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**Application of the Environmental Protection Agency's
Data Quality Objective Process to
Environmental Monitoring Quality Control**

Lucinda M. Garcia

November 1995

Lawrence
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Laboratory

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Application of the Environmental Protection Agency's Data Quality Objective Process to Environmental Monitoring Quality Control

**Lucinda M. Garcia
University of San Francisco**

Master of Science Thesis

Manuscript date: November 1995

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ABSTRACT

Application of the Environmental Protection Agency's Data Quality Objective Process to Environmental Monitoring Quality Control

The United States Environmental Protection Agency's (EPA) Data Quality Objectives (DQO) process was applied to two environmental monitoring networks for the purpose of optimizing field quality control sampling to give the highest quality monitoring data with minimal impact on resources. The DQO process, developed primarily to aid in cleanup and restoration activities, is a systematic approach to designing sampling and analysis programs with improved efficiency, cost savings, and measureable and traceable data quality. The two monitoring networks studied had not been subjected to the systematic review and analysis of the DQO process defined by the EPA.

The two monitoring networks studied had relied upon field duplicates or replicates as the main source of field quality control data. Sometimes, both duplicate and routine sample were analyzed by the same analytical laboratory; at other times they were analyzed by different laboratories. This study identified some potential inconsistencies between analytical data and reporting limits from two different laboratories.

Application of the EPA DQO process resulted in recommendations for changes in the field quality control sampling program, allowed new insight into the monitoring data, and raised several issues that should be the subject of further investigation.

Application of the Environmental Protection Agency's Data Quality Objective
Process to Environmental Monitoring Quality Control

This thesis is Written by

Lucinda M. Garcia

The thesis, written under the guidance of the Faculty Advisory Committee and approved by all its members, has been accepted in partial fulfillment of the requirements for the degree of:

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at the
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CHAPTER 1

INTRODUCTION

Background

Lawrence Livermore National Laboratory (LLNL) is a U.S. Department of Energy (DOE) facility operated by the University of California as a national resource of scientific, technical, and engineering capability with a special focus on national security (Gallegos, et al. 1993). As a part of its comprehensive environmental monitoring program, LLNL conducts aquatic monitoring in response to federal, state, and DOE mandates both at its Livermore Site and at its Experimental Test Site (Site 300), located in the Altamont Hills near the city of Tracy. Thousands of aquatic samples are collected and analyzed each year as a part of LLNL compliance and surveillance monitoring programs for rain, storm water runoff, surface water, and ground water. Most of these monitoring programs have been in place for a number of years and the different aqueous media have been well characterized. Contaminant levels in all these media are extremely low and temporal variations are considered to be well known and understood.

When environmental data are to be used to make decisions, it is necessary to understand the uncertainty associated with those data and Data Quality Objectives (DQOs) must be developed based on the end use of the data (USEPA 1987b). The collection and analysis of environmental samples are subject to both systematic and random errors. Bias and precision are the parameters used most often to quantify uncertainty in environmental data, thus assuring that the monitoring data are of acceptable quality (Keith 1991). Bias is the systematic error inherent in a method or caused by some artifact or

idiosyncrasy of the measurement system while precision is the degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specific conditions (Taylor 1987). The information necessary to determine bias and precision of a particular data set is obtained through the use of Quality Control (QC) samples. Data from field QC samples are used to estimate errors that arise during sampling, preservation, storage, and shipment to the laboratory, as well as the total error of the sampling and analysis process. When combined with data from analytical laboratory QC samples, these data allow an estimation of the total uncertainty of the sampling and analysis process.

Data Quality Objectives (DQOs) are qualitative and quantitative statements that clarify the study objective, define the most appropriate types of data, determine the most appropriate conditions from which to collect data, and specify acceptable levels of decision error (USEPA 1993a). In order to ensure that DQOs are determined systematically for projects performed under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), the United States Environmental Protection Agency (USEPA) first published a method for determining DQOs for remedial response activities, in 1987 (USEPA 1987b). Additional guidance documents, which provided revised and expanded processes for defining DQOs, were published in 1993 (USEPA 1993a, 1993b). These guidance documents include minimum guidelines for the types and frequencies of field QC samples.

The LLNL environmental monitoring networks that will be studied in this research are not governed by CERCLA, however, the guidelines for field quality assurance sampling published in the 1987 EPA DQO guidance document (USEPA 1987b) were adopted as goals for field QC sampling for

these networks in 1993. These levels are not always achieved and, in addition, formal DQOs have not been systematically established for these networks, so the adequacy or inadequacy of these goals has not been evaluated. This research will attempt to show that using a formal process to develop DQOs will result in more cost-effective field QC sampling and a better understanding of the quality of the associated monitoring data.

Because water occurs naturally in various forms, and has a variety of uses, it is subject to diverse regulations and regulators; hence, the LLNL aquatic monitoring program is broad and diverse. Some of the regulations governing LLNL aquatic monitoring programs include the Clean Water Act, CERCLA, the Resource Conservation and Recovery Act (RCRA), California State Waste Discharge Requirements (WDRs), National Pollutant Discharge Elimination System (NPDES) Permits, and DOE Orders. LLNL monitors ground water, surface water, water from the LLNL on-site swimming pool, tap water, rain, and storm water runoff. Because the issues related to the development of DQOs will be similar for all aquatic monitoring networks, this study will be limited to two of them: storm water runoff monitoring at the Livermore site and rain monitoring at and around the Livermore site. Rain and storm water runoff monitoring have diverse regulatory requirements and goals and the study of these two networks should give a broad perspective of the effectiveness of formally developed DQOs and the use of QC samples to evaluate attainment of those objectives.

This research represents the first attempt to apply a formal DQOs development process to rain and storm water runoff monitoring at LLNL and the first attempt to evaluate the adequacy of field QC samples that have been collected and analyzed for those networks.

Statement of Research Problem

This thesis research will systematically define the data quality requirements for monitoring of selected parameters in the LLNL rain and storm water runoff to determine the extent to which data of improved quality can be produced without a significant increases in resource requirements.

Subproblem One

The first subproblem will use the first six steps of the United States Environmental Protection Agency's Data Quality Objectives development process to define Data Quality Objectives for selected analytes in the LLNL rain and storm water runoff monitoring networks.

Subproblem Two

The second subproblem will evaluate analytical data for samples collected for the LLNL rain and storm water runoff monitoring networks from 1992 through 1994 and determine whether the field QC samples that were taken during that period can be used to verify that the specified Data Quality Objectives were met.

Subproblem Three

The third subproblem will determine the optimum field Quality Control sampling program required to ensure the specified Data Quality Objectives are met for the LLNL rain and storm water runoff monitoring networks and define the resources required to implement those measures.

Research Hypothesis

The main hypothesis to be evaluated in this study is that use of a systematic method for the design and analysis of field Quality Control samples for the LLNL rain and storm water monitoring programs can result in improved data quality with minimal impact on resources.

Subhypothesis One

The first subhypothesis is that current field QC sampling results for the two monitoring networks that will be studied have not been correlated with Data Quality Objectives.

Subhypothesis Two

The second subhypothesis is that the results of field Quality Control samples for LLNL rain and storm water runoff samples collected from 1992 through 1994 can be used to evaluate the data acquired for those networks against specified Data Quality Objectives.

Subhypothesis Three

The third subhypothesis is that systematic definition of data quality goals for LLNL rain and storm water runoff samples collected from 1992 through 1994 and evaluation of data against those goals will allow LLNL to improve the understanding of the quality of the data being produced without impacting resources required to implement the monitoring.

Assumptions

It is assumed that data collected between January 1, 1992 and December 31, 1994 provide a valid representation of the LLNL rain and storm water runoff monitoring networks.

Quality Control measures used by analytical laboratories are assumed to be adequate and will not be addressed in this study.

Delimitations

The monitoring networks that will be studied are part of an existing monitoring program. The design of these networks, including sampling locations, sampling frequency, sampling methodology, analyses performed, and analytical methodology, will not be subject to change as a part of this research.

Data Quality Objectives for the LLNL rain and storm water runoff monitoring networks will be developed using the DQO process developed by the US EPA (USEPA 1987b, USEPA 1993a, USEPA 1993b).

Data for samples collected prior to January 1, 1992, or after December 31, 1994, will not be included in this study.

Storm water is analyzed for many different analytes. This study will focus on the results of analysis for two metals (copper and zinc), the pesticides that are measured by EPA Method 608 (Aldrin; alpha, beta, delta, and gamma isomers of BHC; Chlordane; Dieldrin; Endosulfan I and II; Endrin; Endrin Aldehyde; Heptachlor; Heptachlor Epoxide; Methoxychlor; p,p'-DDD; p,p'-DDE; p,p'-DDT; and Toxaphene), and tritium in storm water. Copper and zinc were chosen because they are of particular regulatory importance to LLNL, being common pollutants associated with urban runoff and industrial operations. Pesticides were chosen because the storm water monitoring

program was initially created to evaluate the levels of pesticides leaving the LLNL site, because off site farms have the capability of contributing pesticides to storm water runoff influent to LLNL, and because pesticides are still used on site by LLNL. Tritium was chosen because it is the only analyte measured in rain. Looking at tritium levels in both rain and runoff will allow a comparison of the two networks.

Abbreviations and Acronyms

A list of abbreviations and acronyms used in this research is given in Appendix A.

Definitions

Quality control vocabulary is often imprecise. In practice, two professionals may seriously disagree as to the meaning of certain QC terms. For this reason, concepts that are critical to this research are defined here.

Quality Control

Quality control is the overall system of activities that ensures the quality of a product meets the needs of its user in a way that is satisfactory, adequate, dependable, and economic (Keith 1994). QC encompasses all of the techniques used to encourage reproducibility of the output of a measurement system. What may be considered "high quality" in one situation may be unacceptable in another, and tolerable limits for error must be established that will, in the judgment of the end user, represent the best estimate of the limits within which the measured property must be known to be useful for its intended purpose. Limits must also be realistic and based on cost-benefit

considerations (Taylor 1981). QC data are used to estimate and evaluate the quality of analytical data and determine the necessity or effect of taking corrective action. Means of estimating data quality include precision, accuracy, detection limit, and other quantifiable and qualitative indicators (USEPA 1986). Uniform interpretation and implementation of QC samples are required to maintain quality across multiple environmental projects within a program (Luedtke 1992).

The EPA Data Quality Objectives Process

Few methods are available for systematically defining the optimum type and number of field QC samples required for an environmental monitoring program. By far the most comprehensive method available is the USEPA DQO process. The DQO process is a series of planning steps, based on the scientific method, designed to ensure that the type, quantity, and quality of environmental data are appropriate for their intended application.

The Quality Assurance Management Staff (QAMS) of the USEPA began developing a formal DQO planning process in the spring of 1984 (Blacker 1993). The goal of the project was to provide a structure for directing the design of environmental data operations and provide general assistance for planning data collection programs related to Remedial Response activities under CERCLA. EPA guidance for the preparation of DQOs was first issued in 1987 (USEPA 1987b) and revised guidance was published in 1993 (USEPA 1993a, 1993b). EPA guidance for the preparation of DQOs provides a set of management and technical tools for articulating technical objectives to facilitate communication among diverse players in complex projects and for optimizing the collection and use of data in environmental decision making.

DQOs are intended to save significant amounts of time and money in cleanups, while still achieving the risk-based cleanup standards expected by the public and regulators (Blacker and Goodman 1994). A more detailed description of the DQO process, including the specific steps that are required and the outputs from the process, is given in Chapter 4.

Data Quality

Data quality is a measure or description of the types and amounts of uncertainty associated with a data set (Blacker and Brantly 1984). Data quality is also defined as the magnitude of error associated with a particular data set. As the magnitude of error associated with a particular data set increases, its data quality decreases (Peters 1988). Important factors in defining data quality include intended data uses, required analytical levels, contaminants and levels of concern, and detection limits. It is extremely important that the detection limits of analytical techniques used are well below the level of concern since sampling accuracy is hard to evaluate or control (USEPA 1987b).

Uncertainty in Environmental Monitoring

Uncertainty describes the likelihood of all types of errors associated with a particular decision (USEPA 1987b). Environmental data are subject to many different types of uncertainty. Some can be controlled and quantified while others can only be described qualitatively (Blacker and Brantly 1984). The total uncertainty of a measurement is the combination of all the possible deviations, either estimated or measured, from the true value (Casey, Larson, and Harris 1989). Total error is composed of sampling variability and measurement error (USEPA 1993c). Data uncertainty may be divided into

random and systematic components. Figure 1.1 illustrates random and systematic errors for a measurement process. Figure 1.2 shows the dependence of uncertainty on analyte concentration near the detection limit.

Random Error or Precision

Random errors are those errors that can be estimated by the use of standard statistical techniques (Black 1988). Random errors are caused by random fluctuations inherent in the sampling and analysis system and the system being sampled. Other common names for random error are objective error and precision. Random error can be measured using replicates, repeated measurements of the same quantity, or other means. Random error is typically expressed as a variance or estimated standard deviation (Casey, Larson, and Harris 1989).

Precision is a measure of the reproducibility of measurements under a given set of conditions. Precision is a quantitative measure of the variability of a group of measurements compared to their average value. Precision is usually stated in terms of standard deviation but is sometimes reported in other ways such as coefficient of variation, relative standard deviation, range, and relative range. Overall precision is a mixture of sampling and analytical factors. Analytical precision is much easier to control and quantify than sampling precision (USEPA 1987b).

Figure 2.1. Unbiased measurement processes. The distributions of results from three unbiased processes are shown. The precision decreases in the order $A > B > C$. While the limiting means of all will approach the "true value," process C is relatively inaccurate (compared with A) due to its large imprecision.

Figure 2.2. Biased measurement processes. All of the processes are biased and hence inaccurate since the limiting means do not coincide with the "true value" in each case. However, it will be noted that most of the results for process A' will be more accurate than those of process C and even B (Figure 2.1), due to precision considerations.

Figure 1.1. Precision and Bias in Measurement Processes
(from Taylor 1987)

**Figure 1.2. Uncertainty of Measurements Close to the Limit of Detection
(from Taylor 1987)**

Systematic Error

Systematic errors usually result in a consistent deviation (bias) in a final result and cannot be estimated statistically (Black 1988). Systematic error arises from sources such as faulty operations, use of erroneous constants, incorrect calculation methods, improper units of measurement or reporting of data, and non-rectifiable matrix effects (Ramamoorthy and Baddaloo 1991). and includes all types of error that are not caused by random fluctuations in the field or measurement system. Systematic error must generally be estimated, at least in part, because the "true value" is not known

Accuracy and Bias

Accuracy is a measure of the amount by which the measured mean differs from the true value (Casey, Larson, and Harris 1989). Bias is a systematic error inherent in a method or caused by some artifact or idiosyncrasy of the measurement system depends on both random and systematic errors (Taylor 1987). Sources of bias in a measurement system include the sampling process, field contamination, preservation, handling, the sample matrix, sample preparation, and analysis techniques (USEPA 1987b). Bias is a function of the adequacy of the sampling plan design (Smith et al. 1988).

Measurement Error

Measurement error represents the difference between the true sampling values and the reported value. Measurement error has components from both sampling and analysis and is estimated using the results of QC sample analysis (USEPA 1993c).

Sampling Variability

Sampling variability represents the variation between true sample values and is a function of the spatial variation of the pollutant concentrations (USEPA 1993c). Sample variance and measurement variance are both significant for most cases of environmental analysis (Taylor 1986).

Contamination

Contamination is something inadvertently added to the sample during sampling or analysis. This results in data that do not give an accurate representation of the measured characteristic of the medium from which the sample was taken. Contamination is a common source of error in all types of environmental measurements. Most sampling and analytical schemes present numerous opportunities for sample contamination from a variety of sources. Contamination during sample collection, transport, and storage can arise from equipment and apparatus, handling (filtration, compositing, aliquotting), preservatives, ambient contamination, sample containers, cross contamination from other samples or reagents (Lewis 1988).

Cross contamination occurs when material from one sample enters a second sample during sampling, shipping, or storage (Mills 1992). Cross contamination during analysis can be caused by carry-over from high-level samples contaminating subsequent low-level samples, careless sample handling, and dirty sampling equipment. Sporadic contamination most often introduces false positives but false negatives can result when negative interference occurs (Lewis 1988).

Interferences

Additive interferences result when a sample constituent generates a signal that adds to the analyte signal. Additive interferences cause change in intercept but not slope, meaning their effect is most pronounced at low concentrations.

Multiplicative interferences result when a sample constituent increases or decreases the analyte signal by some factor without generating a signal of its own. Multiplicative interferences change the slope but not the intercept of the calibration curve.

Negative interference occurs when contamination results in a decreased analyte signal. Common causes for negative interference are adsorption and volatilization.

Representativeness

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition (USEPA 1980). Representativeness is a qualitative parameter that is dependent upon proper design of the sampling program. Representativeness is controlled by proper selection of sampling locations and collection of a sufficient number of samples (USEPA 1987b) and is also affected by the use of standard procedures for the collection and analysis of samples (Keck et al. 1993) and the use of pilot studies and systematic sampling (Barth 1992). For representing an average concentration over a region, representativeness is assured by random sampling from the target population. For estimating a maximum

concentration over the same region, scientific judgment is commonly applied to choose sampling locations at or near the maximum (Smith et al. 1988).

Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct normal conditions (USEPA 1980, Smith et al. 1988). Completeness is evaluated by determining the percentage of measurements made that are judged to be valid measurements (USEPA 1987b).

Comparability

Comparability is a qualitative parameter that expresses the confidence with which one data set can be compared to another (USEPA 1987b). Comparability is intended to provide the degree of control over total measurement process that is required to insure different studies can be compared. Comparability is achieved by using standard techniques for sampling and analysis and reporting results in appropriate units (USEPA 1987b). Comparability is assessed by evaluating field collection methods, analyzing field and laboratory QC samples, and comparing sample matrix and detection limits (Keck et al. 1993). Comparability is best evaluated through the use of field audit samples (Barth 1992).

Types and Purposes of Field QC Samples

Field QC samples include blanks, duplicates, spikes, and background samples that are used to determine and evaluate the quality of environmental data. Because there is some variability in the literature

regarding the definitions and recommendations for use of field QC samples, the major types and their primary uses are discussed here. Additional QC samples required for or added during analytical laboratory analysis will not be discussed.

Blank

A blank is a sample expected to contain negligible or unmeasurable amounts of the substance of interest (Black 1988). Blanks are used to determine some of the uncertainty caused by random error and to assess and control sample contamination. The use of blanks for assessing and controlling contamination is limited to contaminants causing additive interferences (Lewis 1988), but blanks should be used whenever the possibility of introducing contaminants exists (Keith 1994). Due to the high cost of analysis, it is sometimes recommended that a full suite of blanks be collected, but only the field blanks be analyzed (Keith 1991). If a problem is discovered, the rest of the blanks can be analyzed to locate the source of the problem. When this occurs, holding times are likely exceeded for the unanalyzed blanks, but resampling will usually be required in any case.

Bottle Blank

Bottle blanks are prepared by filling sample containers with analyte free deionized water, then adding the same preservatives as are added to the samples. Bottle blanks are used to ensure that contamination is not introduced by the sample containers. Bottle blanks are only used when an independent QC program does not exist for sample containers (Burger and Jordan 1988).

Trip Blank

Trip blanks are prepared by filling sample containers with analyte free water, transporting them to the sampling site, and returning them unopened to the laboratory. Trip blanks are kept near the samples throughout collection, transportation, storage, and the analytical process (Luedtke 1992). Trip blanks are used to determine contamination during sample collection and transportation (improperly cleaned sample containers, contaminated reagents, airborne contamination during transportation, etc.) (Csuros 1994). and measure cross-contamination from the container and preservative during transport, field handling, and storage (Keith 1994): Trip blanks are generally used only when Volatile Organic Analysis (VOA) will be performed. The recommended frequency for use of trip blanks varies. Typical frequencies include at least one for each VOA method for each cooler used to store and transport VOA samples (Csuros 1994); one per cooler, primarily for VOAs, but also when there is a concern that concentration of the parameter is biased by contamination (DOE 1994b); at least one per day per type of sample analyzed for volatile organic compounds (Keith 1991); daily, when VOA samples are collected (USEPA 1986); and one per day of sampling or as appropriate (USEPA 1987b).

Equipment Blank or Equipment Rinsate Blank

Equipment, field source water, or rinsate blanks are prepared by passing ASTM Type II (analyte free) water through decontaminated sampling equipment (DOE 1994b) or by collecting water or solvents used to rinse sampling equipment during decontamination (Lewis 1988). Equipment

blanks are used to assess the effectiveness of decontamination between sampling locations (Burger and Jordan 1988) and determine types of contaminants that may have been introduced through contact with sampling equipment such as filters, traps, and sample bottles, and verify effectiveness of cleaning procedures (Lewis 1988). As for trip blanks, the recommended frequency for equipment blanks varies. Some recommended frequencies include at least one for every twenty samples per parameter group per matrix per type of sampling equipment (Csuros 1994); one per 20 samples collected (Keck et al. 1993); at least one per day of sampling for each matrix sampled (USEPA 1986); and one sample for each source of water for a given event for each type of water used for decontamination (DOE 1994b).

Field Blank

A field blank is created by transferring analyte free media similar to the sampling matrix from one vessel to another or exposing analyte free media to the sampling environment at the sampling site (Keith 1994). Field blanks are used to identify contamination from sampling and analysis procedures, field conditions, containers, preservatives, shipping, storage, sample preparation, and measurement (Prasad 1994). Again the recommended frequency varies significantly. Some of the frequencies recommended for the use of field blanks in the literature include: one per 20 samples collected (Keck et al. 1993); one per matrix per day or one for every 20 investigation samples, whichever is less (USEPA 1987b); at least two during each round of sampling (DOE 1989); one with each set of samples from a given source (ASTM 1988); one per day per collection apparatus (Keith 1991), and "at frequencies specified according to the probability of contamination" (Mills 1992).

