15. Quality Assurance

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Introduction

Quality assurance (QA) is a system of activities and processes put in place to assure that monitoring and measurement data meet user requirements and needs. Quality Control (QC) consists of procedures used to verify that prescribed standards of performance in the monitoring and measurement process are attained. QA requirements for environmental monitoring of DOE facilities are mandated by DOE Orders and guidance. DOE Order 5400.1 identifies QA requirements for radiological effluent and surveillance monitoring and specifies that a QA program consistent with DOE Order 5700.6 be established. The latter Order sets forth policy, requirements, and responsibilities for the establishment and maintenance of plans and actions that assure quality achievement in DOE programs. The DOE *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (U.S. Department of Energy 1991) requires that an Environmental Monitoring Plan be prepared that contains a QA section discussing the applicable elements of the American National Standards Institute / American Society of Mechanical Engineers (ANSI / ASME) NQA-1, *Quality Assurance Program Requirements for Nuclear Facilities* (ASME 1989).

LLNL conducted QA activities in 1995 at the Livermore site and Site 300 in accordance with a plan based on DOE Order 5700.6C (Garcia and Failor 1993). DOE Order 5700.6C prescribes a risk-based, graded approach to QA. This process promotes the selective application of QA and management controls based on the risk associated with each activity, maximizing the effectiveness and efficiency in resource use.

LLNL environmental sampling is conducted according to procedures published in an appendix to the LLNL *Environmental Monitoring Plan* (Tate et al. 1995). Environmental monitoring samples are analyzed by LLNL or commercial laboratories using EPA standard methods when available. When EPA standard methods are not available, custom analytical procedures, usually developed at LLNL, are used. The radiochemical methods used by LLNL laboratories are described in procedures unique to the laboratory performing the analyses. When analyses are performed by independent contractors, LLNL requires that their laboratories be certified by the State of California for the analyses performed for LLNL. In addition, LLNL requires all analytical laboratories to maintain adequate QA programs and documentation of methods.

15. Quality Assurance

Quality Assurance Activities

The LLNL environmental monitoring program was audited successfully by the Department of Energy in 1995.

During 1995, 132 Nonconformance Reports (NCRs) related to environmental monitoring were written by the environmental monitoring staff. The major sources of NCRs were air particulate sampling equipment failures and analytical laboratory problems. Air particulate sampling equipment problems are ongoing and cannot be eliminated without a major resource expenditure for upgraded equipment. Analytical laboratory issues are addressed as they arise. It is anticipated that the detailed Statement of Work developed for the contracts starting in 1996 will result in improved data quality from off-site analytical laboratories.

Discrepancies and inconsistent results for radiological samples analyzed by off-site contract laboratories during 1995 led to an extensive performance evaluation study of these laboratories. Because results of this evaluation were inconclusive, a joint EPD / CES Performance Evaluation Committee will continue to study this issue.

Analytical Laboratories

In April of 1995, reorganization within LLNL and EPD affected the Radiation Analytical Sciences (RAS) analytical laboratory. This laboratory, which had been a part of the Environmental Protection Department (EPD), was transferred to the Chemistry and Materials Science Directorate and combined with a nonradiological laboratory that had also been a part of EPD to form Chemistry and Materials Science Environmental Services (CES). This laboratory continues to perform radiological analyses of extremely low-level environmental samples.

The off-site contract analytical laboratory that had been analyzing nonradiological Quality Control (QC) duplicates was also reorganized during 1995. This reorganization made it impossible for that laboratory to continue analyzing LLNL samples. In June of 1995, a replacement laboratory was audited and qualified for use as a QC lab until existing analytical contracts expired in January of 1996.

Three of the remaining four off-site contract analytical laboratories were audited by EPD and CES QA and technical personnel during 1995 under the terms of the existing contract. Audit reports were prepared detailing the results of these audits. The fourth laboratory was audited in late 1994.

