessments and compliance reporting under NESHAPs are in place at all LLNL facilities having continuous air monitoring systems (see Chapter 3), as well as in the Radiological Measurements Laboratory (RML) and Analytical Laboratory of the Hazards Control Department, and within EPD.

For continuously monitored facilities, integration work sheets, facility safety procedures, safety analysis reports, discipline action plans, NESHAPs Agreements of Roles and Responsibilities (NARRs), and QA manuals address such items as organizational structure, responsibilities for sampling locations, and procedures for monitoring air emissions, as well as procedures to be followed in the event of unplanned releases of radioactive material. For RML, the QA program describes laboratory analysis procedures, precision, accuracy, and completeness objectives, sample tracking procedures, sample handling, QC sampling, and data reporting. Continuously monitored facilities that have NARRs with EPD include the Tritium Facility, Plutonium Facility, and Heavy Elements Facility.

EPD performs QC on all data tables and figures appearing in annual Environmental Reports. TAMM Group in ORAD, which is responsible for NESHAPs compliance, performs QC on model runs and radionuclide usage inventory data in accordance with a quality assurance project plan (Hall and Biermann 2000). TAMM also maintains detailed records of radionuclide usage inventories, environmental measurements, model runs and other calculations.

14.10 Glossary

Absorbed dose: The amount of energy imparted to matter by ionizing radiation per unit mass of irradiated material. The absorbed dose is expressed in units of rad or gray (l rad = 0.01 gray = 0.01 joule per kilogram).

Becquerel (Bq): The Système International (SI) unit of activity of a radionuclide, equal to the activity of a radionuclide having one spontaneous nuclear transition per second.

Collective dose equivalent and collective effective dose equivalent: The sums of the dose equivalents or effective dose equivalents to all individuals in an exposed population within 80 km (50 miles) of the radiation source. These are evaluated by multiplying the dose received by an individual

at each location by the number of individuals receiving that dose, and summing over all such products for locations within 80 km of the source. They are expressed in units of person-rem or person-sievert. The collective EDE is also referred to as the "population dose."

Committed dose equivalent: The predicted total dose equivalent to a tissue or organ over a 50-year period after an intake of a radionuclide into the body. It does not include contributions from external dose. Committed dose equivalent is expressed in units of rem or sievert (100 rem = 1 sievert).

Committed effective dose equivalent: The sum of the committed dose equivalents to various tissues in the body, each multiplied by an appropriate weighting factor representing the relative vulnerability of different parts of the body to radiation. Committed effective dose equivalent is expressed in units of rem or sievert (100 rem = 1 sievert).

Curie (Ci): A unit of measurement of radioactivity, defined as the amount of radioactive material in which the decay rate is 37 billion disintegrations per second; 1 curie is approximately equal to the decay rate of 1 gram of pure radium.

Dose commitment: The dose which an organ or tissue would receive during a specified period of time (e.g., 50 or 70 years) as a result of a year's intake of one or more radionuclides.

Dose equivalent: The product of absorbed dose in tissue and a quality factor representing the relative damage caused to living tissue by different kinds of radiation, and perhaps other modifying factors representing the distribution of radiation, etc. Dose equivalent is expressed in units of rem or sievert (100 rem = 1 sievert).

Effective dose equivalent (EDE): An estimate of the total risk of potential effects from radiation exposure. It is the summation of the products of the dose equivalent and weighting factor for each tissue. The weighting factor is the decimal fraction of the risk arising from irradiation of a selected tissue to the total risk when the whole body is irradiated uniformly to the same dose equivalent. These factors permit dose equivalents from nonuniform exposure of the body to be expressed in terms of an effective dose equivalent that is numerically equal to the dose from a uniform exposure of the whole body that entails the same risk as the internal exposure. For our use, the effective dose equivalent includes the committed effective dose equivalent from internal deposition of radionuclides and the effective dose equivalent due to penetrating radiation from sources external to the body (i.e., EDE is taken to be the sum of the committed EDE from internal deposition and the EDE from external penetrating radiation received during one calendar year). EDE is expressed in units of rem or sievert (100 rem = 1 sievert).

Maximally exposed individual (MEI): The maximally exposed individual is a hypothetical member of the public at a fixed location who, over an entire year, receives the maximum effective dose equivalent (summed over all pathways) from a given source of radionuclide releases to air. Generally, the MEI is different for each source at a site.

Quality factor: The factor by which the absorbed dose is multiplied to obtain a quantity that expresses (on a common scale for all ionizing radiation) the biological damage to exposed persons. Quality factor is used because some types of radiation, such as alpha particles, are biologically more damaging than others. Quality factors for alpha, beta, and gamma radiation are in the ratio 20:1:1.