Duplicate or Collocated Samples

Duplicate or collocated samples are samples collected independently, as close as possible to the same point in space and time, and intended to be identical in all respects. The only sources of difference between the two samples are homogeneity of the medium being sampled and the sampling technique employed (Luedtke 1992). Duplicate samples are often presented to the laboratory "blind" (the laboratory is not made aware that the batch contains duplicate samples) (Bryden and Smith 1989). Duplicates are used to assess the variability of sample collection procedures and its impact on data (Burger and Jordan 1988). To obtain an accurate estimate of precision, collocated samples should be separated after collection and allowed to pass through the shipment, analysis, and handling phases at time intervals similar to those experienced by study samples. If collocated samples are not separated in time, they may vary in the same manner and at the same rate as the study samples and give an optimistic estimate for precision (Smith et al. 1988). Collocated samples processed and analyzed by the same organization provide intralaboratory precision information for the entire measurement system including sample acquisition, homogeneity, handling, shipping, storage, preparation, and analysis. Collocated samples processed and analyzed by different organizations provide interlaboratory precision information for the entire measurement system (USEPA 1987b).

Various frequencies are recommended for taking duplicate samples. Typical recommendations include at least one sample or 10% of the samples, whichever is greater for each parameter group and matrix sampled (Csuros 1994); at least one for each day of sampling for each matrix sampled (USEPA

1986); and one in 20 samples, spread out over the sampling event, preferably at least one per day of sampling (USEPA 1987b).

Replicated Samples

Replicate samples are samples that have been divided into two or more portions at some step in the measurement process. Field replicates give precision information on homogeneity, handling, shipping, storage, preparation, and analysis. Analytical replicates give precision information on preparation and analysis (USEPA 1987b). For large batches, a fixed frequency such as one in 10 or 20 is recommended. For small batches, more frequent repetition may be desirable to ensure adequate data to assess precision (Smith et al. 1988).

Splits

Split samples are replicate samples sent to different laboratories and subjected to the same environmental conditions and steps. Split samples serve as an oversight function in assessing the analytical portion of the measurement system (USEPA 1987b). They are used to indicate sample homogeneity and evaluate analytical process precision (Luedtke 1992). Field splits are normally collected at a frequency of 5 to 10% of the routine samples (DOE 1994b).

Field Spikes

Field Spikes are selected field samples to which a known amount of specific analytes of interest is added during collection in the field (Keith 1991). Although field spikes are useful, they are difficult to prepare because of the

technical procedures required to prepare them accurately. Because of this, most spikes are made after samples have been returned to a laboratory, possibly hours, days, or even longer periods of time after the samples were taken (Keith et al. 1983). If spiking is not practical, blind reference materials are sometimes used (Smith et al. 1988). Simulated or synthetic field blanks may be spiked when suitable blanks from control sites are unavailable.

Bias can be estimated from recovery of spiked samples, however, spiked samples may not fully simulate natural samples and the recovery information should be interpreted with this in mind (Keith et al. 1983). Field spikes provide a measure of sampling, handling, and preservation error, giving the best overall assessment of accuracy for the entire measurement system (USEPA 1987b). Some sources recommend that field spikes be used infrequently or not at all (USEPA 1986, USEPA 1987b). Spikes should be used when feasible (Keith et al. 1983) based on the data quality needs of the program, bias and precision of the measurement system, size of sample lot, and other considerations (Smith et al. 1988).

Background Samples

Background samples are samples of media similar to the test sample matrix taken near in time and place to where analytes of interest may exist at background, naturally occurring, or typically encountered levels (Keith 1994). They are taken from media characteristic of the site but outside the zone of contamination (USEPA 1987b) and used to identify the presence of analytes of interest in the sample matrix from which the samples are obtained (determine whether the site is contaminated or truly different from the norm) (Keith 1991). Background samples are necessary for valid scientific

comparison of samples suspected of containing environmental contaminants with samples containing low or acceptably low levels (Keith 1991).

Action Level

An action level is the minimum change in concentration of an analyte in an environmental medium at which some action must be taken. Action levels can be triggered by such situations as numerical limits that are not to be exceeded as well as significant changes from historical results.

Data Grooming

Data grooming is a set of procedures performed on data received electronically from an analytical laboratory to ensure that the data are complete and correctly formatted prior to entry into the LLNL environmental monitoring database.

Abbreviations

Abbreviations used in this research are summarized in Appendix A.

Methodology

This research will use both qualitative and quantitative methods. Most data used will be secondary data but some primary data will also be required. DQOs will be developed from existing documents, procedures, and reports and from information gathered from subject matter experts. The adequacy of current field QC practices will be evaluated by statistical analysis of existing monitoring data. Finally, an optimized field QC sampling program will be

developed by comparing the cost of collection the field QC samples required to meet specified DQOs to the risks associated with not taking those samples.

CHAPTER 2

REVIEW OF THE RELATED LITERATURE

Goals of Environmental Monitoring

Environmental monitoring is performed for various reasons. The overall goal of a well-designed sampling and analytical program is to measure what is really there (Mills 1992). Blacker and Brantly (1984) discuss monitoring programs intended to determine compliance with regulatory standards or requirements, determine the effectiveness of pollution control strategies, identify and evaluate long-term trends in pollutant concentrations, determine the highest concentrations of pollutants expected to occur in a geographical area, determine the highest concentrations of pollutants in areas of high population density, determine the impact of significant sources or source categories on ambient pollution levels, or determine background concentration levels. The USEPA (1987b) describes additional uses of monitoring programs, including attempting to determine the presence or absence of contaminants, identifying existing types of contaminants, determining quantities (concentrations) of contaminants, defining contaminant release mechanisms, determining the direction of contaminant transport, and determining source boundaries.

Federal and state agencies rely heavily on monitoring data to assess the status of and trends in the quality of the nation's natural waters. Moreover, public officials at all levels are pressing to increase monitoring efforts to establish long-term trends for chemicals that affect the environment. Unfortunately, the fact that data obtained in many monitoring studies are typically so compromised in one or more respects that they are of little value is neither well known nor well-appreciated (D'Elia, Sanders, and Capone 1989).

Environmental Monitoring at LLNL

LLNL has performed environmental monitoring and reported the results annually every year since 1971 (Gudiksen et al. 1972). Monitoring at the Laboratory was originally driven only by the Atomic Energy Manual's Standards for Radiation Protection and intended to provide assurance of the effectiveness of the Laboratory's effluent control program for potentially hazardous radioactive materials (Gudiksen et al. 1972). As environmental regulatory control increased and environmental regulations and reporting requirements increased, the Laboratory's monitoring program expanded to include non-radiological parameters. In addition to Federal, State, and local regulations, drivers for LLNL's environmental monitoring programs include DOE Orders, State of California and city of Livermore permits, and public concern.

The Importance of Understanding and Controlling Environmental Data Quality

Bottrell (1993) has pointed out that many environmental program managers face a nearly impossible task. They are required to make the "right" decisions within accepted levels of uncertainty while conserving and making the best use of limited resources. In order to avoid making erroneous decisions leading to wasted resources or unnecessary exposure to hazardous materials, it is important to understand and control the uncertainty inherent in environmental sampling and analysis as much as possible (Blacker and Goodman 1994). Possible consequences of a wrong decision based on the data from a field sampling program include economic costs, court costs, and loss of public confidence (Barth 1992). Federal and state funding for monitoring programs is decreasing, while at the same time, enforcement actions, including both fines and criminal penalties,

are becoming more and more common. The DOE has many environmental concerns due to the scope and complexity of contamination throughout the weapons complex. Lillian et al. (1992) have estimated the cost of cleanup at DOE facilities to be \$200 billion over 30 years, with approximately \$15 to \$45 billion required to obtain reliable environmental monitoring data. According to Thomas P. Grumbly (1994), collection of credible and cost-effective environmental data is critical to the success of DOE management programs. Michael, Neptune, and Barr (1992) also discuss the significant impact that data quality can have on the cost-effectiveness of a monitoring program.

The cost of obtaining data is related to the quality of those data. Ramamoorthy and Baddaloo (1991) discuss the impact of defining data quality requirements before beginning a monitoring program on the resources required for program implementation. Understanding that data used to develop standards, reinforce enforcement actions, or support health impact studies must be of higher quality than data collected for environmental trend analysis during the design of a monitoring program allows for the use of less precise (and significantly less costly) analytical techniques or for the collection of considerably fewer samples. In addition to the cost of monitoring itself, data of unknown quality can result in extremely costly compliance programs that being mandated unnecessarily. Kratochvil and Taylor (1981) recommend the use of a rapid, approximate analytical method if uncertainty inherent in the sampling process is large and cannot be reduced, since further refinement of the measurement step may be of negligible aid in improving the overall results.

The impact of understanding and controlling data quality on data defensibility, and the resultant ability to avoid enforcement actions are discussed by Wallin, Hamilton, and Wait (1994). Enforcement actions resulting in fines or

criminal penalties are increasingly common in the 1990s. Analytical data are generally of central importance to allegations regarding permit violations and other illegal practices. For example, the Clean Water Act requires that Discharge Monitoring Reports be accompanied by certification that the permittee understands the quality of the data provided and that the sampling and analytical procedures used to generate the data were in accordance with 40 CFR Part 136. Failure to provide this certification or providing false information in a monitoring report can result in civil or criminal penalties.

Finally, Ramamoorthy and Baddaloo (1991) report that high quality environmental analytic data are essential to protect ecosystems and human health from exposure to toxic chemicals in the environment. Regulatory agencies rely heavily on monitoring data for development of standards.

Keith et al. (1983) cite many factors that have the ability to affect the cost and reliability of environmental data, including the level of confidence required regarding the identity of the material being analyzed, qualitative and quantitative levels of measurement required, the degree of confidence needed, and the requisite degree of quality assurance. If a cost-effective sampling plan is to be developed, the magnitude and characteristics of random and systematic error associated with a system must be known and the major sources of error should receive the most emphasis in sampling plan design.

Difficulties in Understanding and Controlling Environmental Data Quality

Some of the elements contributing to uncertainty in environmental monitoring discussed by Botrell (1993) include variability inherent in the material being sampled, the ability to define and collect representative samples, and uncertainty introduced by sample handling, analysis, data recording,

transcription, and modeling. All of these factors must be identified, quantified, understood, and managed to understand the quality of the data. Environmental measurements are a special class with special problems including relatively large inherent uncertainties. According to Taylor (1986), the fact that the quantity of data available to make decisions that are typically controversial is generally less than the optimum increases the importance of technical soundness and legally defensibility. Burger and Jordan (1988) report that it is not possible to develop a "standard" environmental monitoring program. The mix of stakeholders, their perceived needs, and the level of decision uncertainty that can be tolerated varies considerably, both within and between projects.

Ramamoorthy and Baddaloo (1991) describe a number of sources of uncertainty in environmental monitoring data including inappropriate, outdated, or nonexistent analytical protocol; limited financial or human resources; improper sampling technique; poor choice of detection limit; and misconception of the goal for which data are intended. The American Chemical Society (ACS) Committee on Environmental Improvement (1980) also cites the large number of organic compounds in the environment, the fact that the composition of a sample may be influenced by uncontrollable environmental variables that can complicate measurement and evaluation, gaps in technical knowledge, sampling bias, undetected flaws in the measurement system, and errors in human performance as contributors to uncertainty.

The Impact of Sampling on the Quality of Environmental Data

Keith (1994) has divided the uncertainty of environmental monitoring data into six major components: pollutant distribution, field sampling, field sample handling, laboratory sample preparation, laboratory analysis, and data

handling. The relative contribution of each of these components is illustrated qualitatively in Figure 2.1.

Kratochvil and Taylor (1981) have found that the total variability in environmental monitoring results is likely to be controlled by sampling variability. Several researchers (Barcelona 1988, Bottrell 1993, Burger and Jordan 1988, Haeberer 1993, Kratochvil and Taylor 1981, Keith 1988, Keith 1991, and Ramamoorthy and Baddaloo 1991) discuss the fact that sampling has traditionally received minimal attention while the focus of error control in environmental measurement has been on analytical techniques. It is a common misconception that one can simply take a sample and bring it to a laboratory to find out if it is contaminated. According to Bryden and Smith (1989), this approach can lead to wasted effort, excessive laboratory costs, and flawed data. In reality, the analysis step normally accounts for only about 5% of the total error. Bottrell (1993) reports that sampling contributes about 80% of the variability with 15% due to sub-sampling error. Barcelona (1988) states that this is particularly true for trace level concentrations (i.e., <1 mg/L). Haeberer (1993) discusses the false sense of security regarding quality of data that has been generated by lack of attention to sources of error that occur prior to analysis.

According to Keith et al. (1983), the quality and utility of analytical data depend critically on the validity of the sample and the adequacy of the sampling program. Barcelona (1988) stresses careful planning, refinement, and

Sources of Error (Variability)

Figure 2.1. Sources of Error in Environmental Monitoring Data

(from Keith 1994)

documentation, despite the apparent simplicity of the sampling process, if truly representative samples are to be provided for the purposes of investigation. Kratochvil, Wallace, and Taylor (1984) discuss recent improvement in analytical methodology and instrumental methods and the use of smaller and smaller analytical test portions and the resultant increase in the impact of sampling error and trace component heterogeneity.

Elements of a sampling operation may cause serious errors that cannot be handled by statistics. According to Barcelona (1988), sources of systematic error that can be very difficult to identify and control include sampling locations, sampling mechanisms, and sampling materials. Keith (1990) stresses that contamination is always a problem with water samples, especially as concentration levels of the analytes decrease.

Sources of Variability in Environmental Data Due to Sampling

Smith et al. (1988) describe three sources of variability in the results of environmental sampling and analysis: design of the sampling plan, sampling implementation, and sample analysis and reporting. Each source of error has random and systematic components. Sample uncertainty may contain systematic and random components arising from population and sampling considerations. Taylor (1988) recommends the design and execution of measurement and sampling plans that allow individual components of uncertainty to be evaluated.

Keith (1994) reports that the greatest contributors to variability in environmental data are the actual distribution of pollutants in the environment, field sampling, and field sample handling. Systematic and random components of uncertainty are discussed by Taylor (1988). Systematic components of uncertainty that can result from sampling operations include loss of analyte due

to adsorption or reaction with container materials, sampling equipment, or sample transfer lines; deterioration due to atmospheric contact, temperature, instability, radiation effects, or interactions with other analytes; disturbance of stable or metastable equilibria caused by removal of the sample from its environment; and subtle carryover effects from the memory of previous samples in sample containers. Random components include variability of all the sources of bias mentioned above. Kratochvil and Taylor (1981) recommend proper use of blanks, standards and reference samples to control many sources of poor analytical results, however, these blanks cannot compensate for an invalid sample. Silverstein et al. (1987) mention seasonal variations in water chemistry, field components associated with sample collection or short-term localized water variability as sources of sampling variability specific to water monitoring.

Control and Measure of Uncertainty in Environmental Data

According to Michael and Brown (1992), the two decision errors of most concern when treating environmental data are incorrectly classifying an area as a problem and incorrectly classifying an area as acceptable. To manage uncertainty, the basis upon which decisions will be made must be understood and focus must be placed on the elements of the decision that can be affected during the time available for decision making. Michael, Neptune, and Barr (1992) report that uncertainty can often be limited to an acceptable level through careful planning and management of the expenditures of resources used for data collection and analysis. Accuracy is usually assured by incorporating some form of randomness into the sample selection process. Precision controlled by varying the number of samples taken and measured (USEPA 1986).

The first step in developing uncertainty constraints is to identify the types of decision errors that might result (Michael and Brown 1992). These are defined in Table 2.1.

A judgment must be made as to the degree of sampling accuracy and precision that are required to estimate reliably the chemical characteristics of an environmental medium for the purpose of comparing those characteristics with applicable regulatory thresholds. Generally, high accuracy and high precision are both required if one or more chemical contaminants are present at a concentration that is close to the applicable regulatory threshold. Alternatively, relatively low accuracy and low precision can be tolerated if the contaminants of concern occur at levels far below or far above their applicable thresholds (USEPA 1986).

Bottrell (1993) suggests two methods that can be used to overcome sampling and analysis error: substantially increasing the number of samples that are taken and analyzed and using an appropriate statistical design to develop the sampling and analysis plan. Substantial work has been done in defining statistical methodology for the design of environmental sampling programs (Barcelona 1988, Blackwood 1991, Gilbert 1993, Kratochvil and Taylor 1981, Provost 1984, Smith et al. 1988, USEPA 1993a).

Whenever possible, measurements should be conducted in such a way that the components of variance arising from sample variability and measurement variability can be evaluated separately. Ramamoorthy and Baddaloo (1991) suggest that most sampling and analytical error can be traced and controlled by proper use of blanks, reagents, standards, and reference materials. If the measurement process is demonstrated to be in a state of statistical control and its variability is known, the variability of the entire system

Table 2.1. Decision Table (from Keith 1991)

Decision	When the analyte is really NOT PRESENT	When the analyte is really PRESENT
Analyte Detected	INCORRECT DECISION FALSE POSITIVE (TYPE I ERROR)	CORRECT DECISION
Analyte NOT Detected	CORRECT DECISION	INCORRECT DECISION FALSE NEGATIVE (TYPE II ERROR)

can be determined from the samples. Otherwise, Kratochvil and Taylor (1981) have determined that an appropriate series of replicate measurements and samples can be devised to permit separate evaluations of the standard deviations due to sample variability and measurement variability. If necessary, field and laboratory uncertainties may be differentiated from one another by analyzing both field duplicates and laboratory splits (Casey, Larson, and Harris 1983).

Methods for eliminating systematic error sources identified by Casey, Larson, and Harris (1983) include proper calibration of instruments, standard operating procedures for sample collection and analysis developed by experts in the field and carried out by trained personnel, monitoring of field and laboratory contamination through the use of blanks, and monitoring of matrix effects through the use of matrix blanks or matrix spikes. Potential sources of contamination must be identified and eliminated wherever possible (Lewis 1988).

The Importance of Field Quality Control Samples

Until recently, most quality control samples generated in support of monitoring programs have been related to instrumental analytical procedures. Barth and Mason (1984) found this level of quality control to be inadequate when the medium being sampled is not homogeneous. Barcelona (1988) reports that laboratory oriented QC measures can only account for errors that occur after sample collection, regardless of the purpose of the study or investigation.

Field quality control samples can be used to monitor the adequacy of the sampling system and the integrity of samples during their journey from the field collection point through laboratory analysis (DOE 1994b). Field quality control activities are intended to assure that the sampling process is in control and that the highest quality in field work and sample collection is maintained. According

to Csuros (1994), the validity of data from field measurements can be proven through proper quality control.

The precise composition and frequency of QC samples are dependent upon sampling program objectives and existing guidelines (USEPA 1993c). The level of quality control required to achieve data quality goals should be determined when those goals are established. Taylor(1986) stresses the importance of identifying sources of excessive random and systematic error and developing protocols to reduce error to acceptable levels.

Determination of Appropriate Field QC Samples

Methodology for determining the optimum type and number of field QC samples for an environmental monitoring program is conspicuously lacking in the literature. Although many papers (USEPA 1987b, Blacker and Goodman 1994, Kratochvil and Taylor 1981) stress the importance of determining QC sample loads systematically, guidance regarding the method to be used in making that determination is minimal. Barth (1992) recognizes that various rules of thumb have been devised for determining the number and types of QC samples needed in a particular study, and recommends that these rules be used with great caution, if at all. Several published case studies (DOE 1989, Keck et al. 1993, Luedtke 1992, and Silverstein et al. 1987) describe the QC sample load that is used, but no basis or rationale for their determination is given.

Several documents are available from the USEPA that either address field QC sampling directly or provide information that can be used to determine optimum QC sampling requirements. In 1984, the Quality Assurance Management and Special Studies Staff published a manual for the calculation of precision and bias of chemical and physical measurements (USEPA 1984) that

provides a clear discussion of statistical concepts as they relate to environmental data and provides models, formulas, and examples that can be used to determine the different components of uncertainty in monitoring data. The original guidance document for developing Data Quality Objectives (USEPA 1987b) and its accompanying case study (USEPA 1987a) discuss field quality control samples, define levels at which they should be taken, and provide a method for evaluating the resultant data. The basis for the stated levels is not given, however.

Specific methods for evaluating data to determine whether or not cleanup standards have been met (USEPA 1989) and for determining its usability in risk assessment (USEPA 1990) are in the process of being developed and are not yet available. Finally, the most recent revision of the USEPA data quality objectives guidance process provides a method for assessing and defining required levels of uncertainty (USEPA 1993a).

The USEPA Data Quality Objectives Process

The Data Quality Objectives (DQO) process developed by the USEPA presents a systematic methodology for specifying tolerable uncertainty and using statistical design methods in the design of a data collection program. When combined with statistical methods in the interpretation of the results, this process provides a mechanism for limiting uncertainty to acceptable levels.

The DQO process was developed by the USEPA to help project managers and planners determine the type, quantity, and quality of data needed to make decisions (USEPA 1993b). The guidance for this process was originally issued in 1987 (USEPA 1987b) as a tool to be used in the design of CERCLA remediation studies. Until recently, its application has been mostly limited to Superfund

projects, although broader applicability has been recognized and a few non-CERCLA projects have been managed using this process (Daniels and Tardiff 1992).

The original DQO guidance (USEPA 1987b) was recently superseded. The revised guidance (USEPA 1993a) expanded the process, provided more specific examples of implementation, and offered additional techniques that can be used in defining data quality objectives. Additional new guidance from the USEPA Quality Assurance Management Staff (USEPA 1993b) formally expanded the applicability of the DQO process to non-CERCLA projects and provided a case study in which DQOs were determined for a RCRA project.

Benefits of the DQO Process

Many benefits of using the DQO process have been discussed in the literature. The three main benefits are improved sampling and analysis design, resource savings, and improved decision making. Because this process is based on the scientific method, legal defensibility of decisions is also improved (USEPA 1993a).

Use of the DQO process ensures that data are sufficient and of adequate quality for their intended uses (USEPA 1987b); and improves planning effectiveness, data collection design efficiency, and the defensibility of decisions to which data are applied (Haeberer 1993). Use of the DQO planning process forces the problem and the action requiring attention and the quality and quantity needed for problem resolution to be clearly defined (Bottrell 1993). Sampling and analysis plans are developed systematically, and quality goals that can be easily monitored are established (Daniels and Tardiff 1992).