In April of 1995, LLNL began preparations to rebid its contracts for external analytical services. These contracts were originally intended to include all EPD off-site environmental analyses, including environmental and hazardous waste samples. Late in the rebid process, the scope of the contracts was expanded to

include samples from Lawrence Berkeley National Laboratory (LBNL). A detailed Statement of Work was developed, requests for proposals were sent out, and candidate laboratories were evaluated. The top three candidates for each of two bid packages (nonradiological environmental samples and full service radiological and nonradiological) were evaluated by performance evaluation samples and audits. Two primary laboratories and one QC laboratory were selected for each bid package in late 1995 for contracts scheduled to begin in early 1996.

Participation in Laboratory Intercomparison Studies

During 1995, the CES Environmental Monitoring Radiation Laboratory (CES EMRL) and the Hazards Control Department's Analytical Laboratory (HCAL) participated in both the EPA's Environmental Monitoring Systems Laboratory (EMSL) intercomparison studies program and the DOE Environmental Monitoring Laboratory (EML) intercomparison studies program. In the EMSL program, CES EMRL successfully analyzed 28 of 30 samples within established acceptance control limits, and HCAL successfully analyzed 6 of 8 samples. In the EML program, 54 of 54 sample results from the CES EMRL were within acceptance control limits as were 10 of 10 samples from the HCAL.

The HCAL also participated in four EPA Water Pollution and Water Supply studies during 1995. Of 70 samples that were analyzed, 68 fell within established acceptance control limits.

The intercomparison study results, as well as the follow-up explanation and response for data that fell outside the acceptance control limits are presented in Volume 2. Contract laboratories are also required to participate in laboratory intercomparison programs; however, permission to publish their results for comparison purposes was not granted for 1995.

The potential effects of unacceptable intercomparison study results on routine data have not been fully determined or evaluated. A joint EPD/CES performance evaluation committee has been formed to create a systematic process for evaluating laboratory performance using traceable standards. A method for evaluating the results of intercomparison studies will be developed by that committee.

Duplicate Analyses

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. 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). Collocated samples may also be used to identify errors—for example, mislabeled samples and data entry errors.

Tables 15-1 through **15-3** present data generated by collocated sample pairs, grouped by sample matrix and analyte. Samples from both the Livermore site and Site 300 are included. **Tables 15-1** and **15-2** contain data pairs in which both values are above the detection limit and all radiological results for which a reported value was available. The tables exclude radiological values for which only a minimum detectable activity was reported. In addition, **Table 15-2** excludes radiological results for which the reported value was negative. **Table 15-3** contains data pairs in which either or both values are below the detection limit.

If there were more than eight data pairs with both results above the detection limit, precision and regression analyses were performed; the results are presented in **Table 15-1**. Precision is measured by the percent relative standard deviation (%RSD); see the EPA *Data Quality Objectives for Remedial Response Activities: Development Process,* Section 4.6 (U.S. Environmental Protection Agency 1987).

Acceptable values for %RSD vary greatly with matrix, analyte, and analytical method; however, values above 30% are common. The results for %RSD given in **Table 15-1** are the 75th percentile of the individual precision values. Regression analysis consists of fitting a straight line to the collocated sample pairs. Good agreement is indicated when the data lie close to a line with slope equal to one and intercept equal to zero, as illustrated in **Figure 15-1**. Allowing for normal analytical variation, the slope of the fitted line should be between 0.7 and 1.3, and the absolute value of the intercept should be less than the detection limit. The coefficient of determination (r^2) should be >0.8.

If there are eight or fewer data pairs with both results above the detection limit, the ratios of the individual duplicate sample pairs are averaged; the average, minimum, and maximum ratios for selected analytes are given in **Table 15-2.** The mean ratio should be between 0.7 and 1.3.

If one of the results in a pair is below the detection limit, then the other result should be less than two times the detection limit. **Table 15-3** identifies the sample media and analytes for which at least one pair failed this criterion. Analytes with fewer than four pairs total are omitted from the table.

Table 15-1. Quality assurance duplicate sampling. Summary statistics for analytes with more than eight pairs in which both results were above the detection limit.