Rad: The unit of absorbed dose. It is the quantity of energy imparted by ionizing radiation to a unit mass of matter, such as tissue; 1 rad = 0.01 joules per kilogram.

Rem: A unit of radiation dose equivalent and effective dose equivalent, describing the effectiveness of a type of radiation to produce biological effects, coined from the phrase "roentgen equivalent man." It is the product of the absorbed dose (rad), a quality factor (Q), a distribution factor, and other necessary modifying factors; 1 rem = 0.01 sievert.

Roentgen: A unit of measurement used to express radiation exposure in terms of the amount of ionization produced in a volume of air.

Sievert (Sv): The SI unit of radiation dose equivalent and effective dose equivalent. This is the product of the absorbed dose, quality factor, distribution factor, and other necessary modifying factors; 1 sievert = 100 rem.

Site-wide maximally exposed individual (SW-MEI): The site-wide maximally exposed individual member of the public is defined as the hypothetical person who receives, at the location of a publicly accessible facility (such as a church, school, business, or residence), the greatest LLNL-induced effective dose equivalent (summed over all pathways) from all sources of radionuclide releases to air at a site. The SW-MEI dose sums the contributions of all stack and diffuse area sources. The hypothetical person is assumed to reside at the specified location 24 hours per day, 365 days per year, continuously breathing air having the ground-level radionuclide concentration, and consuming a specified fraction of food and drinking water that is affected by the releases of radioactivity from the site. Thus, the SW-MEI dose is not received by any actual individual and is used as a health-conservative estimate (i.e., over-estimate) of the highest possible dose to any member of the public.

Weighting factor: A value used to calculate dose equivalents. It is tissue-specific, representing the fraction of the total health risk resulting from uniform, whole-body irradiation that could be contributed to that particular tissue.

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Appendix A. Acronyms

1,1,1-TCA	1,1,1-trichloroethane
1,1-DCA	1,1-dichloroethane
1,1-DCE	1,1-dichloroethene
1,2-DCA	1,2-dichloroethane
1,2-DCE	1,2-dichloroethene
ACMT	Analytical contract management team
AF	Air filter
ALARA	As low as reasonably achievable
ALP	Arroyo Las Positas
ANOVA	Analysis of variance
ANSI	American National Standards Institute
ARAC	Atmospheric Release Advisory Capability
ARAR	Appropriate, relevant, and applicable requirement
ARO	Assurance Review Office
ASTM	American Society for Testing and Materials
ATA	Advanced Test Accelerator
ATSDR	Agency for Toxic Substances and Disease Registry
BAAQMD	Bay Area Air Quality Management District
BAT	Best available technology
BMP	Best management practice
BOA	Blanket order agreement
BOD	Biochemical oxygen demand
BSA	Blanket Service Agreement
BTEX	Sum of benzene, ethylbenzene, toluene, and xylene isomers
C&MS	Chemistry & Materials Science (Directorate)
CAELAP	California Department of Health Services Environmental Laboratory Accreditation Program

	Accreditation Program
Cal-EPA	California Environmental Protection Agency
CAM	Continuous air monitors
CC	Control chart
CCR	California Code of Regulations
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CES	Chemistry & Materials Science Environmental Services Laboratory
CFF	Contained Firing Facility
CFR	Code of Federal Regulations
cis-1,2-DCE	*cis*-1,2-dichloroethane
COC	Constituent of concern
CoC	Chain of custody
COD	Chemical oxygen demand
CRWQCB	California Regional Water Quality Control Board
CVRWQCB	Central Valley Regional Water Quality Control Board
DAP	Discipline Action Plan
DCG	Derived concentration guide
DHS	(California) Department of Health Services
DLM	Designated level methodology
DMSO	Dimethyl sulfoxide
DMT	Data Management Team
DO	Dissolved oxygen
DOE	U.S. Department of Energy
DOE-OAK	U.S. Department of Energy Operations Office, Oakland, California
DOELAP	Department of Energy Laboratory Accreditation Program
DOT	U.S. Department of Transportation
DQO	Data quality objective
DRB	Drainage retention basin
DS	Dosimeter