Michael and Brown (1992) have determined that the DQO process forces an up front recognition of the existence of uncertainty arising data collection activities. Creating DQOs also requires the decision maker to specify the degree to which uncertainty must be controlled. According to Haeberer (1993), use of the EPA's DQO process forces the data user to become aware of the uncertainties associated with their data early in the process and provides opportunities for addressing concerns related to both sampling and analysis. The DQO process results in a well thought-out sampling and analysis plan that specifies the chosen sampling and analysis option as well as statements of confidence based on statistical techniques about the decisions made (USEPA 1987b). It also assists the user and planning team in determining the quality and quantity of data that are required for the intended application by focusing on and defining decision errors acceptable to the user. This directs the development of a statistical design for data collection that will meet the user's needs, emphasizes acceptable errors in decision making, quantifies the acceptable level of data uncertainty, and provides a logical structure for planning data collection based on the intended use of the data (Haeberer 1993).

Blacker and Goodman (1994) report that the goal of any environmental data collection effort should be to invest as efficiently as possible in reducing risk to levels acceptable to regulators and the public while not overindulging in activities that do not effectively reduce risk. The cost of an environmental monitoring program is influenced by accessibility to sampling points numbers, kinds and complexity of samples, and frequency of sampling (Keith 1994). The DQO process ensures that only the data necessary to meet program objectives are collected, resulting in improved efficiency, cost savings, and measurable and traceable data quality (Daniels and Tardiff 1992). Applying DQO methods

should save significant amounts of time and money, while still achieving the standards expected by the public and regulators. Separation between policy calls about "risk goals" and technical discussion of alternatives for implementation, translation of regulatory policy calls (including the definition of tolerances for "uncertainty") into specific, concrete, measurable cleanup criteria, documentation of agreements reached among all stakeholders on the critical requirements for the cleanup, and use of all available optimization methodology to develop the most efficient design for the remediation are essential elements in reducing the resource requirements. In addition, the flexibility inherent in the DQO development process creates opportunities for cost savings (Blacker and Goodman 1994).

One of the major strengths of the DQO process is that it brings together the right people at the right time to agree on what data are needed and what is the best way to obtain them. This helps to clearly and precisely define necessary decisions and how they should be addressed, ensures a technically sound and cost-effective data collection effort, promotes buy-in from all stakeholders, minimizes repeated data collection and criticism from outside stakeholders, and can result in significant time and cost savings (Blacker and Harrington 1994). Collecting the right amount and kind of data to answer the program's needs can help stakeholders sort through their initial myriad concerns to reach consensus on a focused statement of the problem (Blacker and Goodman 1994). Time spent planning and building consensus up front will frequently save both time and dollars in the long run as well as improving data defensibility (Michael, Neptune, and Barr 1992).

Drawbacks to the DQO Process

The most significant drawback of the DQO process is the time and resources that it consumes prior to data collection (Daniels and Tardiff 1992). In addition, if the DQO process is to be effective, stakeholders must demonstrate respect for one another, and come to the table with an open mind and a willingness to change. This requires time, patience, and desire and is not always easy to achieve (Michael, Neptune, and Barr 1992). Effective communication between highly trained specialists who traditionally have not interacted and who are not likely to speak one another's technical jargon can also be difficult (Neptune 1994).

Application of the DQO Process to Monitoring at LLNL

The environmental monitoring program at LLNL has never used a formal DQO process. Parts of the process have been done but they have never been formally documented and put together into a formal set of DQOs. A recent audit of LLNL environmental monitoring activities (DOE 1994a) requested that formal DQOs be set. A graded approach application of the DQO process to this program is expected to result in significant resource savings and improved understanding of the meaning of data collected. The recently published Environmental Monitoring Plan (Tate et al. 1995) begins the assessment process that will be necessary for developing and implementing DQOs for environmental monitoring at LLNL.

Comparison of Data to DQOs

Two things must be done in order to assess the quality of environmental data. Data must be validated by determining the uncertainty associated with the

measurement activity and the data must be evaluated to determine if they can be used to make a decision with an acceptable level of uncertainty. The data validation process includes the determination of a statistical distribution of errors for each reported concentration value (USEPA 1987b).

Formal methodology is also available for evaluating data once it has been taken. Many statistical models are available for evaluating data quality. The USEPA is in the process of defining a methodology for data quality evaluation.

CHAPTER 3

METHODS OF CONDUCTING THE RESEARCH

This research was conducted using both qualitative and quantitative methods. Data quality objectives were developed in Subproblem One by reviewing existing documents, procedures, and reports; consulting with subject matter experts; and, to a lesser extent, reviewing existing quantitative data. Subproblem Two determined the adequacy of current field QC practices through analysis of existing monitoring data for two LLNL environmental monitoring networks. Subproblem Three developed an optimized field QC sampling program for those networks based on the results of the first two Subproblems.

Types of Data Used

The majority of the data used in this study was secondary data. Much of the information that was used to determine the data quality objectives for the rain and storm water runoff monitoring networks has been documented in reports, procedures, plans, and permits. This information was augmented, where necessary, with information obtained in interviews with subject matter experts and the primary decision maker for LLNL environmental monitoring programs. Subproblem Two evaluated existing data from the rain and storm water runoff monitoring networks to determine whether the field QC samples that were taken can be used to determine whether those data meet the data quality objectives. Subproblem Three used the results of Subproblem Two to define the optimum quality control sampling requirements for the monitoring programs that were studied.

Criteria for Admissibility of the Data

All documents produced by the LLNL Environmental Monitoring Program (EMP) are subject to peer review and, at a minimum, first line management review and approval. Most plans, permits, and reports are also subject to review and approval by higher levels of management, and, in some cases, the LLNL Legal Department. LLNL Site Annual Environmental Reports (SAERs) are also subject to review by the Department of Energy. For the purposes of this research, it was assumed that this level of review is adequate and that data published in these documents were admissible.

Because one of the goals of this research was to examine and evaluate the quality of environmental monitoring data, the only criteria for admissibility of those data was that the samples were taken within the time period specified. The data management process is shown in Figure 3.1. Data traceability is maintained through the use of Chain of Custody (COC) and Field Tracking Forms (FTF). The COC accompanies the samples to the analytical laboratory and subsequently accompanies the resultant analytical data back to the responsible Environmental Analyst. The EMP's Data Management Team (DMT) accepts and distributes the data to the responsible Analyst. The Analyst reviews the data and accepts them only after any unusual results are explained or revised.

After acceptance, the DMT enters the data into an INGRES relational database maintained on a VAX 6310 mainframe. Most data are downloaded electronically from analytical laboratories but some are entered manually by DMT members. Data are first entered into personal work space tables where they are groomed and verified prior to entry into the database. Data are groomed using several procedures that automatically check most data fields against acceptable values and report invalid or missing data so that DMT members can

**Figure 3.1. Data Management of Monitoring Activities
(from MacQueen and Hankla 1995)**

correct any mistake before appending data to the database. New data must also be thoroughly checked against hard-copy before they are appended. To minimize errors, data are verified by a DMT member other than the one who entered the data. One hundred percent of the data that are manually entered must be proofed against hard-copy reports. When data are received electronically, all sample records are proofed, but only 20% of the analysis records, selected randomly, require verification. This is because analytical laboratories are required by contract to use the same information system to generate hard-copy reports that they use to generate the electronic data download (MacQueen and Hankla 1995).

Collection and Treatment of Data for the Research Problem

The Data for Subproblem One

The Subproblem

The first Subproblem used the first six steps of the United States Environmental Protection Agency's Data Quality Objectives (DQO) development process to define data quality objectives for selected analytes in the LLNL rain and storm water runoff monitoring networks.

The Data Needed

Data required for Subproblem One included:

- Sufficient information about both monitoring networks to develop a clear description of their purpose, drivers, history, and status;
- A description of how monitoring is conducted for both networks, including monitoring frequency, sampling locations, analytes of interest, sampling methodology, and sample control;

- Action levels and alternative actions for each parameter of interest for both monitoring networks;
- Potential consequences of false positive and false negative errors for each parameter of interest for both monitoring networks; and
- Acceptable probabilities for the occurrence of decision errors for each parameter of interest for both monitoring networks.

The Location and Means of Obtaining the Data

LLNL publishes the results of its environmental monitoring studies annually in a Site Annual Environmental Report (SAER). In addition, an Environmental Monitoring Plan (Tate et. al 1995), required by Department of Energy Order 5400.1, was revised and reissued in 1995. This document includes rationale and design criteria for the monitoring program, extent and frequency of monitoring and measurements, procedures for laboratory analyses, quality assurance requirements, program implementation procedures, and direction for the preparation and distribution of reports. (DOE 1990, DOE 1991). Descriptive information regarding monitoring networks was obtained primarily from SAERs and from the EMP. Additional information for the storm water runoff network was obtained from the LLNL Storm Water Pollution Prevention Plan (Eccher et al. 1994). Where necessary, this was supplemented by discussions with the Environmental Analyst assigned to the network or with the EMP Leader.

The methods used for environmental monitoring at LLNL are described in procedures that contain detailed descriptions of how, when, and where samples are collected, and which analytes are measured.

Recommendations for action levels and alternative actions for each parameter of interest for both monitoring networks, potential consequences of

false positive and false negative errors for each parameter of interest for both monitoring networks, and acceptable probabilities for the occurrence of decision errors for each parameter of interest for both monitoring networks were developed as a part of this research and approved by the EMP Leader (the primary decision maker).

The Treatment of the Data

The first Subproblem used the first six steps of the DQO process to define data quality objectives for the LLNL rain and storm water runoff monitoring networks. The EMP Leader, who has ultimate responsibility for all activities carried out by the EMP, was considered the primary decision maker for this study. Because most of the information and decisions required for establishing DQOs for these networks had already been accumulated and published, a formal planning team was not established.

The first step towards implementing the DQO development process in this research was the development of a list of questions that had to be answered to set action levels and determine DQOs. Existing documents were reviewed and as many of these questions as possible were answered based on published information. When necessary, appropriate subject matter experts were consulted to obtain missing information and finish answering the requisite questions.

A historical summary of both networks as well as a description of current monitoring activities were presented to more clearly define the rationale for each program. Informational inputs to the decision and the boundaries of the study were also summarized.

Decision rules, acceptable limits on decision errors, and proposed field QC sampling were developed for each parameter of interest based on the

information gathered. These proposals were reviewed with the primary decision maker and other relevant personnel, and changes were made as appropriate. A staff statistician was consulted as needed.

The Data for Subproblem Two

The Subproblem

The second Subproblem evaluated analytical data for samples collected for the LLNL rain and storm water runoff monitoring networks from 1992 through 1994 to determine whether the field quality control samples that were taken during that period could be used to verify that the specified data quality objectives were met.

The Data Needed

The analyses performed in Subproblem Two required the data quality objectives developed in Subproblem One as well as monitoring data for samples collected from the rain and runoff monitoring networks during the specified time period.

The Location of the Data

Monitoring data are stored in the EPDDATA INGRES database described above. Hard-copy data reports are also archived by the DMT and these are stored in the DMT offices or in a Document Retention Center.

The Means of Obtaining the Data

Data were obtained from the EPDDATA INGRES database using DataPrism™ software.

The Treatment of the Data

Once data were retrieved from the database, they were transferred to Microsoft Excel™ 4.0 spreadsheets for manipulation. Routine sampling data were compared to the action levels developed for Subproblem One and, where possible, the precision of each data set was calculated.

Field quality control samples were summarized and the level of sampling effort was compared to that required by the DQOs developed for Subproblem One. The percent relative standard deviation was calculated and plotted for duplicate samples with results above the reporting limit, so that the overall precision of the sampling and analysis process can be estimated. Finally, the quality of the QC data was evaluated qualitatively.

The Data for Subproblem Three

The Subproblem

The third Subproblem determined the optimum field quality control sampling program required to ensure the specified data quality objectives are met for the LLNL rain and storm water runoff monitoring networks and defined additional resources required to implement those measures.

The Data Needed

The data gathered to define data quality objectives for Subproblem One and the results of Subproblem Two were applied to Subproblem Three. Estimated resource requirements for additional field QC sampling were also needed.

The Location of the Data

Estimates of resource requirements were obtained from the EMP Leader, who has budgetary responsibility for rain and storm water runoff monitoring at LLNL.

The Means of Obtaining the Data

Additional data required for Subproblem Three were obtained through discussions with the EMP Leader.

The Treatment of the Data

The primary method of treating the data for Subproblem Three involved discussion of the results of Subproblem Two with the EMP Leader. The EMP Leader evaluated the costs, risks, and benefits of proposed field quality control sampling strategies and approved the recommendations for the system that best met the needs of the Program.

CHAPTER 4

RESEARCH DATA AND ANALYSIS

Subproblem One

The first subproblem uses the first six steps of the United States Environmental Protection Agency's Data Quality Objectives (DQO) development process to define data quality objectives for selected analytes in the LLNL rain and storm water runoff monitoring networks. The purpose of each step of the DQO process as defined by the EPA (USEPA 1993b) is stated below, followed by the information required to fulfill that purpose for LLNL monitoring of tritium, copper, zinc, and pesticides in storm water runoff and monitoring of tritium in rainfall.

Step 1: State the Problem

The purpose of this step is to clearly define the problem that requires new environmental data so that the focus of the study will be clear and unambiguous.

Summary of Existing Information

Environmental monitoring at LLNL began in 1971. In the early years, environmental monitoring was performed to determine to what extent LLNL contributed to levels of radiation in the surrounding environment and to ensure the effectiveness of Laboratory effluent control programs (Gudiksen et al. 1972). The goal of environmental monitoring at LLNL was expanded in 1987 to include assessment of compliance with applicable standards (Holland and Brekke 1988), again in 1990 to determine the contribution of rainfall to tritium levels in storm water runoff, and finally in 1993 to reflect the need to support CERCLA investigation and cleanup efforts (Gallegos et al. 1994).

Storm Water Runoff Monitoring

LLNL originally began monitoring storm water runoff to determine whether pesticides were being transported off-site. Beginning in 1975, quarterly samples were obtained from the drainage ditch at the northwest corner of the site and analyzed for pesticides (Silver et al. 1976). This monitoring program continued unchanged for a number of years (Silver et al. 1977, Silver et al. 1978, Silver et al., 1979, Silver et al. 1980, Toy et al. 1981), with quantitative results for pesticide monitoring first being published in 1978. Beginning in 1981, storm water samples were also analyzed for gross alpha, gross beta, and tritium (Auyong, Griggs, and Buddemeir 1982). In 1982, the storm water monitoring network was expanded from one to three locations (Griggs, Gonzalez, and Buddemeir 1983). This program continued through 1984 (Griggs, Meyers, and Buddemeir 1984, Griggs, Meyers, and Buddemeir 1985). In 1985, the scope of LLNL's storm water monitoring program was broadened once again. Samples were collected at four locations during the first major rain following the dry season and analyzed for gross alpha, gross beta, tritiated water, metals, general water quality parameters, and other priority pollutants (Griggs and Buddemeir 1986). The monitoring network was again expanded in 1986 to include six locations. (Holland, Buddemeir, and Brekke 1987). This program continued through 1989 (Holland and Brekke, 1988, Brekke et al. 1989, Sims et al. 1990).

In March of 1989, tritium in a sample of storm water runoff in taken from the on-site drainage basin was measured at 57,400 pCi/L, or 2.87 times the California State Maximum Concentration Level (MCL) of 20,000 pCi/L. Tritium levels in samples taken at three other on-site locations were at or below the MCL.

No unusual releases of tritium from LLNL or its neighbor, Sandia National Laboratory, Livermore (SNLL), that could have caused these elevated levels were identified and review of analytical data showed no reason to reject them (Sims et al. 1990). The combination of an unexplained exceedence of the MCL for tritium in a storm water runoff sample and a need to develop a database in support of a National Pollutant Discharge Elimination System (NPDES) permit application to be filed in late 1991, resulted in the decision to further expand the LLNL runoff monitoring program in 1990. Three storm water runoff sampling locations were added to make a total of nine. Sampling frequency for storm water runoff, which in previous years had included only the period of active surface water flow following the first major storm of the rainy season, was expanded to include any storm with significant runoff (Sims et al. 1991). Storms are required to be separated by periods of at least 24 hours without rainfall (Gallegos et al. 1993). This special study continued through 1991 (Gallegos et al. 1992) and 1992 (Gallegos et al. 1993).

In 1987, the Federal Clean Water Act added section 402(p), which established a framework for regulating municipal and industrial storm water discharges under the NPDES program. Final regulations for storm water permits were published by the EPA in 1990 requiring that storm water associated with industrial activity discharging directly or indirectly to surface waters be regulated by a NPDES permit. The California State Water Resources Control Board administers this program by a statewide General Permit that applies to all industrial storm water discharges requiring a permit (Brandstetter, Brown, and Christofferson 1995). LLNL submitted a Notice of Intent to operate under the conditions of this General Permit in March of 1992 and the State Board subsequently issued permit CAS00001 to LLNL, authorizing storm water

discharges associated with "industrial activity" to surface waters and requiring a specific storm water runoff monitoring program as part of its terms (Welsh 1992).

To reduce analytical costs and to comply with the conditions of the General Permit, the LLNL storm water monitoring network underwent significant changes again in 1993. Four of five on-site sampling locations were eliminated in the fall of 1993 and the frequency of monitoring was reduced from every storm with significant runoff to four storms per year (Gallegos et al. 1994).

Rain Monitoring

Tritium levels in rainfall at LLNL have been monitored and reported since 1971. Until 1990, LLNL collected rainfall from a single on-site location. In 1989, when elevated tritium levels were identified in storm water runoff samples at four of six runoff sampling locations during one of the two storms sampled that year, the tritium level in the rain sample was similar to that measured in previous years (Sims et al. 1990).

In 1990, LLNL expanded both its rain and storm water runoff monitoring programs as part of a special study designed to develop a better understanding of the migration of tritium through the environment. The rain sampling program was enlarged to include seven on-site and ten off-site locations in the Livermore Valley and, instead of monthly composites, rain was sampled and tritium levels were measured after every major rainstorm (major rainstorms must be separated by at least 24 hours without rain). Although not much rain fell in 1990, it was concluded on the basis of that year's data that, although tritium concentration varied widely over on-site locations, elevated concentrations of tritium in rainfall, very localized to LLNL and SNLL, could be identified (Sims et al. 1991). A simple correlation with facility emissions could not, however, be made.

The special study of tritium in rainfall continued into 1991. On April 4, 1991, all but safety related operations were suspended at the LLNL Tritium Facility. The resultant decrease in tritium emissions was quickly followed by a decrease in tritium levels in rainfall (Gallegos et al. 1992). This trend has continued and is illustrated in Figure 4.1.

In early 1993, graphical analyses were performed on tritium levels of rain sampled at 19 locations following 53 rain events between October 1990 and December 1992 (Brandstetter, Brown, and Christofferson 1995). These analyses demonstrated an exponential decrease in tritium activity with distance from the LLNL tritium facility and the former Tritium Research Laboratory at SNLL. Tritium levels in rain were demonstrated to be reduced to background levels at a distance of about 4 km from these sources. Based on these results, and a desire to eliminate redundant sampling and reduce analytical costs, the rain sampling program was significantly reduced in 1993. Eight of nine off-site locations at a distance of greater than 3 km from the LLNL site were eliminated and the sampling frequency was reduced to the same four storm per year schedule as storm water runoff sampling (Gallegos et al. 1994). Five storms were monitored during 1993 (Gallegos et al. 1994). While the mean tritium concentration in rain was significantly different from historical levels, one location exhibited tritium at 147,000 pCi/L, over 7 times the drinking water MCL and 7 times the previously recorded single value (19,500 pCi/L in 1990). On-site locations exhibited elevated tritium levels during the period this sample was collected, but off-site locations did not. The location at which the sample containing elevated levels of tritium was taken is adjacent to the LLNL Tritium Facility. It has been hypothesized that the high level of tritium in rainfall could have been caused by diffuse tritium

Figure 4.1. Decreasing Tritium Concentration in Rainfall at LLNL over Time

emissions caused by routine decommissioning operations in the Tritium Facility yard (Gallegos et al. 1994).

Prior to the start of the rainy season in 1994, one additional off-site rain collection station was added to the monitoring network. This was done after a study of wind directions during rainfall events revealed a gap in the rainfall sampling (Brandstetter, Brown, and Christofferson 1995). Six storms were sampled in 1994 and no unusual results were identified.

Concise Description of the Problem

Storm water runoff monitoring at LLNL addresses two specific problems. The first is to determine the effects, if any, of LLNL activities on onsite and offsite environmental and natural resources as required by DOE Order 5400.1 (DOE 1990, 1991). The second is to ensure compliance with the California Water Resources Control Board Industrial Activities Storm Water General Permit (SWRCB 1992).

Rain monitoring at LLNL is intended to determine the effects, if any, of LLNL activities on the concentration of tritium in onsite and offsite rain, as required by DOE Order 5400.1 (DOE 1990, 1991).

Planning Team and Decision Maker

Because this research relied heavily on existing information, a formal planning team was not established. The LLNL Environmental Monitoring Program Leader served as the primary Decision Maker for this DQO development process. The Environmental Monitoring Program Leader has been assigned the responsibility for ensuring that LLNL's environmental monitoring programs meet all regulatory and DOE requirements. She also manages all

resources required for LLNL environmental monitoring. Relevant personnel, including the responsible Environmental Analyst and a staff statistician, were consulted as needed during the Data Quality Objectives development process.

Available Resources

Environmental monitoring at LLNL is the responsibility of the LLNL Environmental Protection Department (EPD). Day-to-day responsibilities for each monitoring network have been assigned to an Environmental Analyst who oversees sampling activities, analyzes and interprets analytical results, investigates inconsistencies in the data, and prepares any reports required by the Department of Energy or regulatory agencies. Samples are collected by EPD sampling technologists. Tritium analysis is performed by an on-site analytical laboratory. Analysis for metals and pesticides is performed by an off-site contract analytical laboratory. Data are interpreted by the responsible Environmental Analyst and archived both electronically and as hard-copy by EPD data management personnel.