Medium	Analyte	N[a]	%RSD[b]	Slope	r^2[c]	Intercept	Units
Air	Beryllium[d]	21	16.3	1.08	0.82	–0.45	pg/m^3
	Gross alpha[d]	93	82.8	0.328	0.12	-2.33×10^{-7}	pCi/L
	Gross beta	93	28.9	0.823	0.81	2.053×10^{-6}	pCi/L
	Tritium	33	21.3	0.946	0.95	–0.00006	pCi/L (air)
Radiation dose	Radiation dose[d]	27	2.95	0.943	0.78	112	µSv
Ground water	Arsenic	25	9.43	1.00	1.0	0.00013	mg/L
	Bicarbonate alkalinity (as $CaCO_3$)[e]	18	4.56	0.892	0.65	22.1	mg/L
	Calcium	18	1.96	0.896	0.85	2.64	mg/L
	Chloride	18	2.31	1.03	1.0	–1.86	mg/L
	Fluoride	18	3.11	0.977	0.99	0.00532	mg/L
	Gross alpha[d]	17	60.6	0.399	0.48	0.729	pCi/L
	Gross beta[d]	17	25.6	0.217	0.28	3.88	pCi/L
	Magnesium	18	3.45	0.972	0.99	0.149	mg/L
	Nitrate (as NO_3)	15	1.69	0.989	1.0	0.578	mg/L
	Potassium	18	6.61	0.959	0.99	–0.0440	mg/L
	Sodium	18	2.77	0.989	1.0	–0.561	mg/L
	Specific conductance	18	3.77	1.01	0.99	–6.99	µmhos/cm
	Sulfate	18	3.14	0.990	1.0	1.15	mg/L
	TDS[e]	18	3.37	1.25	0.018	525.	mg/L
	Total alkalinity[d] (as $CaCO_3$)	18	4.56	0.892	0.65	22.1	mg/L
	Total hardness (as $CaCO_3$)	18	2.67	0.917	0.92	8.82	mg/L
	Vanadium	9	5.24	1.12	1.0	–0.00546	mg/L
	pH	19	0.949	0.942	0.97	0.466	Units
Sewer	Gross alpha[d]	32	99.3	0.0981	0.0073	0.852	pCi/L
	Gross beta	51	19.5	1.15	1.0	–2.78	pCi/L
	Tritium	34	56.4	1.02	0.96	–53.9	pCi/L

a Number of duplicate pairs included in regression analysis.

b 75th percentile of percent relative standard deviation (%RSD), where %RSD = $\left(200/\sqrt{2}\right)\left(|x_1 - x_2| / (x_1 + x_2)\right)$ and x_1 and x_2 are the reported concentrations of each routine-duplicate pair.

c Coefficient of determination.

d Outside acceptable range of slope or r^2 due to variability.

e Outside acceptable range of slope or r^2 due to outliers.

Table 15-2. Quality assurance duplicate sampling. Summary statistics for selected analytes with eight or fewer pairs in which both results were above the detection limit.

Medium	Analyte	N[a]	Mean ratio	Minimum ratio	Maximum ratio
Air	Plutonium-239[b]	8	0.69	0.10	1.6
Ground water	Chromium	4	1.0	0.97	1.1
	Thorium-230	2	1.3	0.41	2.2
	Thorium-232[b]	1	2.9	2.9	2.9
	Uranium-234, Uranium-233	7	1.1	0.72	1.4
	Uranium-235, Uranium-236[b]	5	1.9	0.57	5.5
	Uranium-238	7	1.1	0.71	1.4
Rain	Tritium	4	0.99	0.79	1.2
Runoff (from rain)	Gross alpha[b]	4	0.57	0.20	0.95
	Gross beta	4	1.1	0.86	1.3
	Tritium	2	0.73	0.73	0.73
Other water	Gross alpha[b]	4	2.0	0.33	5.5
	Gross beta[b]	4	0.68	0.42	1.1
	Tritium	3	0.91	0.86	0.95
Soil	Beryllium[b]	1	2.4	2.4	2.4
	Cesium-137	2	0.75	0.45	1.0
	Plutonium-239	2	0.81	0.47	1.1
	Plutonium-239, Plutonium-240[b]	4	2.2	0.21	6.2
Vegetation	Tritium	5	1.1	0.66	1.7
	Tritium, per gram dry weight	5	1.1	0.69	2.0

a Number of data pairs.

b Outside acceptable range of 0.7–1.3, for mean ratio.