DTSC	Department of Toxic Substances Control
DWTF	Decontamination and Waste Treatment Facility
EDD	Electronic data deliverables
EDE	Effective dose equivalent
EDO	Environmental Duty Officer
EEG	Environmental Evaluations Group
EIS/EIR	Environmental Impact Statement and Environmental Impact Report
ELAP	Environmental Laboratory Accreditation Program
EMCAP	Environmental Management Consolidated Auditing Program
EML	Environmental Monitoring Laboratory
EMP	Environmental Monitoring Plan
EMRL	Environmental Monitoring Radiation Laboratory
EMT	Emergency Management Team
EOG	Environmental Operations Group
EPA	(U.S.) Environmental Protection Agency
EPD	Environmental Protection Department
ERD	Environmental Restoration Division
ES&H	Environment, Safety, and Health
EST	Environmental Support Team
EWFA	East and West Firing Area
FFA	Federal Facility Agreement
FSP	Facility safety plan
FTF	Field Tracking Form
FY	Fiscal Year
GC/MS	Gas chromatography/mass spectrometry
GSA	General Services Area (Site 300)
HASL	Health and Safety Laboratory
HCAL	Hazards Control Analytical Laboratory
HCD	Hazards Control Department

HCl	Hydrochloric acid
HE	High explosive
HEPA	High efficiency particulate air (filter)
HSU	Hydrostratrigraphic units
HT	Molecular tritium gas
HTO	Tritiated water
HWCSA	Hazardous waste container storage area
HWM	Hazardous Waste Management (Division)
ICPT	Integrated Contractor Purchasing Team
ICRP	International Commission on Radiological Protection
ID	Identifier
IEEE	Institute of Electrical and Electronics Engineers
IWS	Integration work sheet
LBNL	Lawrence Berkeley National Laboratory
LCD	Liquid crystal display
LCRS	Leachate Collection and Removal System
LCS	Laboratory control sample
LCSD	Laboratory control samples duplicate
LIMS	Laboratory Information Management System
LLNL	Lawrence Livermore National Laboratory
LTRAIN	Livermore Training Records and Information Network
LWRP	Livermore Water Reclamation Plant
MAL	Management action level
MAPEP	Mixed Analyte Performance Evaluation Program
MCL	Maximum contaminant level
MDA	Minimum detectable activity
MDC	Minimum detectible concentration
MDL	Method detection limit
MEI	Maximally exposed individual

MOU	Memorandum of Understanding
MPN	Most probable number of organisms
MRP	Monitoring and Reporting Plan
MS	Matrix spike
MSD	Matrix spike duplicate
MT&E	Measuring and test equipment
NAMP	National Analytical Management Program
NARRs	NESHAPs Agreements of Roles and Responsibilities
NCR	Nonconformance Report
NCRP	National Council on Radiation Protection
NEPA	National Environmental Policy Act
NESHAPs	National Emission Standards for Hazardous Air Pollutants
NGSL	Noble Gas Spectometry Laboratory
NIF	National Ignition Facility
NIST	National Institute for Standards and Technology
NPDES	National Pollutant Discharge Elimination System
NRC	(U.S.) Nuclear Regulatory Commission
NSPS	New source performance standards
NTLF	National Tritium Labeling Facility
NWS	National Weather Service
OBT	Organically bound tritium
ORAD	Operations and Regulatory Affairs Division
OSP	Operational safety plan
OU	Operational unit
PCB	Polychlorinated biphenyl
PCE	Tetrachloroethene
PCMP	Post-closure monitoring plan
PDL	Personnel Dosimeter Laboratory
PE	Performance evaluation

PETN	Pentaerythritol tetranitrate
POC	Point of contact
POTW	Publicly Owned Treatment Works
ppm	Parts per million
PQL	Practical quantitation limit
PRAG	Permits and Regulatory Affairs Group
PT	Pretreatment
QA	Quality Assurance
QAMP	Quality Assurance Management Plan
QAP	Quality Assurance Plan
QAPP	Quality Assurance Project Plan
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RL	Reporting limit
RML	Radiation Measurements Laboratory
RMMA	Radioactive Materials Management Area
RO	Storm water runoff
ROD	Record of decision
RPD	Relative percent difference
RSDR	Retention System Disposition Record
RTAL	Retention Tank Analysis List
RWQCB	Regional Water Quality Control Board
SAER	Site Annual Environmental Report
SAR	Safety analysis report
SARA	Superfund Amendments and Reauthorization Act
SC	Specific conductivity
SC/I	Suspect counterfeit or indeterminate
SDF	Sewer Diversion Facility