The LLNL Environmental Monitoring Program Leader manages resources in five categories: people, time, space, equipment, and money.

People

Oversight for the storm water runoff and rain monitoring networks is provided by the Environmental Monitoring Program Leader and the Water Guidance and Monitoring Group (WGMG) Leader. The WGMG Leader supervises the Environmental Analysts assigned to these networks. Sampling and data management are provided by the EPD Technical Support Group (TSG).

A Quality Assurance Coordinator ensures that appropriate QA controls are in place. Statistical support is provided by a staff statistician.

Time

The Environmental Analyst assigned to storm water monitoring spends approximately 30% of his time on this network. The Environmental Analyst assigned to rain monitoring spends approximately 5% of his time working on that network (Hoppe 1995). Runoff sampling requires approximately 35 days of a sampling technologists time per year; rain sampling requires approximately 14 days. Data management for both rain and storm water runoff combined requires 15 days per year (Rueppel 1995). Laboratory analysis and preparation of reports for tritium requires approximately 3 days per sample batch and turn around time from the time the sample is submitted to the laboratory to the time the data report is generally received within about 45 days. Laboratory analysis and preparation of data reports for metals and pesticides require approximately 30 days.

Money

Managing the budget for environmental monitoring has become an increasing challenge as Department of Energy funding continues to decline. Funding for this effort is from the overhead portion of LLNL's budget and, as such, it declines when the overall LLNL budget declines. The DOE budget cycle runs from October 1 through September 30 each year. The budget request for environmental monitoring at LLNL is prepared each summer and submitted to Laboratory management. Monitoring required for regulatory compliance, such as storm water monitoring to fulfill NPDES permit requirements, typically takes

priority over surveillance monitoring required by DOE orders. The Environmental Monitoring Program Leader is responsible for preparing and submitting proposals and for managing the environmental monitoring budget.

Space

The storm water runoff and rain monitoring programs are part of a comprehensive monitoring program at LLNL. Space requirements for rain and storm water runoff monitoring are included with those of that program. Space needed includes housing for management, environmental analysts, data management personnel, and sampling technologists; storage space for sample bottles; and storage space for analytical data and monitoring reports.

Equipment

The following equipment is required for sampling storm water runoff: rain suits, rubber boots, safety line and harness, sample bottles, tags and labels for sample bottles, indelible marking pens, Kimwipes or equivalent, disposable rubber gloves, ice chests with double-bagged ice, a field filtration unit with supply of disposable filters (for metals samples), a stainless-steel dip sampler a gasoline-powered generator, detergent for decontaminating equipment, a flashlight, a pH meter, calibration buffer pillows (for calibrating pH meter), Field Tracking Forms, and Chain-of-Custody Forms. Rain sampling requires stainless-steel 13-quart buckets, plastic rain collection gauges, rain-collection bottles, tags and labels for bottles, Kimwipes or equivalent, Chain-of-Custody Forms, and Field Tracking Forms. Both networks require the use of a 4-wheel drive vehicle to access sampling locations. On-site and off-site analytical laboratories are required to have the equipment that is required to prepare and

analyze samples using the analytical methods specified by the responsible LLNL Environmental Analyst.

Relevant Deadlines

Storm water runoff and rain monitoring at LLNL are ongoing. Both storm water runoff and rain monitoring data must be reported in the LLNL Site Annual Environmental Report (SAER), due to the Department of Energy by September 1 of each year. In addition, an annual storm water monitoring report is due to the San Francisco Regional Water Quality Control Board by July 1 of each year.

Step 2: Identify the Decision

The purpose of this step is to define the decision that will be resolved using data to address the problem.

This step and the one that follows will treat tritium separately from copper, zinc, and pesticides. The analytical methodology for tritium has been refined at LLNL to allow extremely low quantitation limits so numerical results for tritium are readily available while the majority of the results for copper, zinc, and pesticides are reported to be less than the analytical laboratory's reporting limit. This, combined with the fact that analytical laboratory reporting limits vary over time and the fact that very few data points are available for these analytes, makes the statistical manipulation for these data much different than for the tritium data. In addition, as a radionuclide, the perceived risk associated with tritium is much different from that associated with nonradiological contaminants so acceptable errors and their consequences as well as the actions that must be taken when the decision is made that tritium has exceeded an action level are quite different.

Decision to be Resolved

Three decisions must be made based on the results of LLNL monitoring of storm water runoff and rain water for tritium. These are

1. Does any one measurement exceed the California MCL of 20,000 pCi/L?
2. Do the data indicate an upward trend in the concentration of tritium in storm water runoff or rainfall at or near the LLNL Livermore Site?
3. Are the data from one or more samples collected during a particular storm significantly different from historical results?

Specific criteria have been identified for determining whether data exhibit an upward trend and whether they are different from historical results. These criteria are defined later in this research.

One major question must be asked based on the results of LLNL monitoring of storm water runoff for copper, zinc, and pesticides. This question is:

- Are the data significantly different from historical results?

Numerical limits for these pollutants in storm water have not been developed, so limit-based actions similar to the one established for tritium are not appropriate for copper, zinc, or pesticides. According to the San Francisco Regional Water Quality Control Board, numerical effluent limitations are not practical for storm water discharges at this time (RWQCB 1995). This decision was made because sources of pollutants and points of discharge for storm water are diffuse and because methods of reducing pollutants in these discharges are in the development stages. Monitoring of storm water discharges is primarily performed to establish baseline values for pollutants of concerns, identify trends, evaluate the effectiveness of best management practices were implemented to

the need for additional control measures, and focus limited resources on the most important problems. The regulated community is quite resistant to numerical limits for storm water and the regulators have been hesitant to propose them. Even the environmental lobbyists seem willing to negotiate away from numerical limits in favor of strong management controls (Folks 1995).

Possible Outcomes from Resolution of Decision Statement

The First Action Level for Tritium

If the concentration of tritium in any sample exceeds the California Maximum Contaminant Level (MCL), a DOE Occurrence Report must be initiated. Occurrence Reporting is a system established by the DOE for providing information regarding critical operations related to DOE owned or operated facilities to DOE management. This system is defined in DOE Order 5000.3B (DOE 1993) which requires that critical information be documented and reported if and when particular activities specified in the Order occur. This information must also be reported to the San Francisco Regional Water Quality Control Board and, through a press release, to the public. Each time the MCL has been exceeded in rain or storm water runoff to date, it has been reported in local newspapers and EPD personnel have been required to answer questions from media personnel as well as members of local environmental activist groups. If a release of tritium by LLNL or by its neighbor SNLL is ever identified as the cause of tritium levels in storm water runoff or rainfall exceeding the MCL, this fact may have a significant impact on Laboratory operations. Actions that will be taken whenever the tritium concentration in any storm water runoff or rain sample exceeds the MCL include notification of EPD and LLNL management, a thorough investigation of the sampling and analytical processes to ensure that no

discrepancies can be identified, reanalysis of the sample, and analysis of additional water from the same sample, if possible. If none of the above activities can explain the elevated levels, the results will be reported to the regulatory agencies mentioned above, and investigation of any potential releases of tritium by LLNL or SNLL that could have caused the increased level of tritium will be initiated.

If the concentration of tritium is found to be below the California MCL, the data will be evaluated for trends and consistency with historical results.

The Second Action Level for Tritium

Tritium levels in storm water runoff rainfall at and around LLNL have historically been well below the MCL. Since 1991, when operations at the LLNL tritium facility were ceased, the concentration of tritium in rainfall has decreased steadily, with the exception of rainfall samples from one storm in 1993. If this trend is reversed, and tritium levels begin to show a steady increase, sampling and analytical methodology will be reviewed to ensure that no systematic problems can be found there that would explain the upward trend. If no sampling or analytical inconsistencies are found, management will be notified and an investigation of tritium activities at LLNL and SNLL will be undertaken to attempt to identify the source of the increase.

If no upward trend in tritium concentration is identified using the criteria that are defined later in this research, no action will be required.

The Third Action Level for Tritium

If tritium data are determined to be significantly different from historical results, sampling and analytical methodology will first be reviewed to ensure

The Third Action Level for Tritium

If tritium data are determined to be significantly different from historical results, sampling and analytical methodology will first be reviewed to ensure that no errors or process inconsistencies can be identified. If no discrepancies with sampling or analysis are found, future results will be monitored to determine whether they are significantly different from historical levels or whether they indicate the start of a new trend. The same actions as those required when an upward trend is identified will be required when results differ significantly from historical levels.

The Action Level for Metals or Pesticides

Metal and pesticide concentrations in storm water runoff are to be measured using the most sensitive method available and data typically fall slightly above or below analytical laboratory reporting limits. This is not an ideal situation, especially since analytical laboratory reporting limits can vary from sample to sample. When analytical laboratory reporting limits decrease, analytes that have never been detected in a particular medium or at a particular location may suddenly become quantifiable. If analytical laboratory reporting limits are later raised, the concentration of those analytes may be below the new limits and they may be reported as nondetects, although the actual concentrations may be the same, or even higher than they were when the reporting limit was lower.

The system of best management practices for control of pollutants in storm water defined in the LLNL Storm Water Pollution Prevention Plan (SWPPP) (Eccher et al. 1994) is expected to result in decreasing or, at worst, unchanging levels of these analytes over time. If the concentration of one of these analytes begins to show a steady increase that cannot be explained by sampling

upward trend is reversed. The results of such an incident would be reported in the Site Annual Environmental Report to the DOE and the annual Storm Water report to the Regional Water Quality Control Board. If the incident is determined to be a result of not following the LLNL SWPPP, a 30 day reporting requirement in the General Permit would be activated. If hazardous contaminants are found in storm water above CERCLA or RCRA reporting levels, the immediate reporting requirements of those laws would be activated. A DOE Occurrence Report may be required when unusual results are identified that cannot be explained by sampling or analytical error (DOE 1993, Cochran et. al 1994).

If pesticides, copper, or zinc are not found at concentrations significantly different from historical results according to the criteria defined later in this research, no action will be required.

Step 3: Identify the Inputs to the Decision

The purpose of this step is to identify the information that will be required to resolve the decision and determine the environmental measurements required to obtain this information.

Information Necessary to Resolve the Decision

To resolve the specified decisions for storm water runoff, samples of LLNL storm water influent and effluent at the LLNL Livermore site must be collected and analyzed for tritium, copper, zinc, and pesticides. To resolve the specified decisions for rain water, samples of rainfall at and around the LLNL Livermore site must be collected and analyzed for tritium content.

Sources of Data or Information

Storm water runoff and rain monitoring at and around the Livermore site are ongoing and historical data are readily available in the Environmental Monitoring Program database and in published reports.

Information Necessary to Establish Action Levels

Tritium

The first action level for tritium is met when the California MCL of 20,000 pCi/L is exceeded in any one sample of rain or storm water runoff. The second action level is achieved when an upward trend in the level of tritium in rain or storm water runoff is identified. Establishing this level will require a rule for determining when an upward trend is occurring. The third action level is reached when the level of tritium in one or more samples collected during a particular storm differs significantly from historical values for that parameter at that location. A set of rules for determining values that are significantly different from historical levels will be required to establish this level. Specific actions to be taken when action levels are exceeded must be defined for all three levels.

Copper, Zinc and Pesticides

Action is required when the level of copper, zinc, or pesticides in storm water runoff at a particular sampling location is determined to be significantly different from historical results. A set of rules for determining values that are significantly different from historical levels will be required to establish this level. Specific actions to be taken when the action level is exceeded must also be defined.

Field Sampling Methods

Field sampling for rain and storm water sampling is conducted according to standard operating procedures (Christofferson 1994a, Christofferson 1994b, Hoppes 1994, Welsh 1994).

Storm Water Runoff Sampling

Storm water runoff is sampled at six locations to characterize influent, effluent, and on-site runoff. Storm water sampling locations are illustrated in Figure 4.2. Storm water runoff sampling at LLNL is performed either by dip sampling or by grab sampling. The method to be used depends upon access, water flow, and other conditions and usually must be determined by the technologist at the time of sampling. When dip sampling is performed, a stainless-steel sampling bucket is triple rinsed with the water to be sampled then dipped or submerged in the water to be sampled and withdrawn in a smooth motion. Sampling near the edge of surface water bodies is avoided to minimize the collection of sediment that may be present in the sample matrix. Samples to be analyzed for metals are filtered using a field filtration unit. Bottles are stored in an ice chest for transportation to the analytical laboratory. Equipment is decontaminated between sampling locations with deionized water and cleaned with detergent and deionized water then rinsed with deionized water prior to storage.

If the water to be sampled is accessible to the technologist and bottles have not been preacidified, grab sampling can be used in place of dip sampling. Grab samples are collected by partially submerging sample bottles directly into the water, allowing them to fill with the sample water.

Figure 8-1. Storm water runoff sampling locations, Livermore site and vicinity.

Figure 4.2. Storm Water Runoff Sampling Locations at LLNL (Tate et al. 1995)

A duplicate sampling location is selected from the routine sampling locations using a random number table before the beginning of the quarter in which storm water runoff sampling will occur. The duplicate sample should be taken in an equivalent manner to a routine sample and is submitted "single blind" to the analytical laboratory (an artificial sample location designator is assigned to the duplicate sample so the analytical laboratory is unaware that it is a duplicate.)

Rain Sampling

Rainwater is collected in rain gauges and stainless-steel collection buckets that are left in place year-round at 7 on-site and 6 off-site sampling locations illustrated in Figure 4.3. Rain is decanted from the buckets after each storm but only required to be sampled during four storms each year. Rain gauges are read and sample buckets are emptied by LLNL technical staff each time there is at least a 12-hr break between rain storms. When rain is to be sampled, it is poured into 500 ml flint glass bottles with stoppers. Quality assurance replicate samples for rain are taken at one randomly determined location for each sampling event. The replicate sample is submitted "single blind" to the analytical laboratory (an artificial sample location designator is assigned to the replicate sample so the analytical laboratory is unaware that it is a replicate.)

Analytical Methods

Tritium

Rain and storm water runoff samples are analyzed for tritium by an LLNL analytical laboratory. Samples can be vacuum distilled under argon to purify the water and electrolytically enriched to improve accuracy, however, enrichment is seldom done for rain or storm water runoff samples (Edwards 1995). The

Figure 4.3. Rain Sampling Locations, Livermore Site and Livermore Valley
(Tate et al. 1995)

electrolytical enrichment procedure is used when tritium content is suspected to be less than or equal to 0.1 pCi/mL or if results below this detection limit are required. The HTO (tritiated water) content in rain and storm water runoff samples is usually determined by liquid scintillation or internal gas-conversion proportional counting when sample volumes are small (Bazan 1995). This method can give a detection limit of around 100 pCi/L.

Samples are delivered directly to the on-site laboratory for tritium analysis by the sampling technologists. If samples must be stored overnight before they can be delivered, they are stored in a secure location until they can be delivered. Refrigeration is not required for samples that will be analyzed for tritium.

Metals

Copper and zinc are analyzed by an off-site analytical laboratory under contract to LLNL using EPA Method 200.7, Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES). This is a high sensitivity, multi-element method of metals analysis.

All samples that are sent to contract analytical laboratories for metals analysis are packaged in ice chests along with double-bagged ice or blue-ice, sealed, and delivered to a courier for transportation to the laboratory for analysis.

Pesticides

Pesticides are analyzed by an off-site analytical laboratory under contract to LLNL using EPA Method 608. In this method, the sample is first solvent extracted with methylene chloride using a separatory funnel. The extract is then dried and exchanged to hexane during a concentration to 10 mL or less. The

.specified list of 25 pesticides and PCBs is then separated and measured by electron capture gas chromatography (USEPA 1982).

All samples that are sent to contract analytical laboratories are packaged in ice chests along with double-bagged ice or blue-ice, sealed, and delivered to a courier for transportation to the laboratory for analysis. The specified hold time for this method is 7 days for extraction and 40 days after extraction for analysis.

STEP 4: DEFINE THE BOUNDARIES OF THE STUDY

The purpose of this step is to specify the spatial and temporal circumstances that are covered by the decision.

Spatial and Temporal Boundaries of the Decision

Geographic Boundaries for Storm Water Runoff

The natural drainage of the LLNL Livermore Site flows northwest from the southeast corner. The main channel of the Arroyo Seco, as shown in Figure 4.4, crosses the center of the Sandia National Laboratory/California site, located directly to the south of the LLNL site, then cuts diagonally across the southwest corner of the LLNL site, carrying drainage in a northwesterly direction. Arroyo Las Positas enters the site on its eastern boundary, near the northeast corner. From there, it has been channeled towards the northeast until it crosses the northern boundary of the site near the northeast corner and then west along the north perimeter to an outlet at the northwest corner where it carries drainage in a northerly direction (Eccher et al. 1994). This outlet, which constitutes the main pathway for the site's surface drainage (storm and irrigation runoff) runs north to the Western Pacific railroad tracks, then west, where it joins the Arroyo Seco. Both arroyos are dry year-round except for storm water runoff.

Figure 4.4. Livermore Site Storm Water Influent and Effluent

On-site drainage for developed areas of the site can be divided into three segments. Drainage from the southeast portion flows through conduits and unlined open channels into siltation basins and then into a lined retention basin. Retention basin outflow is controlled by a weir that can be used to release water to Arroyo Las Positas as desired. A small portion of the drainage from the southwest portion of the site flows through unlined open channels and conduits to the Arroyo Seco. The westerly and northerly portions flow through conduits and unlined open channels into Arroyo Las Positas (Eccher et al. 1994).

On-site drainage for undeveloped portion of the site is divided into two segments. The northern area sheet flows west along Patterson Pass Road into Arroyo Las Positas. The western area sheet flows to and through conduits and unlined open channels northward along Vasco Road and into Arroyo Las Positas (Eccher et al. 1994).

The overall storm water monitoring program characterizes influent to and effluent from the LLNL site. Two monitoring locations are required by the NPDES General Permit to characterize site effluent; four additional locations characterize influent to the site and flow into the Central Drainage Basin, which collects storm water runoff from a large percentage of the site.

The two sampling locations required by the NPDES general permit are L-WPDC and L-ASW. Location L-WPDC monitors discharges into Arroyo Las Positas from drainage channels that collect effluent from internal site channels and the Central Drainage Basin. This effluent then passes eastward through undeveloped land via a drainage channel and exits LLNL at Patterson Pass Road. Location L-ASW characterizes Arroyo Seco effluent in the southwest area of the Site.

Influent to the site is monitored at locations L-ASS2, L-ALPE, and L-GRNE. Location L-ASS2 characterizes influent in the Arroyo Seco near the southwest corner of the site. L-ALPE is near the intersection of East Gate Drive and Greenville Road, on the eastern edge of the site, and L-GRNE is on Greenville Road at the northwest corner of the site. These two locations monitor influent in Arroyo Las Positas. A final monitoring location, L-CDB, is located at the point where site runoff enters the Central Drainage Basin.

LLNL storm water runoff monitoring locations are illustrated in Figure 4.2.

Geographic Boundaries for Rain

Recent analysis of monitoring and meteorological data from on-site and off-site rain monitoring locations led to the conclusion that the concentration of tritium in rainfall decreases quickly with distance from the source of tritium (Gallegos et al. 1994). Tritium levels were found to decrease to background levels at a distance of 3 to 4 kilometers from the LLNL and SNLL/CA sites. Once this analysis was completed, the number of off-site monitoring locations for rain was significantly decreased. Based on this information, the geographic area within which the decision must apply is limited to a circle with a radius of 4 km and its center at the LLNL tritium facility (see Figure 4.3).

Temporal Boundaries

Rain and storm water runoff samples are collected during a minimum of four storm events per year. The first event sampled should be the first storm of the wet season in which there is significant discharge (continuous flow for at least one hour). The fourth and final event should preferably be the final storm of

the wet season in which there is significant discharge. If samples have been obtained and flow ceases before one hour of significant discharge, samples should be discarded. Sampling can only take place during or up to two hours after scheduled facility operating hours (8 am to 5 PM, Monday through Friday, excluding holidays). Two additional storms should also be sampled. Sampling should occur in alternate months, if possible. Sampled storms should be separated from one another by at least one month, and should not exceed four storms per year. Additional storms may be sampled at the discretion of the responsible Environmental Analyst.

Time Frame to which Data Apply

Since this is an ongoing monitoring program, there is no specific time frame to which the data apply, however, this research is limited to data collected between January 1, 1992, and December 31, 1994.

Data are reviewed and reported to DOE, regulatory agencies, and the public at least annually.

Practical Constraints on Data Collection

Any storm water monitoring is dependent upon the availability of sufficient precipitation for sampling. Historically, not all locations have been sampled during the requisite number of storms due to insufficient rainfall or storm water runoff. In addition, the safety of the sampling technologist is of utmost concern and sampling is not done when unsafe conditions exist.

Step 5: Develop a Decision Rule

The purpose of this step is to integrate the outputs from previous steps into a single statement for each action level that describes the logical basis for choosing among alternative actions.

Tritium

The First Action Level for Tritium

The first action level for tritium is reached when the level of tritium in any storm water runoff or rainfall sample collected at or near LLNL exceeds the California MCL of 20,000 pCi/L.

When this occurs, the following steps will be taken.

1. Sampling and analysis records, including field and analytical QC data, will be reviewed to ensure that no activities occurred that could have contributed to artificially high levels of tritium being reported;
2. If nothing is identified that satisfactorily explains the elevated level, the WGMG Leader and the EMP Leader will be notified, the sample or samples will be reanalyzed and, if possible, a second subsample from the same storm and location will be analyzed; and
3. If the concentration in the reanalyzed sample or the second subsample is still above the MCL, the WGMG Leader and the EMP Leader will be notified, a DOE Occurrence Report will be initiated, a full investigation into the root cause of the elevated concentration will be carried out, and a corrective action program will be designed and implemented.

The LLNL Public Affairs Office will be contacted and they will determine the course of action to be taken with respect to notifying the media and the public.