Table 15-3. Quality assurance duplicate sampling. Summary statistics for analytes with at least four pairs in which one or both results were below the detection limit.

Medium	Analyte	Number of inconsistent pairs	Number of pairs	Percent of inconsistent pairs
Air	Tritium	4	12	33.3
Ground water	Copper	1	18	5.6
	Freon 113	1	18	5.6
	Tritium	1	13	7.7
Runoff (from rain)	Copper	1	5	20
	Nickel	1	5	20
Sewer	Methylene chloride	1	4	25
Other water	Iron	2	4	50
	Manganese	1	5	20
	Silver	1	7	14.3
	Zinc	1	5	20
Vegetation	Tritium	1	7	14.3

These analyses show generally good agreement between routine samples and quality assurance duplicates: approximately 84% of the pairs have a precision better than 30%. Data sets not meeting our precision criteria generally fall into one of two categories. The first category, outliers, can occur because of data transcription errors, measurement errors, or real but anomalous results. Of 29 data sets reported in **Table 15-1**, four did not meet the criterion for acceptability because of outliers. **Figure 15-1** illustrates a set of collocated pairs with a single outlier. The other category of results that does not meet the criterion for acceptability consists of data sets in which there is a lot of scatter. This tends to be typical of measurements at extremely low concentrations as illustrated in **Figure 15-2.**

Low concentrations of radionuclides on particulates in air highlight this effect even more because one or two radionuclide-containing particles on an air filter can significantly impact results. Another cause of high variability is sampling and analytical methodology. Analyses of total organic carbon and total organic halides in water are particularly difficult to control. Of the 26 data sets in **Table 15-1**, seven show sufficient variability in results to make them fall outside of the acceptable range.

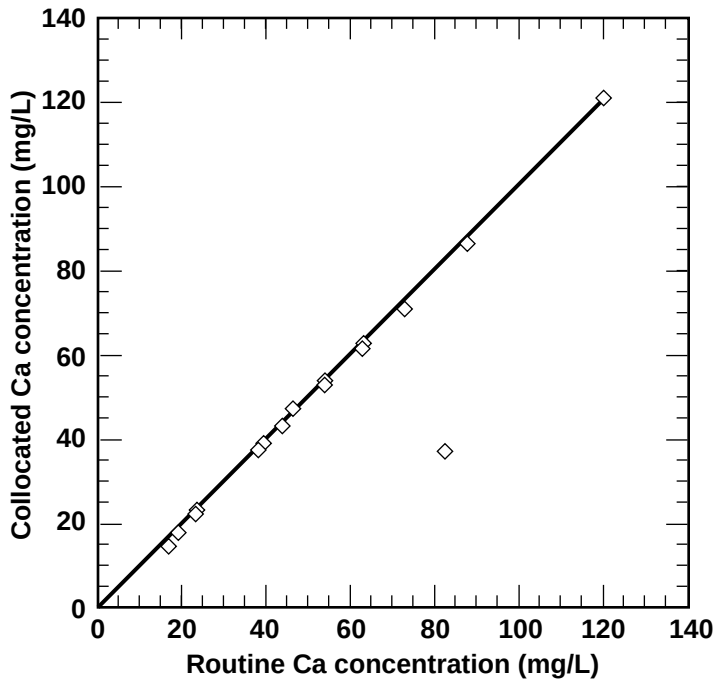

Figure 15-1. Calcium concentration in ground water from collocated samples. For each pair of samples, one result is plotted on ordinate (collocated) and the other result on the abscissa (routine). Data are shown with a line having a slope equal to one and intercept equal to zero. The measure of acceptability is determined by how well the data fall on the line.

Deviations and Changes to the Sampling Program

The sections that follow summarize changes to the environmental sampling effort made during 1995, deviations from planned environmental sampling, and omissions of data expected from regularly scheduled samples.