SFBRWQCB	San Francisco Bay Regional Water Quality Control Board
SJVUAPCD	San Joaquin Valley Unified Air Pollution Control District
SL	Statistical limit of concentration
SM	Standard Method
SMS	Sewer monitoring station
SNL/CA	Sandia National Laboratories, California
SOP	Standard operating procedure
SOW	Statement of Work
SQL	Standard Query Language
STAR	Sample Tracking and Receiving system (Hazards Control)
STLC	Soluble Threshold Limit Concentration
SW	Sewer water
SW-MEI	Sitewide maximally exposed individual
SWPPP	Storm Water Pollution Prevention Plan
SWRCB	State Water Resources Control Board
T-BOS	Tetra-2-ethylbutylorthosilicate
TAMM	Terrestrial and Atmospheric Monitoring and Modeling (Group)
TATB	2,4,6-trinitro-1,3,5-benzenetriamine
TBD	To be determined
TCE	Trichloroethene
TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total dissolved solids
TID	Technical Information Department
TLD	Thermoluminescent dosimeter
TMDL	Total maximum daily load
TOC	Total organic carbon
TOX	Total organic halides
TRR	Technical Release Representative
TRU	Transuranic

TSG	Technical Support Group
TSS	Total suspended solids
TTO	Total toxic organics
TTU	Transportable Treatment Unit
U.S.	United States
UC	University of California
USC	United States Code
VOC	Volatile organic compound
WAA	Waste Accumulation Area
WDAR	Wastewater Discharge Authorization Record
WDRs	Waste Discharge Requirements
WGMG	Water Guidance and Monitoring Group
WMU	Waste management unit
WP	Water pollution
WS	Water supply
WSS	Work smart standards
XRF	x-ray fluorescence
XRFS	x-ray fluorescence spectroscopy

Appendix B. Environmental Work Smart Standards

Work Smart Standard	Description
A12	40 CFR 61.90-61.97, National Emission Standards for Hazardous Air Pollutants, National Emission Standards for Emissions of Radionuclides Other Than Radon from Department of Energy Facilities - included in 40 CFR 61, National Emission Standards for Hazardous Air Pollutants (WSS No. A24)
A23	40 CFR 60, Standards of Performance for New Stationary Sources
A27	Bay Area Air Quality Management District (BAAQMD) Regulations 1-12, Regulations and permitting requirements
A37	San Joaquin Valley Unified Air Pollution Control District (SJVUAPCD) Regulations Rules 1010-9120, Regulations and Permitting Requirements
A130 ??	40 CFR 264, Standards for Owners and Operators of Hazardous Waste, Treatment, Storage, and Disposal Facilities
A131	40 CFR 265, Interim Status Standards for Owners and Operators of Hazardous Waste Treatment, Storage and Disposal Facilities
B81	ANSI N13.1-1969, Sampling and Monitoring Releases of Airborne Radioactive Substances from the Stacks and Ducts of Nuclear Facilities
B89	DOE O 414.1A, Quality Assurance, Attachment 1, Contractor Requirements Document
B92	DOE O 231.1, Paragraph 5.d.2, Annual Site Environmental reports (requires report on annual basis) - included in DOE O 231.1 Chg. 2, ES&H Reporting, Paragraph 3. Applicability, and Attachment 1, Contractor Requirements Document (WSS No. B182)
B93	DOE O 5400.1 Chapter III, Paragraph 4.a., Groundwater Protection Management Program, and Chapter IV, paragraph 1.a. Requirement for Environmental Monitoring, 3. Preoperational Monitoring of facilities, sites, and opertions, 4. Environmental Monitoring Plan 5. Environmental Monitoring General Requirements, 6. Meteorological Monitoring Requirements and 10c. Laboratory Quality Assessment - included in DOE O 5400.1 Chg. 1, Chapter III, Paragraph 4(a), 4(b), 4(c) and Chapter IV, Paragraph 1(a), 3, 4, 5, 6, and 10(c). (WSS No. B253)

Work Smart Standard	Description
B94	DOE O 5400.5 Chg. 2, Chapter II, Requirements for Radiation Protection of the Public and the Environment, Paragraph 1 (except 1.a.3.c. and 1.c), Public Dose Limits, 2. ALARA, 5. Release of property having residual radioactive material, 6. Demonstration of compliance with the Dose Limits, and 8a, Records
B95	DOE O 5400.5 Chg. 2, Chapter III, Derived Concentration Guides for Air and Water
B180	DOE O 151.1 Chg. 2, Comprehensive Emergency Management System, Paragraph 3. Applicability, and Attachment 1, Contractor Requirements Document
B183	DOE O 232.1A, Occurrence Reporting and Processing of Operations Information, Attachment 1, Contractor Requirements Document (8/1/97)