The Second Action Level for Tritium

The second action level for tritium is reached when the level of tritium in storm water runoff or rainfall sample collected at a particular location shows a consistent upward trend:

In order to determine whether trends exist in LLNL rain or storm water runoff samples, a control chart showing the natural logarithm of the concentration of tritium ($\ln [T]$) versus time will be made for each monitoring location. Control limits will be calculated using the method presented by Lindsay (1990) for $\bar{X}$ and R_m charts. This type of chart is typically used for individual values when an independent estimate of variability is not available at any instant. Control limits are based on a moving range which is calculated for each pair of data points. For the purposes of this research, an upward trend will be identified by either (1) six data points in a row showing an increase in $\ln [T]$; (2) eight of ten data points in a row showing an increase in $\ln [T]$; or (3) seven data points in a row above the centerline.

When a consistent upward trend in the tritium concentration at one or more locations is identified, the following steps will be taken.

1. Sampling and analysis records, including field and analytical laboratory QC data, will be reviewed to ensure that no activities occurred that could have contributed to artificially high levels of the analyte being reported;
2. If nothing is identified that satisfactorily explains the upward trend, the WGMG Leader and the EMP Leader will be notified and the trend will be closely monitored. If a trend continues for at least one year without reaching the regulatory limit associated with the First Action

Level, an investigation of the source of the trend will be initiated by the responsible Environmental Analyst. If no source is identified, the trend will continue to be monitored and the attempt to find it will be revisited periodically.

The Third Action Level for Tritium

The third action level for tritium is reached when the level of tritium in one or more samples collected during a particular storm differs significantly from historical values for tritium at that location. The control charts developed for identifying upward trends can also be used to make this determination. Data are determined to be significantly different from historical results when (1) any single data point falls outside the control limits; (2) four of five consecutive data points fall beyond one standard deviation (on the same side of the centerline); or (3) two of three consecutive data points fall beyond two standard deviations (on the same side of the centerline).

When this occurs, the following steps will be taken.

1. Sampling and analysis records, including field and analytical laboratory QC data, will be reviewed to ensure that no activities occurred that could have contributed to artificially high levels of the analyte being reported;
2. If nothing is identified that satisfactorily explains the inconsistency, the WGMG Leader and the EMP Leader will be notified and the location or locations at which the inconsistent result occurred will be closely monitored. If a trend is identified, it will be investigated as described above.

Metals and Pesticides

The action level for copper, zinc, or pesticides is reached when the level of copper, zinc, or pesticides in storm water runoff or rainfall sample collected at a particular location is significantly different from historical results.

Historically, these analytes are either found to be (1) consistently below the analytical laboratory reporting limit, or (2) slightly above the analytical laboratory reporting limit with some values below that limit.

Unlike tritium, which was measured in every storm during 1992 and 1993, resulting in a relatively large data set, copper, zinc, and most pesticides were not measured prior to 1993. This means that few data are available and, since the LLNL standard operating procedure only requires monitoring in four storms per year, the amount of data is not growing quickly. Since 25 points are required to construct a control chart (Lindsay 1990), the methods of data evaluation developed for tritium cannot be applied to metals or pesticides. Instead, more qualitative decision criteria were developed.

When the results for a particular analyte at a particular location typically fall below the analytical laboratory's reporting limit, the decision will be made that results are significantly different from historical values and action will be taken when (1) two storms in a row show data above the analytical laboratory reporting limit (assuming the reporting limit has not been decreased significantly) or (2) two of the four storms measured during a particular rain year (October through May) show results above the analytical reporting limit.

When the results for a particular analyte at a particular location are typically slightly above the analytical laboratory reporting limit with the possibility of some values falling below that limit, the decision will be made that data are significantly different from historical results and action will be required

when (1) the frequency of results above the reporting limit increases by two or more over that measured during the previous rain year (assuming the reporting limit has not been decreased significantly), or (2) a plot of the average concentration of the analyte at that location (using the laboratory reporting limit for results reported as less than that value) appears to show an upward trend.

The action level will also be reached when any single data point is greater than or equal to 10 times the laboratory reporting limit. These criteria are summarized in Table 4.1.

When the concentration of copper, zinc, or pesticides at one or more locations is determined to be significantly different from historical results, the following steps will be taken.

1. Sampling and analysis records, including field and QC data, will be reviewed to ensure that no activities occurred that could have contributed to erroneously high levels of the analyte being reported;
2. If nothing is identified that satisfactorily explains the inconsistent results, the WGMG Leader and the EMP Leader will be notified, and future data for that analyte at that location will be closely monitored. If a trend is established that continues for at least one year (four storms), an investigation will be initiated by the responsible Environmental Analyst. If no source is identified, the data will continue to be monitored and the attempt to find an explanation will be revisited periodically.
3. If the increase is traced to a particular source, action will be taken to minimize or eliminate that source through management controls.

Table 4.1. Criteria for Identifying Copper, Zinc, or Pesticide Concentrations that are Significantly different from Historical Results

IF the true condition is...	AND...	THEN
The results for an analyte at a location are typically below the analytical laboratory reporting limit	The analyte is detected in one storm (only)	Gray Area (not of concern to primary decision maker)
The results for an analyte at a location are typically below the analytical laboratory reporting limit	The analyte is detected in two of four storms during one rain year	Data are significantly different from historical results
The results for an analyte at a location are typically below the analytical laboratory reporting limit	The analyte is detected in two storms in a row	Data are significantly different from historical results
The results for an analyte at a location are typically slightly above the analytical laboratory reporting limit with some values below that limit	The frequency of results above the laboratory reporting limit during a particular rain year increases by one per year or less	Gray Area (not of concern to primary decision maker)
The results for an analyte at a location are typically slightly above the analytical laboratory reporting limit with some values below that limit	A visual inspection of a plot of the concentration of the analyte over time shows no apparent upward trend	Gray Area (not of concern to primary decision maker)
The results for an analyte at a location are typically slightly above the analytical laboratory reporting limit with some values below that limit	The frequency of results above the laboratory reporting limit during a particular rain year increases by two or more per year	Data are significantly different from historical results
The results for an analyte at a location are typically slightly above the analytical laboratory reporting limit with some values below that limit	A visual inspection of a plot of the concentration of the analyte over time shows an apparent upward trend	Data are significantly different from historical results
Any analyte is measured at a concentration greater than 10 times the analytical laboratory reporting limit	—	Data are significantly different from historical results

4. The upward trend and any action taken to eliminate it will be reported to the RWQCB in the annual Storm Water Monitoring Report and to the DOE in the Site Annual Environmental Report.

Step 6: Specify Acceptable Limits on Decision Errors

The purpose of this step is to specify the decision maker's acceptable limits on decision errors, which are used to establish appropriate performance goals for limiting uncertainty in the data.

The activities that must be undertaken to complete this step include:

- Determining the possible range of the parameter of interest;
- Defining both types of decision errors (false positive and false negative errors) and identifying the potential consequences of each;
- Specifying a range of possible parameter values where the consequences of decision errors are relatively minor (gray region);
- Assigning probability values to points above and below the action level that reflect the acceptable probability for the occurrence of decision errors; and
- Checking the limits on decision errors to ensure that they accurately reflect the decision maker's concern about the relative consequences for each type of decision error.

The required outputs from this step include:

- The decision maker's acceptable decision error rates based on a consideration of the consequences of making an incorrect decision.

Possible Range of Tritium

The lowest level of tritium that has been measured in storm water runoff or rainfall is less than the detection limit of approximately 100 pCi/L. The highest level that has been measured since 1971 is 147,000 pCi/L, measured in rain from a February 1993 storm.

Decision Errors For Tritium Action Levels

This section attempts to quantify the willingness of the primary decision maker to accept error, based upon the associated consequences and the difference between the measured value and the true value.

The First Action Level for Tritium

Error Types and Consequences

The two types of decision errors are (1) deciding that the level of tritium in rain or storm water runoff has exceeded the MCL of 20,000 pCi/L when it has not, or (2) deciding that the level of tritium has not exceeded the MCL when it has.

The consequences of deciding that the level of tritium in rain or storm water runoff has exceeded the MCL when it has not are extremely negative: publicity for the laboratory; loss of public confidence; loss of confidence with the regulatory community; and costs associated with additional sampling, analysis, and investigations required to verify or disprove the high tritium values as well as preparing and completing a DOE Occurrence Report.

The consequences of deciding that the level of tritium in rain or storm water runoff has not exceeded the MCL when it has are a potential for a very slightly increased dose to onsite and off-site populations in the affected areas.

The drinking water MCL for tritium is based on consumption of 2 liters per day of water containing 20,000 pCi/L of tritium.

There are two exposure routes to consider for tritium in rainfall. The first is ingestion. Though rain is not a source of drinking water for the Livermore Valley, some individuals might consume a small amount of rainwater. The drinking water MCL for tritium is based on consumption of 2 liters per day of water containing 20,000 pCi/L of tritium to give an effective dose equivalent of 1 mrem per year (Gallegos et al. 1993). If an individual consumed one liter of rainwater containing 20,000 pCi of tritium, the effective dose equivalent would be $\{1/(2 \times 365)\}$ or 0.05 mrem; substantially below the 300 mrem per year background dose for residents of the Livermore Valley (Failor 1995). Ingestion of tritium could also occur by consumption of meat from animals that have been drinking rainwater. This pathway would be a much smaller source of tritium due to the relatively small amount of meat consumed and the small amount of tritium that would be retained in the meat. (The biological half-life, or the time it takes for the body to eliminate half of the tritium consumed is known to range from three to 12 days, with a most frequently occurring value of 8 days. This means that animals consuming water containing tritium will eliminate that tritium from their bodies at a rate of one half approximately every 8 days.)

The second exposure pathway for tritium is absorption through the skin when water containing tritium wets the skin or clothing. Since tritium exposure would be very small via either of these pathways, the public exposure consequence of deciding that the level of tritium has not exceeded the MCL when it has would be very minor. Additionally, it is unlikely that a tritium release that would noticeably affect the tritium concentration in rainfall would not be detected by LLNL's air effluent and air surveillance monitoring networks.

The primary decision maker has decided that the first decision error (deciding that the level of tritium in rain or storm water runoff has exceeded the MCL when it has not) has the more severe consequences.

The true state of nature when the more severe decision error occurs (the tritium level in a single measurement is determined to exceed the MCL when it does not) is that the tritium level is below the MCL. The baseline condition or null hypothesis (H_0) is: the tritium level is below the MCL. The false positive decision error occurs when H_0 is rejected when it is in fact true. In this case, the false positive decision occurs when the Environmental Analyst decides that the tritium level is above the MCL when it is not.

The true state of nature when the less severe decision error occurs (the tritium level in a single measurement is determined not to exceed the MCL when it does) is that the tritium level is above the MCL. The alternative hypothesis (H_a) is: the tritium level is above the MCL. The false negative decision error occurs when H_0 is accepted when it is not true. In this case, the false negative decision occurs when the Environmental Analyst decides that the tritium level is below the MCL when it is not.

Gray Region

The gray region is the area adjacent to the action level where the primary decision maker feels that the consequences of a false negative decision error are minimal. In this case, the primary decision maker has determined that the gray region lies between 20,000 and 25,000 pCi/L.

Design Performance Goal Table

The Design Performance Goal Table for the first action level for tritium, exceeding the California MCL of 20,000 pCi/L, is given in Table 4.2. The percent values shown in that table represent the percentage of the time that the primary decision maker can accept an incorrect decision.

The Second Action Level for Tritium

Error Types and Consequences

The two types of decision errors are (1) deciding that an upward trend in tritium concentration has been established in rain or storm water runoff when it has not, and (2) deciding that a trend has not been established when it has.

The consequences of deciding that an upward trend in the level of tritium in rain or storm water runoff exists when it has not are additional resource expenditures related to investigation of the problem. These would include the time spent by the responsible Environmental Analyst and other staff investigating the problem as well as reanalysis of existing samples or possible expansion of monitoring to include more storms, more sampling locations, or additional quality control samples. Depending on the severity of the trend, consequences could also include the necessity of writing a DOE Occurrence Report or reporting the trend to the Regional Water Quality Control Board. If either of these occurs, negative publicity for the Laboratory will result as well.

The consequences of deciding that no upward trend in tritium concentration exists in rain or storm water runoff when there is an actual upward trend are minimal since existing levels of tritium are typically so far below the MCL (the average tritium concentration in storm water runoff between 1992 and

**Table 4.2. Design Performance Goal Table for First Action Level for Tritium
(Tritium Concentration Exceeds California MCL of 20,000 pCi/L)**

<u>True Concentration</u>	<u>Correct Decision</u>	<u>Acceptable Probability of Making an Incorrect Decision</u>
0 - 20,000 pCi/L	Tritium level is below the MCL	1%
20,000 - 25,000 pCi/L	Tritium level is above the MCL	gray region - no probability specified
25,000 - 30,000 pCi/L	Tritium level is above the MCL	5 %
>30,000 pCi/L	Tritium level is above the MCL	1 %

1994 was 175 pCi/L and that for rain was 325 pCi/L.)

The primary decision maker has decided that the first decision error has the more severe consequences.

The true state of nature when the more severe decision error occurs (an upward trend in the tritium concentration in rain or storm water runoff is determined to exist when it does not) is that there is no upward trend in tritium concentration. The baseline condition or null hypothesis (H_0) is: the tritium levels in rain and storm water runoff are constant or exhibit a downward trend. The false positive decision error occurs when H_0 is rejected when it is in fact true. In this case, the false positive decision occurs when the Environmental Analyst decides that there is an upward trend in the tritium concentration in rain or storm water runoff when such a trend does not exist.

The true state of nature when the less severe decision error occurs (an upward trend in the tritium concentration in rain or storm water runoff is determined not to exist when it does) is that the tritium level in rain or storm water runoff is steadily increasing. The alternative hypothesis (H_a) is: the tritium level in rain or storm water runoff exhibits an upward trend. The false negative decision error occurs when H_0 is accepted when it is not true. In this case, the false negative decision occurs when the Environmental Analyst decides that the tritium levels in rain or storm water runoff are constant or decreasing when, in fact, they are steadily increasing.

Gray Region

The gray region is the area adjacent to the action level where the primary decision maker feels that the consequences of a false negative decision error are minimal. The primary decision maker has determined that the consequences of

not identifying an upward trend in the concentration of tritium in rain or storm water runoff that results in an increase to a level that is less than or equal to three times the historical average tritium concentration during a one year period are minimal. The gray region is defined as shown in the following Design Performance Goal Table.

Design Performance Goal Table

The Design Performance Goal Table for the second action level for tritium, establishment of a consistent upward trend, is given in Table 4.3.

The Third Action Level for Tritium

Error Types and Consequences

The two types of decision errors are deciding that the tritium concentration in one or more rain or storm water runoff samples collected from a single storm are significantly different from historical results when they are not or deciding that results are consistent with historical results when they are significantly different.

The consequences of deciding that the tritium concentration in one or more rain or storm water runoff samples collected from a single storm are significantly different from historical results when they are not include additional resource expenditures related to investigation of the problem. These would include the time spent by the responsible Environmental Analyst and other staff investigating the problem as well as reanalysis of existing samples or possible expansion of monitoring to include more storms, more sampling locations, or additional quality control samples. Depending on the severity of the

Table 4.3. Design Performance Goal Table for Second Action Level for Tritium (Tritium Concentration Exhibits an Upward Trend)

<u>True Condition</u>	<u>Correct Decision</u>	<u>Acceptable Probability of Making an Incorrect Decision</u>
Tritium levels in rain or storm water runoff are constant or decreasing	Upward trend in tritium concentration does not exist	1%
Tritium levels in rain or storm water runoff increase to $\leq 3X$ the historical average during a period of one year or less	Upward trend in tritium concentration exists	gray region - no probability specified
Tritium levels in rain or storm water runoff increase by $\geq 5X$ during period of one year or less	Upward trend in tritium concentration exists	50% for a 5X increase

perceived inconsistency, consequences could also include the necessity of writing a DOE Occurrence Report or reporting the increase to the Regional Water Quality Control Board. If either of these occurs, negative publicity for the Laboratory is likely to result as well.

The consequences of deciding that data do not differ significantly from historical results when they do (assuming that the inconsistent results are not near the MCL) are minimal since existing levels of tritium are typically so far below levels of concern. Inconsistent results that fall near the MCL must be evaluated as described above for the first action level.

The primary decision maker has decided that the first decision error (deciding that the tritium concentration in one or more rain or storm water runoff samples collected from a single storm are significantly different from historical results when they are not) has the more severe consequences.

The true state of nature when the more severe decision error occurs (data are determined to be significantly different from historical results when they are not) is that data are significantly different from historical results. The baseline condition or null hypothesis (H_0) is: the tritium levels in rain and storm water runoff are significantly different from historical results. The false positive decision error occurs when H_0 is rejected when it is in fact true. In this case, the false positive decision occurs when the Environmental Analyst decides that the tritium concentration in one or more samples collected during a single storm is significantly different from historical results when in fact it is not.

The true state of nature when the less severe decision error occurs (data that are significantly different from historical results are determined to be consistent) is that the tritium concentration in rain or storm water runoff is, in fact, significantly different that it has been historically. The alternative hypothesis

(H_a) is: the tritium level in one or more samples collected during a single storm is significantly different from historical results. The false negative decision error occurs when H₀ is accepted when it is not true. In this case, the false negative decision occurs when the Environmental Analyst decides that the tritium levels in rain or storm water runoff sampled during a particular are significantly different from historical results when, in fact, they are not.

Gray Region

The gray region is the area adjacent to the action level where the primary decision maker feels that the consequences of a false negative decision error are minimal. The primary decision maker has determined that the gray region includes a zero to 25% increase over historical levels.

Design Performance Goal Table

The Design Performance Goal Table for the third action level for tritium, one or more data points differing significantly from historical results, is given in Table 4.4.

Copper, Zinc, and Pesticides

Possible Ranges of Copper, Zinc and Pesticides

Copper

The highest level of copper measured in storm water runoff between 1992 and 1994 was 0.97 mg/L, measure at location L-ALPE for a November 10, 1992 storm. The lowest level of copper measured was less than the analytical laboratory's reporting limit of 0.01 mg/L. However, the analytical reporting limit has varied depending on the laboratory, the method used, and the sample.

Analytical laboratory reporting limits that have been specified for copper in storm water runoff include: <0.005 mg/L, <0.01 mg/L, and <0.05 mg/L.

Zinc

The highest level of zinc measured in storm water runoff between 1992 and 1994 was 1.8 mg/L, measure at location L-ASS2 for a November 10, 1993 storm. The lowest level of zinc measured was less than the analytical laboratory's reporting limit of <0.05 mg/L. Unlike the limit for copper, the laboratory reporting limit for zinc remained the same throughout the study period.

Pesticides by EPA Method 608

The highest levels of pesticides measured in storm water runoff by EPA Method 608 between 1992 and 1994 were 0.5 µg/L of Eldrin, measure at location L-WPDC for a February 12, 1992 storm and 0.05 µg/L of Lindane measured at location L-ASW for an October 29, 1992 storm. No other pesticides measured by this method were reported above the analytical laboratory reporting limits, however, those limits varied during this period. Control of analytical laboratory reporting limits has not been tight and has been subject to change by the analytical laboratory without approval by LLNL. A clear explanation of the cause of this variation was not available and is beyond the scope of this research.

The Action Level for Zinc, Copper, and Pesticides

Error Types and Consequences

The two decision errors are (1) deciding that the copper, zinc, or pesticide concentration in one or more storm water runoff samples collected from a single storm are significantly different from historical results when they are not,

**Table 4.4. Design Performance Goal Table for Third Action Level for Tritium
(Tritium Concentration Significantly Different from Historical Results)**

<u>True Condition</u>	<u>Correct Decision</u>	<u>Acceptable Probability of Making an Incorrect Decision</u>
Tritium levels in rain or storm water runoff collected during a particular storm are significantly different from historical results	Concentration significantly different from historical results	1%
Tritium levels in a particular rain or storm water runoff sample differs $\leq 25\%$ from historical levels	Concentration significantly different from historical results	gray region - no probability specified
Tritium levels in rain or storm water runoff differs $> 25\%$ from historical levels	Concentration significantly different from historical results	33%

or (2) deciding that results are consistent with historical results when they are not.

The consequences of deciding that the copper, zinc, or pesticide concentration in one or more storm water runoff samples collected from a single storm is significantly different from historical results when it is not include additional resource expenditures related to investigation of the problem. These would include the time spent by the responsible Environmental Analyst and other staff investigating the problem, as well as the resources required for reanalysis of existing samples or possible expansion of monitoring to include more storms, more sampling locations, or additional quality control samples. Depending on the severity of the perceived inconsistency, consequences could also include the necessity of writing a DOE Occurrence Report or reporting the trend to the Regional Water Quality Control Board. If either of these occurs, negative publicity for the Laboratory is likely to result as well.

The consequences of deciding that data are consistent with historical results when they are not are minimal since existing levels of copper, zinc, or pesticides are typically extremely low and numerical limits for these analytes have not been defined.

The primary decision maker has decided that the first decision error has the more severe consequences.

The true state of nature when the more severe decision error occurs (data are determined to be significantly different from historical results when they are consistent) is that data are significantly different from historical results. The baseline condition or null hypothesis (H_0) is: the copper, zinc, or pesticide levels in rain and storm water runoff are significantly different from historical results. The false positive decision error occurs when H_0 is rejected when it is in fact true.

In this case, the false positive decision occurs when the Environmental Analyst decides that the copper, zinc, or pesticide concentration in one or more samples collected during a single storm is significantly different from historical results when in fact it is not.

The true state of nature when the less severe decision error occurs (data that are significantly different from historical results are determined to be consistent) is that the copper, zinc, or pesticide concentration in storm water runoff is, in fact, significantly different that it has been historically. The alternative hypothesis (H_a) is: the copper, zinc, or pesticide level in one or more samples collected during a single storm is significantly different from historical results. The false negative decision error occurs when H_0 is accepted when it is not true. In this case, the false negative decision occurs when the Environmental Analyst decides that the copper, zinc, or pesticide levels in storm water runoff sampled during a particular are consistent with historical results when, in fact, they are not.