Changes to Environmental Monitoring Networks

Changes that were made to environmental monitoring networks in 1995 are summarized in **Table 15-4**.

The LLNL environmental monitoring program uses alpha-numeric location designator codes to define sampling locations. Volume 2 includes tables that decode these sampling location designators and provide a cross-reference between current designators and those used in previous years. Changes made in 1995 are noted on those tables.

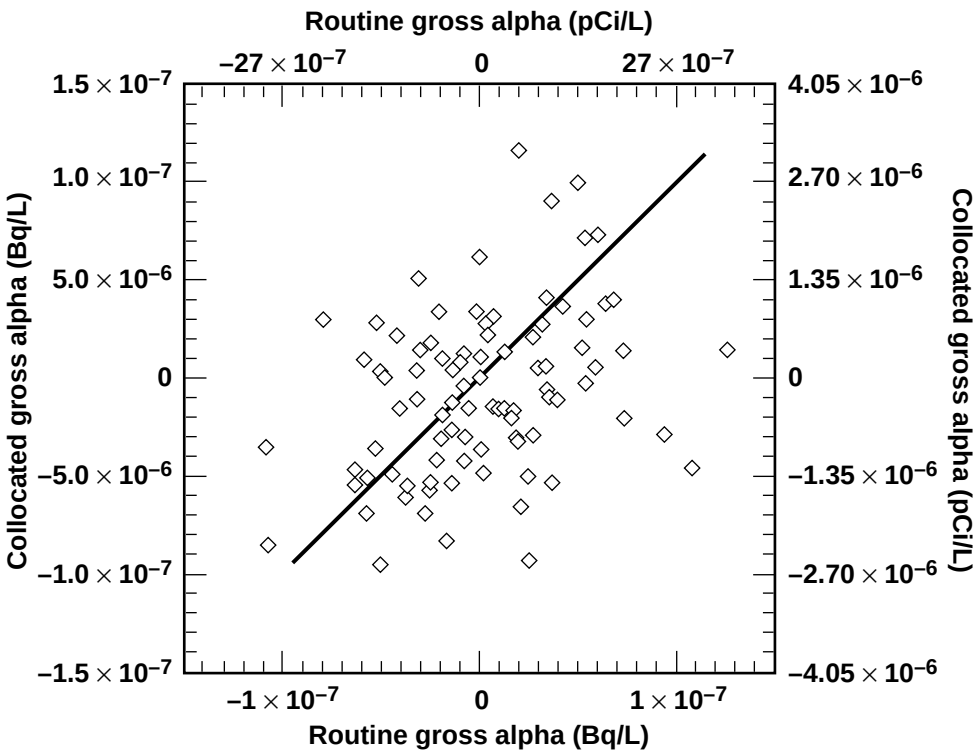

Figure 15-2. Gross alpha data from collocated samples collected on air filters. Data are shown with a line having a slope equal to one and intercept equal to zero.

One off-site air particulate monitoring station was eliminated during 1995 because of problems with electrical safety at that location. Two off-site vegetation monitoring locations were eliminated after 1994 as a result of a technical assessment of the vegetation monitoring network. The two locations that were removed, both of which are more than 25 km from LLNL, are no longer necessary because the remaining background locations are adequate for surveillance purposes.

The LLNL radiation monitoring networks changed significantly at the end of 1994. Neutron monitoring at the Livermore site was eliminated because of the absence of neutron sources requiring monitoring. The need for this monitoring will be reevaluated if new sources of neutrons are introduced. The thermoluminescent dosimeter network was also significantly reduced at the end of 1994, when a technical assessment of that network showed that environmental radiation could be adequately characterized with a smaller number of dosimeters.

Table 15-4. Changes to environmental monitoring networks in 1995.

Environmental medium	Livermore site	Site 300
Air particulate	L-ERCH dropped 10/10/95	No changes
Air tritium	No changes	Not sampled
Soil	No changes	No changes
Arroyo sediment	No changes	Not sampled
Vegetation	Dropped locations L-DAN and C-MOD after 1994	No changes
Wine	No changes	Not sampled
Rain	Reinstated locations L-BVA, L-GTES, and L-VINE in 1995	No changes
Storm water runoff	Reinstated location L-ALPO between 1Q and 4Q 1995	Added locations 3-GEOCRK and 3-CARN between 1Q and 4Q 1995
Drainage Retention Basin	No changes	Not sampled
Other surface water	No changes	Transferred location 3-GEOCRK to runoff network between 1Q and 4Q 1995
Ground water	Network added in 1995	No changes
Cooling towers	Not sampled	No changes
Sewage	No changes	Not sampled
Thermoluminescent dosimeters	Dropped 28 locations after 1994	Added 1 location
	Dropped 6 of 12 duplicates after 1994	Dropped 4 locations after 1994
	Dropped 5 of 7 transit controls after 1994	Dropped 2 additional locations after 1Q 1995
		Dropped 2 transit controls after 1994
Neutrons	Stopped monitoring after 1994	Not sampled

Three rain monitoring stations that had been eliminated in 1994 were reinstated in 1995 when a study of rain and meteorological data revealed that those locations were necessary to completely characterize precipitation of tritium from LLNL and SNL/California sources. Storm water monitoring location L-ALPO was reinstated in 1995 to measure influent to LLNL in response to elevated levels of gross alpha and beta in storm water runoff at another influent location. Two

monitoring locations at Site 300 were transferred from the surface water monitoring network to the storm water monitoring network.

Finally, surveillance monitoring of ground water at the Livermore site was added in 1995. This network is intended to provide data to establish baseline conditions of ground water quality and quantity in response to DOE Order 5400.1 and to meet the ground water monitoring requirements of 40 CFR Part 265, Subpart F.

Explanation of Missing Samples

Planned samples and actual samples collected and analyzed in 1995 are summarized in **Table 15-5.**

Table 15-5. Sampling completeness in 1995, Livermore site and Site 300.

Environmental medium	Samples planned	Samples analyzed	Completeness (%)
Air particulate	2091	2030	97.1
Air tritium	468	447	95.5
Soil	76	76	100
Arroyo sediment	24	24	100
Vegetation	76	76	100
Wine	22	22	100
Rain	110	108	98.2
Storm water runoff			
Site 300	123	82	66.7
Livermore	397	308	77.0
Drainage Retention Basin			
Field Measurements	238	416	54.8
Samples	89	88	98.9
Other surface water	120	116	96.6
Ground water			
Site 300	406	405	99.8
Livermore	1592	1592	100
Sewage	614	595	96.9
Thermoluminescent dosimeters	212	200	94.3
Cooling towers	16	16	100

Sample loss for the air particulate network were caused by a number of factors: tripped ground fault interrupt (GFI) circuits (24%), loss of location L-ERCH (18%), missed maintenance (12%), motor problems (12%), inadequate air flow (11%), access problems due to weather (11%), power off or unit unplugged (8%), samples not collected (2%), and the government shutdown (2%). Lost samples for the air tritium network were due to: flow out of range (24%), broken flasks (24%), motor problems (19%), tripped GFI circuits (19%), and power off upon arrival to collect the sample (14%). Two rain samples were lost because the sample bottles broke before reaching the laboratory. Two surface water samples were also missed because of an oversight on the part of sampling personnel.

The primary cause of lost samples for the Site 300 storm water runoff monitoring network was insufficient flow for sample collection. One set of samples was not analyzed because the sampling location is a spring and the flow at that location was determined to be spring water rather than storm water runoff at the time of sampling. One planned sampling event for storm water runoff was not accomplished at the Livermore site. Typically, the first storm of a rainy season is sampled in October or November and a second storm is sampled in December. Because of the late start of the 1995 – 1996 rainy season, the first storm that could be sampled during this season did not arrive until December, with the result that one less storm than was planned was sampled in 1995. Additional losses for the Livermore site storm water runoff network occurred because total suspended solids and Chrome VI analyses were not requested on the Chain of Custody for one storm.