Gray Region

The gray region is the area adjacent to the action level where the primary decision maker feels that the consequences of a false negative decision error are minimal. The primary decision maker has defined the gray region for copper, zinc, and pesticides in storm water runoff according to the criteria defined previously in Table 4.1.

Design Performance Goal Table

The Design Performance Goal Table for the action level for copper, zinc, or pesticides, one or more data points differing significantly from historical results, is given in Table 4.5.

This completes the first six steps of the DQO process for tritium, copper, zinc, and pesticides in rain and storm water runoff.

Subproblem Two

The second subproblem evaluated analytical data for samples collected for the LLNL rain and storm water runoff monitoring networks from 1992 through 1994 and determine whether the field quality control samples that were taken during that period can be used to verify that the specified data quality objectives were met.

Field Quality Control Samples for Rain and Storm Water Runoff

In order to determine whether field quality control samples analyzed for the LLNL rain and storm water runoff networks between 1992 and 1994 can be used to verify that the data from those networks meet the data quality objectives defined in Subproblem One, the types and numbers of field quality control samples that were collected and analyzed will first be described.

LLNL Standard Operating Procedures require that one of the existing storm water runoff sampling locations be selected randomly for the collection of a duplicate sample for each sampling event (Welsh 1994). Duplicate samples are collected independently, as close as possible to the same point in space and time, and intended to be identical in all respects (Luedtke 1992). Duplicates are used to

Table 4.5. Design Performance Goal Table for Zinc, Copper, and Pesticides (Concentration Significantly Different from Historical Results)

<u>True Condition</u>	<u>Correct Decision</u>	<u>Acceptable Probability of Making an Incorrect Decision</u>
Copper, zinc, or pesticide levels in storm water runoff are constant or decreasing	Copper, zinc, or pesticide concentration significantly different from historical results	1%
See Table 4.1.	Copper, zinc, or pesticide concentration <u>not</u> significantly different from historical results	gray region - no probability specified
See Table 4.1.	Copper, zinc, or pesticide concentration <u>not</u> significantly different from historical results	20%

assess the variability of sample collection procedures and its impact on data (Burger and Jordan 1988).

For rain sampling, one of the existing sampling locations at which sufficient rain water is available is selected randomly for the collection of a replicate sample during each storm sampled. Replicate samples are samples that are divided into two or more portions at some step in the measurement process. Field replicates are used to determine precision based on homogeneity, handling, shipping, storage, preparation, and analysis. (USEPA 1987b). The replicate rain sample is taken from the same collection bucket the routine sample at that location.

Routine and duplicate or replicate sample are sent to the analytical laboratories with the intention that they be treated as similarly as possible throughout the analytical process. Duplicate or replicate samples are sent to the laboratory "single blind." This means that samples are coded in such a way that analytical laboratory personnel may be aware that a sample is a duplicate or replicate but they do not know which routine sample the duplicate or replicate corresponds to at the time of analysis. The on-site laboratory that performs LLNL tritium analysis has asked for decodes of single blind samples after analysis is completed as a way of evaluating their own quality control practices.

Duplicate or replicate samples processed and analyzed by the same organization provide intralaboratory precision information for the entire measurement system including sample acquisition, homogeneity, handling, shipping, storage, preparation, and analysis. Duplicate or replicate samples processed and analyzed by different organizations provide interlaboratory precision information for the entire measurement system (USEPA 1987b). LLNL tritium samples are all analyzed by the same analytical laboratory due to the fact

that no off-site laboratory has been found with the capability of providing the low reporting limits available from the on-site facility. For non-radiological storm water runoff analyses, half of the duplicate samples are sent to the same laboratory as the routine samples, and half are sent to a second laboratory so that interlaboratory precision can be determined.

No other field quality control samples are required or were taken during the time period of interest for either of these networks.

Tritium

Availability of Data from Duplicate or Replicate Tritium Samples

Due to modifications in the sampling networks made over the years as well as sampler error, duplicate and replicate samples were not always taken at the frequency specified in the LLNL Standard Operating Procedures. The actual availability of duplicate or replicate tritium samples in rain or storm water runoff sampled between 1992 and 1994 is given in Tables 4.6 and 4.7.

In some cases, more than one replicate sample rain were analyzed for a particular rain storm. This occurred because of an historic goal that at least 10% of LLNL's routine environmental samples be duplicated or replicated (Holland 1987).

Before the rain network was decreased in size, two replicates were required to achieve this goal. When duplicates or replicate data are missing for a particular runoff or rain sampling event, either the replicate or duplicate was taken from a location that is no longer a part of the network (so it was not included in this study); there was insufficient water available for a duplicate or replicate sample; or the sampling technologist inadvertently failed to take the duplicate or replicate sample.

**Table 4.6. Field Replicate Samples for LLNL Tritium in Rainfall Sampled
Between 1/1/92 and 12/31/94**

Storm Date	Number of Locations Sampled	Number of Replicate Samples
01/07/92	7	1
01/29/92	8	0
02/03/92	8	0
02/08/92	8	1
02/11/92	8	0
02/12/92	9	2
02/18/92	8	1
02/19/92	9	1
02/20/92	9	0
03/03/92	10	0
03/06/92	10	2
03/17/92	10	0
03/26/92	10	1
04/13/92	10	0
06/30/92	10	0
10/21/92	10	1
11/02/92	10	1
12/04/92	10	1
12/10/92	10	1
12/15/92	10	1
01/12/93	10	2
02/22/93	10	1
03/22/93	9	1
10/06/93	4	0
11/11/93	10	2
01/25/94	10	0
03/25/94	9	0
04/11/94	10	0
04/26/94	10	1
05/09/94	9	1
11/07/94	10	1

**Table 4.7. Field Duplicate Samples for LLNL Tritium in Storm Water Runoff
Sampled Between 1/1/92 and 12/31/94**

Storm Date	Number of Locations Sampled	Number of Duplicate Samples
01/05/92	5	0
01/28/92	6	1
02/01/92	6	1
02/06/92	6	0
02/09/92	6	1
02/11/92	6	1
02/14/92	6	0
02/18/92	6	1
03/05/92	6	0
03/16/92	6	1
03/22/92	6	0
03/25/92	5	0
04/12/92	6	1
10/29/92	5	1
12/06/92	4	1
12/10/92	6	0
12/17/92	6	0
12/28/92	6	0
01/06/93	6	1
01/12/93	6	0
02/08/93	6	1
03/25/93	6	1
06/04/93	2	1
10/05/93	3	0
11/10/93	6	1
01/24/94	6	0
04/25/94	6	0
11/05/94	6	1

Results for Duplicate or Replicate and Routine Pairs

Tritium concentrations for the 42 available pairs of routine and duplicate or replicate samples for the rain and storm water runoff monitoring networks during the period from 1992 through 1994 are given in Table 4.8. This Table also includes the natural logarithm (ln) of the tritium concentration (tritium concentration) for each data point and a calculation of the relative percent difference (RPD) between ln [T] in the routine sample and ln [T] in the duplicate sample. RPD, a value commonly used by analytical laboratories to define the precision of duplicate samples (USEPA 1987b), is calculated as follows:

$$RPD = \left\{ \left| \ln [T]_{\text{routine}} - \ln [T]_{\text{duplicate}} \right| / (\ln [T]_{\text{routine}} + \ln [T]_{\text{duplicate}}) \right\} \times 200$$

RPD results for rain and storm water runoff duplicate samples are discussed below.

Evaluation of Routine Data Against Data Quality Objectives

Routine data were next analyzed using the methods described in Subproblem One to determine if they met the DQOs. Field QC data were then evaluated by several different methods to determine their value in confirming that DQOs were or were not achieved.

The First Action Level for Tritium

The first action level for tritium is reached when the level of tritium in any storm water runoff or rainfall sample collected at or near LLNL exceeds the California MCL of 20,000 pCi/L.

Table 4.8. Results of Routine and Duplicate Sampling of Rain and Storm Water Runoff for Tritium (1992 - 1994)

Location Identifier (-RA=rain -RO=runoff)	Storm Date	Duplicate Sample Result (pCi/L)	Ln Duplicate Sample Result	Routine Sample Result (pCi/L)	Ln Routine Sample Result	Relative Percent Difference (RPD)
L-AQUE-RA	10/21/92	2,050	7.63	834	6.73	^a 12.53
L-ASS2-RO	3/16/92	64.3	4.16	<24	<3.18	^a 26.85
L-B291-RA	11/2/92	589	6.38	2,570	7.85	^a 20.71
L-B343-RA	2/23/93	146,000	11.89	147,000	11.9	^a 0.06
L-ZON7-RA	11/11/93	62.4	4.13	121	4.8	^a 14.83
L-ASS2-RO	2/1/92	86	4.45	54	3.99	^b 11.02
L-ALPE-RO	2/18/92	69.6	4.24	103	4.63	^c 8.83
L-SALV-RA	11/11/93	165	5.11	254	5.54	^c 8.83
L-ALPE-RO	3/25/93	136	4.91	150	5.01	1.97
L-ASS2-RO	4/12/92	1,200	7.09	1,320	7.19	1.34
L-ASW-RO	2/9/92	<59.1	<4.08	62.5	4.14	1.36
L-ASW-RO	11/5/94	728	6.59	690	6.54	0.82
L-B291-RA	2/18/92	833	6.73	790	6.67	0.79
L-B291-RA	4/26/94	313	5.75	421	6.04	5.03
L-B343-RA	2/12/92	630	6.45	841	6.73	4.38
L-B343-RA	3/6/92	2,380	7.77	2,120	7.66	1.50
L-B343-RA	5/9/94	1,170	7.06	1,190	7.08	0.24
L-CDB-RA	1/12/93	552	6.31	517	6.25	1.04
L-CDB-RA	3/26/92	329	5.8	337	5.82	0.41
L-CDB-RA	11/7/94	<48.3	<3.88	<49	<3.89	0.37
L-CDB-RA	12/10/92	929	6.83	953	6.86	0.37
L-CDB-RO	1/28/92	97.5	4.58	122	4.8	4.78
L-CDB-RO	2/12/92	112	4.72	144	4.97	5.19
L-CDB-RO	10/29/92	310	5.74	318	5.76	0.44
L-CDB-RO	11/10/93	161	5.08	123	4.81	5.44
L-ESAN-RA	1/12/93	1,150	7.05	1,140	7.04	0.12
L-ESAN-RA	3/6/92	694	6.54	712	6.57	0.39
L-GRNE-RO	2/8/93	139	4.93	146	4.98	4.46
L-GRNE-RO	6/4/93	92.4	4.53	70.2	4.25	6.26
L-GRNE-RO	12/6/92	109	4.69	135	4.91	4.46
L-MET-RA	2/8/92	237	5.47	163	5.09	7.09
L-MET-RA	2/19/92	79.3	4.37	95.5	4.56	4.16
L-SALV-RA	1/7/92	475	6.16	524	6.26	1.58
L-SALV-RA	2/12/92	246	5.51	235	5.46	0.83
L-SLST-RA	2/8/92	473	6.16	429	6.06	1.60
L-SLST-RA	5/9/94	<42.2	<3.74	<41.5	<3.73	0.45
L-SLST-RA	11/7/94	<47.5	<3.86	<47.6	<3.86	0.05
L-SLST-RA	12/10/92	<53.4	<3.98	<52.1	<3.95	0.62
L-VIS-RA	3/22/93	547	6.3	621	6.43	1.99
L-VIS-RA	12/4/92	87	4.47	115	4.74	6.06
L-WPDC-RO	1/6/93	69.2	4.24	75.7	4.33	2.10
L-ZON7-RA	12/15/92	284	5.65	331	5.8	2.67

^a Outlier

^b RPD > UCL

^c RPD > Upper Warning Limit

Evaluation of Routine Data

Only one routine sample collected between 1992 and 1994 exhibited tritium concentration above the MCL. This is shown graphically in Figure 4.5. As described previously, the tritium concentration in rainfall at location L-B343 was measured at 147,000 pCi/L, well above the MCL of 20,000 pCi/L, in a sample taken on February 23, 1993. Coincidentally, a replicate sample was taken for that storm at that location. The tritium concentration for the replicate was 146,000 pCi/L, giving an RPD of 0.06%, which is very low compared to most pairs in Table 4.8.

Evaluation of Field QC Data

The field replicate sample taken on February 23, 1993 supports the decision that the MCL was exceeded at location L-B343. Since replicate sampling locations are selected randomly, it was fortuitous that the replicate location for that storm coincided with the location where the MCL was exceeded. Since the tritium concentration in the replicate closely matched that of the routine sample, and since both values were substantially higher than the MCL (7.35 and 7.30 times the MCL), there is little doubt that the action level was exceeded.

The question remains as to the value of the field QC data in making this determination had the replicate been taken from a different location, specifically, at one where the tritium concentration was far below the MCL. In order to address this question, the results of routine and duplicate or replicate samples collected between 1992 and 1994 were examined.

Plot of Duplicate or Replicate vs. Routine Value

An easy way to determine the correlation between routine and duplicate or replicate sample results is to plot $\ln [T]$ in the duplicate or replicate sample as a function of $\ln [T]$ in the routine sample. A plot of these data, taken from Table

Figure 4.5. Control Chart for Tritium in Rain at Location L-B434

4.8, is shown in Figure 4.6. A linear fit of these data gave a correlation coefficient (r^2) value of 0.94 (where a correlation coefficient of 1.0 indicates a perfect fit) which is indicative of a reasonably good fit, but, as can be seen from the Figure, several data points appear to be outliers.

Evaluation and Elimination of Outliers

Outliers have been defined as observations that do not conform to the pattern established by other observations in the data set. A method described by Gilbert (1987) was used to determine whether outliers existed within these data. A "distance" (D) from the set of data points was calculated for each pair of observations according to the method presented by Gilbert. The D values were then sorted and plotted as a normal probability plot, which is expected to be linear if the data pairs are part of a bivariate normal distribution. If a linear curve does not result, suspected outliers should be identified on the plot and removed from the calculation of D values. If, after removing these points, the probability plot becomes linear, then the values that were removed are assumed to be outliers. If it does not, then the data pairs cannot be assumed to be part of a bivariate normal distribution.

D values for all pairs were plotted in Figure 4.7, but they do not fall along a straight line as would be expected if the data were normally distributed. Observation of this Figure led to the conclusion that the pairs that gave the five highest D values might be outliers. D values were recalculated without the data from these five pairs and plotted in Figure 4.8. This Figure showed a good fit of the data to a linear curve ($r^2 = 0.98$) so the remaining data pairs fit a bivariate normal distribution. A new plot of the $\ln [T]$ in the duplicate sample versus the $\ln [T]$ in the routine sample with the five "outliers" removed is shown in Figure 4.9.

Figure 4.6. Routine vs. Duplicate or Replicate Samples for Tritium in Rain or Storm Water Runoff

As can be seen in Figure 4.9, an improved fit (r^2 increased to 0.99 from 0.94) was achieved. (The five data pairs that were determined to be outliers are footnoted in Table 4.8.)

Calculation of Confidence Values

In order to use duplicate or replicate data to estimate the precision of the routine tritium data, 95% confidence values were calculated for the linear fit of $\ln [T]$ in the duplicate sample versus the $\ln [T]$ in the routine sample with the five "outliers" removed using the method described in Draper and Smith (1981). A 95% confidence level for each observation is calculated using:

$$Y = \hat{Y}_0 \pm t(v, 0.975) \left\{ 1 + \frac{1}{n} + \frac{(X_0 - \bar{X})^2}{\sum (X_i - \bar{X})^2} \right\}^{\frac{1}{2}} s$$

where s^2 is the mean square variability of Y about the residual from the analysis of variance (ANOVA) Table, n is the number of data points used to calculate s^2 , v is $n - 2$, or the number of degrees of freedom on which s^2 is based, t is the appropriate Student's t value, Y is the $\ln [T]$ in the duplicate or replicate sample, and X is the $\ln [T]$ in the routine sample.

Figure 4.10 is a replot of Figure 4.9 showing calculated confidence values for the linear regression fit to the data. As can be seen from the equation above, the size of the confidence interval is dependent on the x -value ($\ln [T]$ in routine sample).

Figure 4.7. Probability Plot of D Values for All Duplicate or Replicate and Routine Pairs Showing Linear Regression Curve

Figure 4.8. Probability Plot of D Values for Duplicate or Replicate and Routine Pairs with Outliers Removed Showing Regression Curve

Figure 4.9. Routine vs. Duplicate or Replicate Samples for Tritium in Rain or Storm Water Runoff Outliers Removed

Dependence of Variability on Location, Sampling Medium, and Tritium Concentration

Two different plots were made in order to evaluate the dependence of RPD on location, sampling medium, and concentration of tritium in the routine sample. Figure 4.11 shows a plot of RPD as a function of $\ln [T]$. As can be seen from this plot, there is no apparent dependence of the relative percent difference between duplicate or replicate and routine samples on the tritium concentration in the routine sample. Figure 4.12 is a plot of RPD as a function of sampling medium (rain or runoff) and location. Again, no apparent correlation exists.

Between-Storm Variability

Plots of $\ln [T]$ in rain as a function of storm date for all storms sampled between 1992 and 1994 are given in Figures 4.13 through 4.23. Duplicate and replicate sample results are also shown on these plots. A review of these plots shows that the variability from storm to storm at a single location is much greater than the variability between the duplicate or replicate sample and the routine sample for a single storm.

Missing Information

Existing field QC data do not provide any means to evaluate contamination that could have been introduced during sampling or transportation to the analytical laboratory. In addition, analytical laboratory quality control data, which were excluded from the scope of this research, would provide additional information regarding the bias and precision of the data that would allow a more quantitative determination of whether data quality objectives were met. These data would have been particularly useful in evaluating a situation where duplicate or replicate and routine results conflicted

Figure 4.10. Duplicate or Replicate vs. Routine Sample for Tritium in Rain or Storm Water Runoff Showing Calculated Confidence Interval

Figure 4.11. Relative Percent Difference Between Routine and Duplicate or Replicate Rain or Storm Water Runoff Samples as a Function of Tritium Concentration in the Routine Sample (Outliers Removed)

Figure 4.12. Relative Percent Difference Between Routine and Duplicate Rain or Storm Water Runoff Samples as a Function of Location and Sampling Medium (Outliers Removed)

Figure 4.13. Control Chart for Tritium in Rain at Location L-B343

Figure 4.14. Control Chart for Tritium in Rain at Location L-B291

Figure 4.15. Control Chart for Tritium in Rain at Location L-CDB

Figure 4.16. Control Chart for Tritium in Rain at Location L-COW

Figure 4.17. Control Chart for Tritium in Rain at Location L-MET

Figure 4.18. Control Chart for Tritium in Rain at Location L-VIS

Figure 4.19. Control Chart for Tritium in Rain at Location L-ZON7

Figure 4.20. Control Chart for Tritium in Rain at Location L-ESAN

Figure 4.21. Control Chart for Tritium in Rain at Location L-SALV

Figure 4.22. Control Chart for Tritium in Rain at Location L-AQUE

Figure 4.23. Control Chart for Tritium in Rain at Location L-SLST

(i.e. one result significantly lower than the MCL while the other was significantly greater than the MCL) or a situation in which the tritium concentration was close to the edge of the gray region.

Use of Historical Data

Historical data also support the decision that the tritium concentration at location L-B343 exceeded the MCL in the storm sampled on February 23, 1993. This was determined by reviewing the plots of $\ln [T]$ as a function of time for other locations.

The specific instance where tritium concentration exceeded the MCL appears in Figure 4.13. Review of the plots for other on-site locations showed an increased tritium concentration in several of them for the February 23, 1993 storm. As can be seen in Figures 4.14, 4.15, 4.16, 4.17, 4.18, and 4.19, the tritium concentration at locations L-B291, L-CDB, L-COW, L-MET, L-VIS, and L-ZON7 appeared significantly higher in that storm than in previous and subsequent storms. Although the tritium MCL was not exceeded at any other location, the Upper Control Limit (UCL) was exceeded at locations L-CDB and L-COW and the 2-sigma warning limit was exceeded at locations L-VIS and L-ZON7. (The UCL and the 2-sigma warning limit will be discussed in more detail as a part of the analysis of the second and third action levels for tritium.) As was discussed earlier, it has been hypothesized that the increase in tritium concentration for this storm was caused by diffuse tritium emissions caused by routine decommissioning operations in the Tritium Facility yard (Gallegos et al. 1994). The fact that sampling locations closest to that facility showed increased tritium levels supports that hypothesis. Remote locations, particularly the background location (L-SLST), showed no effect of those emissions (see Figure 4.23).

Conclusions

Additional data are needed to be able to state definitively that data quality objectives have or have not been met, however, available field QC and historical results allow some observations about the data to be made.

A formula has been developed to calculate 95% confidence levels based on historic data. Due to the lack of correlation between tritium concentration in duplicate or replicate and routine samples and sampling medium, location, or tritium concentration, this formula should be applicable to all data points.

Occasionally, the variability of duplicate or replicate and routine pairs differs sufficiently from the norm that these pairs are determined to be outliers. The cause of this variability needs to be understood before the precision of the data can be quantified with confidence. Adding field QC samples that would evaluate contamination during sampling and transportation to the analytical laboratory and review of laboratory QC data should be helpful in developing this understanding.

The Second Action Level for Tritium

The second action level for tritium is reached when the level of tritium in storm water runoff or rainfall sample collected at a particular location shows a consistent upward trend.

Evaluation of Routine Data

Routine monitoring data were evaluated to determine if upward trends existed in the concentration of tritium in rain or storm water runoff by preparing and analyzing an $\bar{X}$ and moving range (R_m) control chart for each sampling

location. Control charts are commonly used to determine whether current data are consistent with historical results (Gilbert 1987). Control limits are calculated for each control chart to represent the area that includes plus and minus three standard deviations from the center of the distribution, or 99.73% of the data. One- and two-sigma warning limits are calculated by dividing the area between the upper and lower control limits into six equal areas. One-sigma warning limits are expected to contain 68.26% of the data and two-sigma control limits are expected to contain 95.44%.