The lost sample for the Drainage Retention Basin was a QC duplicate that was inadvertently omitted. Field sample losses were due to equipment malfunction (59%) and scheduling problems (41%). These samples are taken for basin management only and are not required for regulatory compliance.

The sample for Site 300 ground water monitoring was lost when a bottle containing a sample for tritium analysis broke. In the past, these bottles were cleaned and reused. The chance of this reoccurring has been minimized by replacing these sample bottles.

Sewer sampling and analysis is performed on a daily, weekly, and monthly basis. Thirteen daily samples could not be collected because of pump failures and planned equipment upgrades. All weekly samples were collected. One monthly sample was not analyzed because the analysis was not requested. Several analyses were not completed on the October monthly sample because the sample was too small after the Livermore Water Reclamation Plant (LWRP) used part of it to verify LLNL results.

Thermoluminescent dosimeters were lost when they were destroyed by vandals or eaten by cows. Because the majority of these samples are located off-site, it is difficult to protect them from people or animals. Unfortunately, these dosimeters have proven to be particularly appetizing to cows.

Statistical Methods

Statistical methods used in this report have been implemented pursuant to the *Environmental Monitoring Plan* (Tate et al. 1995). These methods reduce the large volumes of monitoring data to summary concentration estimates that are suitable for both temporal and spatial comparisons. Attention is given to estimating accuracy, bias, and precision of all data.

Data review and analyses are conducted in accordance with the *Environmental Monitoring Plan* and the Environmental Monitoring Section's Data Analysis Procedure. These documents contain detailed information regarding the acceptability of data and the procedures that are followed for the identification, notification, and correction of suspect data.

Radiological Data

The precision of radiological analytical results is displayed in the Volume 2 data tables as the 2σ counting error. The counting errors are not used in any summary statistic calculations. By convention, any radiological result exhibiting a 2σ counting error greater than 100% is said to be below the detection criterion and is presented in the tables with a less-than symbol (<) to indicate its status. No value of error is reported for values below the detection criterion. The reported concentration is derived from the number of sample counts minus the number of background counts. A sample with a low or zero concentration may therefore be reported to have a negative value; such results are reported in the tables and used in the calculation of summary statistics and statistical comparisons. Some analytical laboratory reports provide a minimum detectable activity rather than a reported value when the radiological result is below the detection criterion.

Nonradiological Data

Nonradiological data that are reported as being below the analytical detection limit also are displayed in the tables with a less-than symbol. The actual detection limit values are used in the calculation of summary statistics as explained below.

Statistical Comparisons

Standard comparison techniques (such as regression, *t*-tests, and analysis of variance) have been used where appropriate to determine the statistical significance of trends or differences between means. All such tests of significance have been performed at the 0.05 level. When such a comparison is made, it is explicitly stated in the text as being "statistically significant" or "not statistically

significant." Other uses of the word "significant" in the text do not imply that statistical tests have been performed. These uses instead relate to the concept of practical significance and are based on professional judgment.

Summary Statistics

Determinations of measures of central tendency and associated measures of dispersion are calculated according to the *Environmental Monitoring Plan* (Tate et al. 1995). For data sets not containing values below the detection criterion, the measures of central tendency and dispersion are the median and interquartile range (IQR). The IQR is the range that encompasses the middle 50% of the data set. Radiological data sets that include values less than zero may have an IQR greater than the median.

For data sets with one or more, but fewer than one half, values below the detection criterion, the measure of central tendency is the median. If the values of the detection limits and the number of values below the detection limit permit (determined on a case-by-case basis), dispersion is reported as the IQR. Otherwise, no measure of dispersion is reported. Statistics are calculated using the reported detection limit value for nonradiological data or the reported value for radiological data.

For data sets with one half or more of the values below the detection criterion, the central tendency is reported as less than the median value. Dispersion is not reported.

Radiation Units

Data for 1995 have been reported in Système Internationale (SI) units to conform with standard scientific practices and federal law. Values in the text are reported in becquerels (Bq) and millisieverts (mSv); equivalent values in picocuries (pCi) and millirems (mrem) are given in parentheses.