First, a plot of $\ln [T]$ for each date between January 1, 1992 and December 31, 1994 that rain or runoff was sampled was made. Control limits were calculated using the method presented by Lindsay (1990) for $\bar{X}$ and moving range (R_m) charts. Control charts for tritium in storm water runoff appear in Figures 4.24 to 4.29. Figures 4.13 through 4.23 are the control charts for tritium in rain. Each control chart shows the upper and lower control limits, as well as upper and lower one- and two-sigma warning limits and the MCL for tritium in drinking water. Results of duplicate or replicate samples were also plotted on each control chart so that the precision of within-storm pairs could be compared to that of between-storm samples. Tables 4.9 and 4.10 shows the centerline, upper control limit, and lower control limit for each storm water runoff and rain sampling location.

In order to determine whether an upward trend in tritium concentration existed, each control chart was examined according to the criteria identified in Subproblem One. Upward trends are established when either (1) six data points consecutive show an increase in $\ln [T]$; (2) eight of ten consecutive data points show an increase in $\ln [T]$; or (3) seven consecutive data points lie above the centerline.

Figure 4.24. Control Chart for Tritium in Storm Water Runoff at
Location L-ALPE

Figure 4.25. Control Chart for Tritium in Storm Water Runoff at Location L-ASS2

Figure 4.26. Control Chart for Tritium in Storm Water Runoff at Location L-ASW

Figure 4.27. Control Chart for Tritium in Storm Water Runoff at Location L-CDB

Figure 4.28. Control Chart for Tritium in Storm Water Runoff at Location L-GRNE

Figure 4.29. Control Chart for Tritium in Storm Water Runoff at Location L-WPDC

No upward trends were found in any of the rain or storm water monitoring tritium data.

Evaluation of Field QC Data

The decision that no upward trends in tritium concentration in rain or storm water runoff were established between 1992 and 1994 was based on a review of historical data. The information gained from field QC data was less useful in supporting this decision than it was for supporting the decision that a single data point exceeded the MCL. The main use of data from duplicate or replicate samples for this action level was to provide added confidence that sampling and analysis are repeatable, thus lending support to the assumption that trends or lack thereof identified in plots of historical data reflect the true situation in the environment.

Conclusions

One of the main limitations of the methodology used for this subproblem is that it does not address the data quality objectives as specified in the Design Performance Goal Table. The Table defines the gray area and the area of concern based on a 3- or 5-fold increase in tritium concentration. These criteria could easily be used in this type of analysis, however, this modification is likely to increase the probability of incorrectly defining a trend when none exists. Since the primary decision maker has determined that failing to identify an existing upward trend is of less concern than incorrectly identifying one, this modification will not be made.

Table 4.9. Mean Values and Upper and Lower Control Limits for Tritium in Storm Water Runoff (1992 - 1994)

Sampling Location	Mean ln [T] ^a	UCL ^{a,b}	LCL ^{b,c}
L-ALPE-RO	4.83	7.23	2.44
L-ASS2-RO	5.10	8.74	1.47
L-ASW-RO	5.11	8.68	1.53
L-CDB-RO	5.26	7.74	2.78
L-GRNE-RO	5.29	8.11	2.67
L-WPDC-RO	5.38	7.53	3.22

^aAll values are ln [T] where [T] is expressed in pCi/L

^bLower Control Limit

^cUpper Control Limit

Table 4.10. Mean Values and Upper and Lower Control Limits for Tritium in Rain (1992 - 1994)

Sampling Location	Mean ln [T] ^a	UCL ^{a,b}	LCL ^{a,c}
L-SLST-RA	4.16	5.58	2.73
L-MET-RA	4.69	6.71	2.67
L-ZON7-RA	5.17	7.15	3.20
L-COW-RA	5.45	8.18	2.72
L-VIS-RA	5.68	7.65	3.71
L-AQUE-RA	5.98	7.79	4.16
L-SALV-RA	6.08	8.46	3.70
L-CDB-RA	6.37	9.24	3.49
L-ESAN-RA	6.43	8.41	4.46
L-B291-RA	6.55	8.59	4.52
L-B343-RA	7.00	9.65	4.35

^aAll values are ln [T] where [T] is expressed in pCi/L

^bLower Control Limit

^cUpper Control Limit

The analysis performed for the first action level for duplicate or replicate tritium samples led to a way of estimating the precision of LLNL rain and storm water tritium monitoring data. This information can be used qualitatively to support decisions that are based on control charts, such as whether or not trends exist, but cannot be used directly or quantitatively to estimate the confidence of such decisions.

The Third Action Level for Tritium

The third action level for tritium is exceeded when the level of tritium in one or more samples collected during a particular storm differs significantly from historical values.

Evaluation of Routine Data

Determination of whether the third action level for tritium was exceeded was done through review of the same control charts that were used for the second action level. In order to determine whether an upward trend in tritium concentration existed, each control chart was examined using the criteria identified in Subproblem One. Results were determined to be inconsistent with historical values when either (1) any one point fell outside the control limits; (2) four of five consecutive points fell outside one standard deviation (on the same side of the centerline); or (3) two of three consecutive points fell beyond two standard deviations (on the same side of the centerline).

Data Points Outside of Control Limits

Review of Figures 4.1 through 4.29 revealed that all data for tritium monitoring of storm water runoff between 1992 and 1994 fell within the control

limits. Four of the six locations showed one data point outside of the 2-sigma warning limits, but in every case, the tritium value both before and after this occurred was within 1-sigma of the centerline.

Figures 4.13 through 4.23 demonstrated that greater variability existed for tritium in rain water than for tritium in storm water runoff. Tritium values for seven rain samples fell outside of control limits. These data, summarized in Table 4.11, represent three storms: three samples taken from the February 23, 1993 storm discussed previously, one sample taken at the background location L-SLST on February 8, 1992; and three samples taken for a November 7, 1994 storm.

No explanation is available for the elevated tritium concentration February 8 sample at SLST. No other locations showed elevated tritium readings during that storm, however, a replicate sample at that location gave similar results.

Nine of the eleven rain sampling locations experienced a significant decrease in tritium concentration for the storm sampled on November 7, 1994. The tritium concentration at three of those locations was below the LCL and the tritium concentration at the other six was outside of the 2-sigma warning limit. The apparent change in tritium concentration was large enough for this storm that further investigation of the analytical data as well as review of data from subsequent storms (the November 7 storm was the first of the 1994-1995 rainy season) is indicated before final conclusions can be drawn.

Evaluation of Field QC Data

The decision that specific data points differed significantly from historical values was based on a review of historical data. The information gained from

Table 4.11. Tritium in Rainfall Where Results are Significantly Different from Historical Values (1992 - 1994)

Date Sampled	Sampling Location	Condition
2/8/92	L-SLST	Value above upper control limit
2/23/93	L-B343	Value above upper control limit and above MCL
2/23/93	L-CDB	Value above upper control limit and above MCL
2/23/93	L-COW	Value equal to upper control limit
11/07/94	L-AQUE	Value below lower control limit
11/07/94	L-B291	Value below lower control limit
11/07/94	L-ESAN	Value below lower control limit

field QC data was less useful in supporting this decision than it was for supporting the decision that a single data point exceeded the MCL. The main use of data from duplicate or replicate samples for this action level was to provide added confidence that sampling and analysis are repeatable. As an example, both routine and replicate samples taken at location L-SLST on February 8, 1992 fell above the upper control limit. This information lends support to the assumption that data that are determined to be significantly different from historical results using plots of historical data reflect the true situation in the environment.

Conclusions

The analysis performed for the first action level for duplicate or replicate tritium samples led to a way of estimating the precision of LLNL rain and storm water tritium monitoring data. This information can be used qualitatively to support decisions that are based on control charts, such as whether or not data are significantly different from historical results, but cannot be used directly or quantitatively to estimate the confidence of such decisions.

Zinc, Copper, and Pesticides

Availability of Data from Duplicate Zinc, Copper, and Pesticide Samples

Due to insufficient rainfall and sampler oversight, duplicate samples for pesticides, copper, and zinc in storm water runoff were not always taken at the frequency specified in LLNL standard operating procedures.

Zinc in storm water runoff has been monitored for four storms since 1992. One field duplicate sample was collected and analyzed for three of the four storms; a duplicate sample was not collected for the fourth storm. One of the three field duplicates was sent to a different analytical laboratory than the routine sample so that interlaboratory precision could be estimated.

Copper in storm water runoff has been monitored in five storms since the beginning of 1992. One field duplicate sample was collected and analyzed for four of the five storms; a duplicate sample was not collected for the fifth storm. One of the four field duplicates was sent to a different analytical laboratory than the routine sample so that interlaboratory precision could be estimated.

A list of the pesticides measured by EPA Method 608 as well as analytical laboratory reporting limits specified for LLNL storm water runoff samples between 1992 and 1994 is given in Table 4.12. Lindane, Methoxychlor, and Endrin were monitored throughout the study period. Monitoring of the other seventeen pesticides began on October 15, 1993, which was the first storm sampled after LLNL changed contract analytical laboratories. Since that time five storms have been sampled. QC field duplicates were collected and analyzed for two of the five storms; duplicate samples were not taken for the remaining three storms. All duplicate samples were analyzed for pesticides by the same analytical laboratory as the routine samples.

The Action Level for Metals or Pesticides

The action level for copper, zinc, or pesticides is reached when the level of copper, zinc, or pesticides in storm water runoff or rainfall sample collected at a particular location is significantly different from historical results.

Evaluation of Routine Data

Routine data were analyzed using the methods described in Subproblem One to determine if they met the DQOs. Field QC data were then evaluated to determine their value in confirming that DQOs were or were not achieved.

Table 4.12. Analytical Laboratory Reporting Limits and Detection History for Pesticides in Storm Water Runoff by EPA Method 608

Pesticide	Specified Analytical Laboratory Reporting Limits (µg/L)	Number Above Reporting Limit/ Total Samples Analyzed
Aldrin	<0.5, <0.25, <0.05	0/28
BHC, alpha isomer	<0.5, <0.25, <0.05	0/28
BHC, beta isomer	<0.5, <0.25, <0.05	0/28
BHC, delta isomer	<0.5, <0.25, <0.05	0/28
BHC, gamma isomer (Lindane)	<0.5, <0.4, <0.25, <0.05, <0.03	1/128
Chlordane	<5, <2.5, <0.5	0/28
Dieldrin	<1, <0.5, <0.1	0/28
Endosulfan I	<0.5, <0.25, <0.05	0/28
Endosulfan II	<1, <0.5, <0.1	0/28
Endosulfan Sulfate	<1, <0.5, <0.1	0/28
Endrin	<1, <0.5, <0.2, <0.1, <0.06, <0.05, <0.04, <0.01	6/128
Endrin Aldehyde	<1, <0.5, <0.1	0/28
Heptachlor	<0.5, <0.25, <0.05	0/28
Heptachlor Epoxide	<0.5, <0.25, <0.05	0/28
Methoxychlor	<10, <5, <2.5, <0.5, <0.2	0/128
p,p'-DDD	<1, <0.5, <0.1	0/28
p,p'-DDE	<1, <0.5, <0.1	0/28
p,p'-DDT	<1, <0.5, <0.1	0/28
Toxaphene	<10, <5, <1, <0.5, <0.1	0/128

Zinc

Because the data set is so small, the results of all Zinc monitoring in storm water runoff between 1992 and 1994 are presented in Table 4.13 and plotted in Figure 4.30.

Because this data set is so small, definitive conclusions cannot be made from it. Evaluating these data using the criteria specified in Table 4.1, led to the following observations:

- zinc concentration was consistent at all sampling locations during the study period.
- zinc concentration in routine samples was consistently below the laboratory reporting limit at locations L-ALPE and L-GRNE, both of which measure influent to the Laboratory via Arroyo Las Positas. (The field duplicate for L-ALPE will be discussed below.)
- zinc concentration in routine samples from all other locations except L-ASW was above the laboratory reporting limit. (Location L-ASW showed zinc above the laboratory reporting limit for all storms except one.) Visual observation of Figure 4.30 led to the conclusion that an upward trend in zinc concentration at all of these locations may have begun in 1994, however, insufficient data are available to state this conclusively.
- November 10, 1993 and November 5, 1994 storms both show elevated zinc concentration when compared to the other storms. Both of these were the first storm monitored for their respective rainy seasons and the apparent increase could be due to the presence of zinc that had built up during the summer. Future monitoring data should be watched closely to determine whether (1) an upward trend in zinc

Table 4.13. Zinc in Storm Water Runoff (1992 - 1994)

Sampling Location	Storm Date	[Zn] (mg/L)
L-ALPE	11/10/93	<0.05
	01/24/94	<0.05
	04/25/94	<0.05
	11/05/94	<0.05
L-ASS2	11/10/93	1.8
	01/24/94	0.056
	04/25/94	0.07
	11/05/94	0.22
L-ASW	11/10/93	0.33
	01/24/94	<0.05
	04/25/94	0.066
	11/05/94	0.085
L-CDB	11/10/93	0.14
	01/24/94	0.084
	04/25/94	0.096
	11/05/94	0.14
L-GRNE	11/10/93	<0.05
	01/24/94	<0.05
	04/25/94	<0.05
	11/05/94	<0.05
L-WPDC	11/10/93	0.24
	01/24/94	0.05
	04/25/94	0.081
	11/05/94	0.12
Duplicate Samples		
L-CDB	11/10/93	0.15
L-ASW	01/24/94	<0.05
L-ALPE	11/05/94	0.12 ^a

^a Analyzed by QC laboratory. All other samples analyzed by primary laboratory.

Figure 4.30. Zinc in Storm Water Runoff

concentration has been established, (2) a seasonal fluctuation of zinc concentration is present, or (3) the apparent upward trend in zinc concentration reverses itself.

- zinc concentration was measured at a concentration greater than 10 times the analytical laboratory reporting limit at one location in one storm (L-ASS2 on November 10, 1993.) Subsequent to that storm, the concentration of zinc at that location dropped and has not returned to that level, although Figure 4.30 shows that a an upward trend in zinc concentration at that location may be starting.

Copper

Because the data set is so small, the results of all Copper monitoring in storm water runoff between 1992 and 1994 are presented in Table 4.14. Again, the data set is too small to allow definitive conclusions to be made. Reviewing these results according to the criteria specified in Table 4.1 led to the following observations:

- Copper was detected at all six sampling locations on March 25, 1993, at concentrations between 0.006 and 0.013 mg/L. The March 1993 samples were analyzed by an off-site contract analytical laboratory whose contract was terminated in July 1993. That laboratory evaluated copper using EPA method 220.2, an atomic absorption (AA) furnace method. LLNL changed to a different contract analytical laboratory in July 1993. The new laboratory evaluated copper using EPA Method 200.7, an ICP method. The analytical laboratory reporting limit for copper increased by five to ten times when the substitution was made.

Table 4.14. Copper in Storm Water Runoff (1992 - 1994)

Sampling Location	Storm Date	[Cu] (mg/L)
L-ALPE	03/25/93	0.0072 ^a
	11/10/93	<0.01 ^b
	11/10/93	<0.05
	01/24/94	<0.05
	04/25/94	<0.05
	11/05/94	<0.05
L-ASS2	03/25/93	0.007 ^a
	11/10/93	<0.01 ^b
	11/10/93	0.052
	01/24/94	<0.05
	04/25/94	<0.05
	11/05/94	<0.05
L-ASW	03/25/93	0.0077 ^a
	11/10/93	<0.01 ^b
	11/10/93	<0.05
	01/24/94	<0.05
	04/25/94	<0.05
	11/05/94	<0.05
L-CDB	03/25/93	0.0064 ^a
	11/10/93	<0.01 ^b
	11/10/93	<0.05
	01/24/94	<0.05
	04/25/94	<0.05
	11/05/94	<0.05
L-GRNE	03/25/93	0.013 ^a
	11/10/93	<0.01 ^b
	11/10/93	<0.05
	01/24/94	<0.05
	04/25/94	<0.05
	11/05/94	<0.05
L-WPDC	03/25/93	0.0089 ^a
	11/10/93	<0.01 ^b
	11/10/93	<0.05
	01/24/94	<0.05
	04/25/94	<0.05
	11/05/94	<0.05
Duplicate Samples		
L-ALPE	03/25/93	0.0062 ^a
L-CDB	11/10/93	<0.01 ^b
L-CDB	11/10/93	<0.05
L-ASW	01/24/94	<0.05
L-ALPE	11/05/94	0.023 ^c

^a Analyzed by previous analytical laboratory

^b Second analysis by primary laboratory

^c Analyzed by QC laboratory

- Copper was measured at a concentration greater than the analytical laboratory reporting limit at location L-ASS2 for a storm sampled November 10, 1993 (0.052 mg/L with an analytical laboratory reporting limit of 0.05 mg/L). Samples from this storm were reanalyzed by same method but using a different analytical laboratory reporting limit (0.01 mg/L). The second analysis (which had the lower reporting limit) did not detect copper at levels above 0.01 mg/L at any location. Analytical laboratory personnel were unable to explain why samples from this storm were analyzed twice or why two different reporting limits were used.
- According to the criteria defined in Subproblem One, no data that are significantly different from historical values can be identified within this data set.

Pesticides

The only pesticides detected in storm water runoff during the study period were Lindane (0.05 ug/L at Location L-ASW on October 29, 1992) and Endrin (0.06 ug/L at location L-CDB, 0.04 ug/L at location L-ASW, and 0.05 ug/L at location L-WPDC, all in a storm sampled on December 12, 1992). According to the criteria specified in Table 4.1, none of these results are significantly different from historical values.

Evaluation of Field QC Data

Zinc

As can be seen in Table 4.13, three field duplicate samples were collected and analyzed for zinc during the time period of interest. LLNL has contracts with two different off-site analytical laboratories for nonradiological analyses. The

first, or primary, laboratory analyzes all routine samples and half of the field duplicate samples. The second, or QC laboratory, analyzes the remaining field duplicate samples in order to verify the results from the primary laboratory and provide an estimate of interlaboratory precision.

The two sets of duplicate and routine samples that were both analyzed by the primary analytical laboratory (L-CDB and L-ASW) showed nearly identical zinc concentration. In the case where the duplicate sample was sent to the QC analytical laboratory, the result from the primary laboratory was <0.05 mg/L and the result from the QC laboratory was 0.12 mg/L. The two laboratories used equivalent analytical methods and a review of laboratory QC data showed no obvious reasons for the different results. The magnitude of the difference and the fact that zinc was detected at a fairly high level at a location where it was measured consistently at levels below the analytical laboratory reporting limit by the primary laboratory could be indicative of a potentially serious problem with all zinc data. As described below, a similar situation occurred for copper. These two data points are indicative of interlaboratory inconsistencies that must be investigated and resolved before the zinc and copper data can be used.

Copper

As can be seen in Table 4.14, five field duplicate samples were collected and analyzed for copper during the time period of interest.

- The four pairs of routine and duplicate samples that were both analyzed by the primary analytical laboratory (L-ALPE sampled on March 25, 1993, both L-CDB samples, and L-ASW) showed nearly identical copper concentration.
- Copper was detected at 0.023 mg/L in a field duplicate sample from location L-ALPE for a November 5, 1994 storm that was analyzed by

the QC laboratory. The primary analytical laboratory reported copper at <0.5 mg/L at all locations for that event. While it is possible (since 0.023 is less than 0.05) that these results may be comparable, the difference in zinc results from the two laboratories that was discussed above makes this less likely.

- The primary analytical laboratory analyzed the samples taken on November 10, 1993 for copper twice. According to analytical laboratory personnel, both subsamples were extracted and analyzed using the same methodology but different laboratory reporting limits (0.01 mg/L and 0.05 mg/L) were reported for the two analyses. The two analyses of the sample from location L-ASS2 gave quite different results. The first analysis reported a copper concentration of <0.01 mg/L, while the other reported 0.052 mg/L. These analyses were performed almost two years before this research was done and, no investigation of the apparent inconsistency was done at the time. Current attempts to obtain an explanation have been unsuccessful.

Pesticides

All field duplicates for pesticides were reported at less than the analytical laboratory reporting limits. While no quantitative analysis of precision can be performed based on these results, they do confirm the results from the routine samples.

Use of Historical Data

Zinc and Copper

A potential upward trend in zinc during 1994 was identified from a plot of historical data. Additional data must be acquired and questions that arose from

QC duplicate results must be resolved before this or any conclusions can be established definitively for zinc or copper.

Pesticides

Based on historic data, pesticides are not likely to be seen at levels above analytical laboratory reporting limits, however, when LLNL changed contract analytical laboratories in July of 1993, those limits for pesticides went up by approximately a factor of ten. No pesticides have been reported in pesticides since December 12, 1992, before the change in laboratories was made. Prior to July of 1993, only three pesticides of those currently measured by EPA Method 608 - Lindane, Methoxychlor, and Endrin - were reported. Two of the three (Lindane and Endrin) were reported at levels above the reporting limit during 1992. This would imply that at least these three pesticides may have been present but not detected in storm water runoff during 1993 and 1994 due to the increased reporting limits. The other 17 pesticides measured by EPA Method 608 were not reported prior to 1993 and have not been detected above analytical laboratory reporting limits since that time.

Subproblem Three

The third subproblem determined the optimum field quality control sampling program required to ensure the specified data quality objectives are met for the LLNL rain and storm water runoff monitoring networks and define the resources required to implement those measures.

Methodology

In order to do this subproblem, the decision errors of most concern to the primary decision maker for the two major types of decisions discussed in this

research - determining whether a data point exceeds a numerical limit and evaluating data with respect to historical results - will be discussed. The information available from current field QC samples will be reviewed with respect to situations that might be expected to result in those decision errors and unresolved issues from current QC field samples will be considered. Likely causes for decision errors will be presented, recommendations for future field QC sampling will be made, and the additional resources that would be required to implement these recommendations will be discussed. Finally, field spikes, a type of field QC sample that is sometimes used, will be discussed and the reasons they are not recommended for these programs will be give.

Field QC Samples not Currently Used by LLNL

Common field QC samples that are not currently a part of the LLNL rain and storm water runoff monitoring programs are field blanks and field spikes.

Blank Samples

Blank samples are used to evaluate contamination that occurs during sampling and transport. A field blank is created by transferring analyte free media similar to the sampling matrix from one vessel to another or exposing analyte free media to the sampling environment at the sampling site (Keith 1994). Field blanks are used to identify contamination from sampling and analysis procedures, field conditions, containers, preservatives, shipping, storage, sample preparation, and measurement (Prasad 1994).

Spiked Samples

The bias of the sampling and analytical process can be evaluated using data acquired from blanks and from field spikes. Field spikes provide a measure

of sampling, handling, and preservation error, giving the best overall assessment of bias for the entire measurement system (USEPA 1987b). Field spikes are typically difficult to prepare due to field conditions and the level of technical expertise required to prepare them properly.

Decision Error for Numerical Limit

The most serious decision error that could occur when LLNL rain and storm water runoff data are being compared to numerical limits would be to determine that the numerical limit had been exceeded for tritium when it had not. As discussed previously, numerical limits have not been established for zinc, copper, or pesticides.

Likely Causes of Decision Error

Likely causes of incorrectly determining that a tritium value is above the numerical limit include field contamination and laboratory error or contamination.

Information Available from Existing Field QC Data

Currently, field QC samples for tritium in rain or storm water runoff consist of one duplicate or replicate sample collected from a randomly selected location during each sampling event. If tritium is measured above the numerical limit in a routine sample and a duplicate or replicate sample taken at the same location confirms that value, then the field QC sample provides added confidence that the correct determination was made. Although the issue of contamination is not addressed by this sampling scheme, reproducible results in a replicate sample lessen the probability that the elevated tritium reading was

due to laboratory error, especially when the laboratory does not know the location from which the replicate sample was taken in advance of the analysis. Review of data from other sampling locations and comparison of those data to historical results can provide added confidence that the elevated tritium measured was not due to laboratory error.

Since the concentration of tritium in rain has been determined to be dependent on the distance of the sample from the LLNL or SNLL Tritium Facilities and the location of the rain replicate sample is chosen at random, it is possible that tritium could be detected above the numerical limit in a sample taken near the LLNL Tritium Facility and the replicate could be taken at a remote location that did not show elevated tritium concentration. In this situation, the data from the replicate would be less useful since the laboratory measurement is not confirmed directly. Although it has been shown that the variability between replicate and routine samples is not dependent on location or on tritium concentration, if only one sample were measured at a value above the numerical limit, the first hypothesis would likely be that analytical laboratory results are suspect.

Information Not Available from Existing Field QC Data

Existing field QC data do not address the issue of field contamination. It is theoretically possible that a sample could be contaminated in the field or during transportation to the analytical laboratory. If this occurred, a sample could contain tritium above numerical limits that was not present in the actual rain or storm water runoff. If it is assumed that laboratory QC measures are good and that the possibility of laboratory error or laboratory introduced contamination could be disproved, samples contaminated in the field would be considered true hits. If field duplicates or replicates were also contaminated, they would support

the decision that tritium levels in the environment exceeded numerical limits. Without field blanks, there is no way to determine whether contamination was introduced during the sampling or transportation process. The fact that each storm event is unique and cannot be resampled directly makes the availability of the information that is obtained from field blanks even more important.

Unresolved Issues From Existing Field QC Data

The main unresolved issue with existing QC data for tritium is the fact that the difference between routine and duplicate or replicate samples is sometimes greater than would be expected when looking at all historical data. As an example, the highest relative percent difference between $\ln [T]$ in routine samples and $\ln [T]$ in replicate rain samples during the study period was 26.85. If the tritium concentration in a routine rain sample was determined to be 30,000 pCi/L and the between the $\ln [T]$ in the routine sample and the $\ln [T]$ in the replicate sample were 26.85, the value of the replicate value would either be 2,614 pCi/L or 744,899 pCi/L. The average RPD for all pairs of rain samples except those that were determined to be outliers was 2.54. At this level of RPD, a routine sample measured to be 30,000 pCi/L would have a replicate result at 23,165 or 39,111 pCi/L. Obviously, the precision indicated by an RPD of 26.85 is unacceptable. The cause of such outliers must be determined and eliminated before decisions about tritium concentrations near the numerical limit can be made with confidence.

Recommendations for Changes to Field QC Sampling

Two changes to the current field QC sampling are recommended in order to increase the confidence in making a decision that tritium in rain or storm

water runoff has exceeded the numerical limit. First, a field blank should be collected during each sampling event. For rainfall, this field blank should be taken at the location most likely to show elevated tritium concentration (L-B343) because this is the location where contamination is most likely to be introduced. In order to conserve resources, field blanks would not need to be analyzed unless the tritium concentration in one or more samples exceeded the MCL or the environmental analyst felt that analyzing the field blank would provide useful information for interpreting the results of a particular storm. Second, a permanent replicate sampling location should be added to the rain monitoring network at L-B343. Data from this sample could provide important information for a storm in which high tritium values were measured. Since this is the location closest to the LLNL Tritium Facility, it is the location most likely to be affected by a tritium release. If a high value were measured at this location, results from the replicate sample should either confirm it or indicate a potential laboratory problem. Again, this sample could be taken, but not analyzed unless a routine sample showed levels of tritium above the MCL.

Additional Resources Required to Implement Recommended Changes

Additional resources required to implement the changes recommended above are minimal, especially if the added samples are not required to be analyzed. Adding both extra samples would require that two additional bottles be obtained and labeled. The sampling technologist would have to fill two bottles at location L-B343 and would have to pour field blank water from one bottle to another at one sampling location. If location L-B343 typically has a low yield of rainfall, an additional sampling bucket might be required at that location to ensure that sufficient rainfall was available for both routine and replicate

samples. In a situation where a tritium value above the MCL was identified, these added samples would have to be analyzed. This would result in additional analytical laboratory costs, however, if the data obtained from this analysis either confirmed the result or provided information that proved the elevated value was due to field contamination, significant savings in the amount of time spent by the Environmental Analyst researching and reporting the issue could be achieved.

Decision Error for Trends or Significant Difference from Historical Results

The most serious decision error for data exhibiting trends or significant difference from historical results would be determining that a trend had been established when none existed or that results were significantly different from historical values when they were not.

Likely Causes of Decision Error

Data significantly different from historical results are likely to be caused by the same circumstances that would result in an erroneous decision that tritium had exceeded the MCL. Analysis of field QC samples and changes to the field QC sampling program recommended previously should address this action level.

The most likely cause of erroneously identifying an upward trend in concentration of a particular analyte in rain or storm water runoff would be laboratory error or laboratory contamination. Field contamination could also cause an upward trend, however, field contamination would probably manifest itself as results that are significantly different from historical values than as a trend, since it is less likely that field contamination would occur systematically as would be required to establish a trend.

Information Available from Existing QC Data

The information available from current field QC data that would be most supportive of a correct decision that a trend had or had not been established would be the results of QC samples that were analyzed by two different analytical laboratories. Since two analytical laboratories are not available for tritium analysis, current field QC samples cannot be used directly to support the existence of an upward trend in tritium concentration.

The other data that would be useful in supporting decisions related to trends are the results of the analytical laboratory's internal quality control program. Although outside the scope of this research, data from laboratory blanks, spikes, control standards, and performance evaluation standards (samples spiked by an outside organization with a known and certified amount of the analyte of interest that are supplied to the laboratory in such a way to be indistinguishable from routine samples) are extremely useful in validating the results achieved by analytical laboratories.

Information Not Available from Existing Field QC Data

The most useful data for confirming the decision that an upward trend in concentration has been established are those that provide for an assessment of the bias of the results provided by the analytical laboratory. Of secondary importance are data that would verify that the apparent trend was not caused by field contamination. This information is not available from existing LLNL field quality control samples.

Unresolved Issues From Existing Field QC Data

The main unresolved issues from current field QC data that could lead to an incorrect decision that an upward trend had been established are the outliers in tritium analysis that were discussed previously and the disagreement between duplicate and routine copper and zinc samples that were analyzed by different analytical laboratories. For zinc in particular, the difference between duplicate samples analyzed by two different laboratories was significant enough to cast a doubt on all zinc analyses. This issue must be resolved before any decisions regarding zinc (and probably copper) can be made with confidence.

Recommendations for Changes to Field QC Sampling

The use of field blanks would provide additional information that could increase confidence that the decision that a trend had been established was correct. It was recommended earlier that field blanks be prepared but not analyzed when sampling for tritium in order to determine whether field contamination had occurred in a case where tritium was detected at levels above the MCL. Field blanks for copper, zinc, and pesticides should also be taken. Since the data set for copper, zinc, and pesticides is so small and since measured concentrations for those analytes are typically at or near the analytical laboratory reporting limit, field blanks should be analyzed regularly, even when potential trends have not been identified, until sufficient data of known quality have been accumulated to define quantitative DQOs for these parameters.

LLNL Standard Operating Procedures currently require that half of the field duplicates for nonradiological parameters be sent to the primary analytical laboratory and the other half be sent to the QC analytical laboratory. The zinc and copper data considered in this study showed that when both samples were

analyzed by the primary analytical laboratory, the results agreed closely. When the QC laboratory was used for the analysis, the results did not agree. This discrepancy must be investigated and resolved before any copper and zinc data can be used to make decisions with confidence. In the meantime, sending all duplicate samples to the QC laboratory could provide information that would help with this investigation.

Additional Resources Required to Implement Recommended Changes

Before implementing long-term changes to field quality control sampling, the issue of inconsistent results between two analytical laboratories for copper and zinc must be resolved. This investigation would begin with a review of the different laboratories' internal quality control data and a comparison of the methodology used for extraction and analysis by each laboratory. If those examinations did not reveal the source of the uncertainty, more extensive evaluations of laboratory practices would be required. If the answer to this question is not found in the early stages of this investigation, significant time could be required from the Environmental Analyst, Quality Assurance Coordinator, and management to resolve it. If visits to analytical laboratories are required, additional costs would be incurred.

Long-term changes recommended to field quality control sampling in order to increase confidence in decisions related to upward trends in data include the collection of one field blank for copper, zinc, and pesticides for each storm water runoff sampling event. To obtain the most benefit from these samples, one set of field blanks should be analyzed at least once a year, whether or not a trend had been established. Additional resources that would be required to implement this include additional bottles to collect the samples, sampling

technologist time to label the bottles, prepare the field blanks during the sampling event, and complete the appropriate paperwork; and analytical laboratory costs to analyze field blanks annually and upon request of the Environmental Analyst. Since there are only six storm water runoff sampling locations (plus one field duplicate), adding a field blank could increase the cost of sampling and analysis by up to 14%. Actual increases will be less, however, because no additional sampling locations are added (meaning that no additional travel time would be involved); preparation of field blanks is less time consuming than actual sampling because it does not have to be performed in locations that may be difficult to access; and, since not all field blanks will be analyzed, the increase in analytical costs will not be as great.

Field Spikes

Field spikes have only received brief consideration for inclusion in the LLNL rain and storm water runoff field Quality Control program. There are several difficulties with taking field spikes and the information gained from them does not justify the resource expenditure that would be required.

Field spikes are a potential source of field contamination. In order to prepare a field spike, an aliquot containing a fairly high concentration of the analyte of interest must be added to a sample in the field. Strict contamination control measures would have to be implemented to ensure that non-spiked samples were not contaminated during the preparation of the field spike and that cross-contamination between the spiked sample and the routine samples did not occur during sampling and transport. In the case where unusually high results appeared in a routine sample, field blank data would be critical to prove that field contamination was not the cause.

Additional difficulties arise because the availability of rain and storm-water runoff is storm-dependent. Sufficient volume of rain or storm water runoff may not always be available to prepare a field spike. If the field spike were prepared by adding a premeasured aliquot to a sample or by adding sample to a prespiked sampling container, inability to fill the container completely with sample water would significantly impact the spiked sample concentration. The opposite extreme would occur if too much sample water were added to a pre-spiked sample container and part of the spiking material were lost. This would not only result in inaccurate results, but could also create other problems if the spiked material were spilled to ground. Since these spikes are prepared in the field, in what are likely to be adverse weather conditions, the possibility that one of these mishaps could occur during spike preparation is fairly high.

The primary use of field spikes is to evaluate the bias of the sampling and analysis process. Since normal analytical laboratory quality control samples routinely include spikes, thus providing data that allow for the determination of bias of the analysis step, and since there are several inherent problems involved in spiking samples in the field that are not easy to resolve, it is not recommended that LLNL include field spikes in its rain or storm water runoff monitoring programs.

Summary of Recommended Changes and Resource Impacts

Several changes are recommended in the field QC samples for the LLNL rain and storm water runoff monitoring networks.

Field Spikes

Field spikes are not recommended at this time due to inherent problems with their preparation and the fact that analytical laboratory QC data provides more reliable data regarding the bias of the analysis. Review of analytical laboratory QC results should provide sufficient information to assess the bias of the results of this monitoring.

Field Blanks

The collection of a field blank should be required for each storm event for each monitoring network. Field blanks should be analyzed annually to provide added confidence in any decisions that were made related to trends. Field blanks should also be analyzed any time a tritium value exceeds the MCL or any time that any data point is significantly higher than would be expected based on historical results. A small resource impact from collecting and analyzing field spikes is expected but this is justified by the additional information these samples provide.

Duplicates and Replicates

The existing program of duplicate and replicate samples is adequate, however, the addition of a fixed replicate rain sample at location L-B343 would increase the likelihood that a tritium value measured above the MCL could be confirmed. Resource impacts of the additional replicate sample would be minimal, since it would not be analyzed unless significantly elevated tritium was measured in a routine sample.

Until the discrepancy between copper and zinc results from the primary and QC analytical laboratories is resolved, it is recommended that duplicate

samples be sent to the QC laboratory for every storm, instead of for every other storm. This will create a larger data set that should provide more information that can be used to research the issue.

Other Recommended Changes

The apparent discrepancy between results for zinc and copper from the primary and QC analytical laboratories must be resolved before decisions can be made from these data with any degree of confidence. Since the data sets for these analytes are so small, it would be difficult to make decisions from them even if interlaboratory results confirmed their bias. Once the analytical laboratory bias has been resolved and sufficient data have been collected, these analytes should be submitted to an analysis similar to the one that was done for tritium in Subproblem Two.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Purpose of the Research

Prior to this research, a systematic evaluation of the field quality control samples from the LLNL rain and storm water monitoring networks had not been performed. The United States Environmental Protection Agency has developed a specific methodology for defining and analyzing Data Quality Objectives for environmental data and it was hypothesized that application of this method to LLNL rain and storm water monitoring data could result in improved data quality without a significant increase in resource requirements. This research was limited to the examination of routine and field quality control sample results and did not include an evaluation of analytical laboratory quality control data.

Summary

Subproblem One

The first subproblem developed Data Quality Objectives for monitoring of tritium in rain and storm water runoff and copper, zinc, and pesticides in storm water runoff using the first six steps of the United States Environmental Protection Agency's Data Quality Objectives development process.

Three action levels were defined for tritium monitoring: data that exceed the California state maximum contaminant level of 20,000 pCi/L; data that exhibit a consistent upward trend; and data that are significantly different from historical results. Means of identifying each of these situations were determined and actions to be taken when an action level is reached were defined based on the level of concern of the LLNL primary decision maker.

Since numerical limits for zinc, copper, and pesticides have not been determined, only one action level was defined for these analytes: data that are significantly different from historical results. Means of identifying these data were defined and actions to be taken when they are identified were defined based upon the level of concern of the LLNL primary decision maker.

Subproblem Two

The second subproblem evaluated data collected between January 1, 1992 and December 31, 1994, with specific focus on the use of field quality control samples to determine if the Data Quality Objectives defined in subproblem one were met. Field quality control samples collected during that period only include sporadic duplicate or replicate samples. Field blanks and field spikes were not taken for either rain or storm water runoff.

A reasonably large data set was available for tritium monitoring during the time period studied, allowing for some statistical analysis. Field QC results were most useful in supporting the decision that the MCL had or had not been exceeded. In general, the field QC samples supported the conclusion that the precision of the data collected was reasonably good, however, occasional pairs of duplicate or replicate and routine samples showed a level of variability that was unacceptable. This issue needs further investigation and resolution.

Review of historical data was also important in supporting a decision that the MCL had been exceeded. Evaluation of trends and comparison of data to historical results relied more on a review of historical data than on the results of field QC samples. For these decisions, the field QC data supported the decision only indirectly by defining the reproducibility of the data.

Very limited data were available for copper, zinc, and pesticides. Interpretation of these data was confounded by the fact that a change in analytical laboratories in June of 1993 resulted in higher analytical laboratory reporting limits for all of these analytes. In addition, the results of copper and zinc analyses provided by an analytical laboratory contacted to measure duplicate samples in order to provide interlaboratory comparison data did not agree with results from the primary analytical laboratory. Additional work must be done to determine whether LLNL should work with the current analytical laboratory to obtain lower reporting limits and to resolve the discrepancy in zinc and copper results before the quality of these data can be assessed and decisions can be made. Once these questions have been resolved, and sufficient data have been collected, an analysis of these data similar to the one performed for tritium should be performed. At the current rate of data collection, it will take two to three years to accumulate sufficient data to do this analysis. Changes to monitoring programs are outside the scope of this research, but the frequency of data collection for these analytes should be evaluated as part of a technical assessment of the storm water runoff monitoring network.

Subproblem Three

The third subproblem used the results of subproblem two to make recommendations for changes in field quality control sampling for LLNL rain and storm water runoff monitoring networks that would provide additional confidence that specified Data Quality Objectives were met and discussed the additional resources that would be required to implement those recommendations.

Some open issues must be resolved in order to determine whether data meet the specified Data Quality Objectives. Before copper and zinc data can be used with confidence, the apparent discrepancy between results from the primary and QC analytical laboratories must be resolved. In addition, since the action level for zinc, copper, and pesticides is based upon a comparison to historical results, a larger data set must be obtained for those analytes before a definitive evaluation of the data can be made.

Changes to the field quality control sampling program for rain and storm water runoff are also recommended in order to better evaluate whether data meet specified DQOs. Field blanks should be added to both monitoring networks. Field blanks should be analyzed annually to provide added confidence in any decisions that are made related to trends as well as any time a tritium value exceeds the MCL or any time that any data point is significantly higher than would be expected based on historical results. A small resource impact from collecting and analyzing field spikes is expected but this is justified by the additional information these samples provide.

The existing program of duplicate and replicate samples is adequate, however, the addition of a fixed replicate rain sample at location L-B343 would increase the likelihood that a tritium value measured above the MCL could be confirmed. Resource impacts of the additional replicate sample would be minimal, since it would not be analyzed unless significantly elevated tritium was measured in a routine sample.

Until the discrepancy between copper and zinc results from the primary and QC analytical laboratories is resolved, it is recommended that duplicate samples be sent to the QC laboratory for every storm, instead of for every other

storm. This will create a larger data set that should provide more information that can be used to research the issue.

Field spikes are not currently used in LLNL environmental monitoring and are not recommended due to the difficulty involved in preparing them properly, the additional resources that would be required to prepare them, and the fact that more valuable information regarding bias can be obtained from data that are part of each analytical laboratory's routine Quality Control program.

Conclusions and Recommendations for Further Work

Several recommendations for additional work can be made based on the results of this research. The systematic approach to environmental monitoring data that was applied in this research revealed some intriguing facts about the monitoring networks that were studied. Environmental monitoring at LLNL incorporates much more than rain and storm water runoff and it is likely that applying this methodology to the remaining networks would be equally enlightening.

Several actions should be taken to specifically address the monitoring networks that were studied. More data should be collected for copper, zinc, and pesticides and those data should be reviewed in a similar fashion to the way the tritium values were analyzed. Apparent discrepancies between duplicate or replicate and routine samples should be resolved, particularly in the case of copper and zinc where results from two analytical laboratories are not comparable. Changes to the field QC program, including the addition of field blanks, that were discussed earlier should be made and these data, as well as analytical laboratory QC results, should be incorporated into the determination of whether data meet Data Quality Objectives. Zinc results should continue to be

monitored, especially after interlaboratory discrepancies have been resolved, to determine if an upward trend has been established or whether a temporal cyclic trend in zinc concentration in storm water runoff exists. Finally, LLNL needs to compare the benefits that might be obtained by requesting lower reporting limits from analytical laboratories to the potential costs of implementing these lower limits and make a determination as to whether lower reporting limits will be requested. Lower reporting limits are more likely to detect significant changes in the concentration of these analytes. Because DOE and RWQCB require that significant changes in pesticide levels be reported, this increased sensitivity could lead to increased cost (and potentially to negative publicity for LLNL). This must be taken into account when determining the approach to be taken.

APPENDIX A

ABBREVIATIONS AND ACRONYMS

ACS	American Chemical Society
ASTM	American Society for Testing and Materials
ANOVA	Analysis of Variance
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
COC	Chain of Custody
DMT	Data Management Team
DOE	United States Department of Energy
DQOs	Data Quality Objectives
EMP	Environmental Monitoring Program (LLNL EPD)
EPA	United States Environmental Protection Agency
EPD	Environmental Protection Department (LLNL)
FTF	Field Tracking Form
HTO	Tritiated Water
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
LCL	Lower Control Limit
LLNL	Lawrence Livermore National Laboratory
MCL	Maximum Contaminant Level
mg/L	milligrams per Liter (unit of concentration for metals)
NPDES	National Pollutant Discharge Elimination System
pCi/L	picoCuries per liter (unit of tritium concentration)
QAMS	Quality Assurance Management Staff
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RWQCB	Regional Water Quality Control Board
SAER	Site Annual Environmental Report
SNLL	Sandia National Laboratories, Livermore
SWPPP	Storm Water Pollution Prevention Plan
SWRCB	State Water Resources Control Board
TSG	Technical Support Group (LLNL EPD)
UCL	Upper Control Limit
ug/L	micrograms per Liter (unit of concentration for pesticides)
USEPA	United States Environmental Protection Agency
VOA	Volatile Organic Analysis
WDR	Waste Discharge Requirement
WGMG	Water Guidance and Monitoring Group (LLNL EPD)

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