Quality Assurance

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Introduction

Quality assurance (QA) is a system of activities and processes put in place to ensure 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 met. U.S. Department of Energy (DOE) orders and guidance mandate QA requirements for environmental monitoring of DOE facilities. DOE Order 5400.1 identifies QA requirements for radiological effluent and surveillance monitoring and specifies that a QA program consistent with the DOE order addressing quality assurance is established. This order sets forth policy, requirements, and responsibilities for the establishment and maintenance of plans and actions that assure quality in DOE programs.

Lawrence Livermore National Laboratory conducted QA activities in 2002 at the Livermore site and Site 300 in accordance with the *Environmental Protection Department Quality Assurance Management Plan* (Revision 4), which is based on DOE Order 414.1A and 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 in order to maximize effectiveness and efficiency in resource use.

The DOE *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance* (U.S. DOE 1991) requires that an environmental monitoring plan be prepared. LLNL environmental monitoring is conducted according to procedures published in Appendix B of the LLNL *Environmental Monitoring Plan* (Tate et al. 1999).

LLNL and commercial laboratories analyze environmental monitoring samples using U.S. Environmental Protection Agency (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. LLNL uses only State of California-certified laboratories to analyze its environmental monitoring samples. In addition, LLNL requires all analytical laboratories to maintain adequate QA programs and documentation of methods.

Quality Assurance Activities

Nonconformance reporting and tracking is a process used for ensuring that Environmental Protection Department (EPD) activities meet the department's QA requirements and that problems are identified, resolved, and prevented from recurring. EPD reports and tracks problems using Nonconformance Reports (NCRs) and Analytical Lab Problem Reporting Forms.

EPD generated 41 NCRs and 12 Analytical Lab Problem Reporting Forms related to environmental monitoring in 2002. These 53 reported problems can be compared to 50 in 2001 and 76 in 2000. The primary reason for the decrease in reported problems in 2002 appears to be an inconsistent interpretation of which problems require NCRs. Environmental monitoring and QA staff are currently working on developing better criteria to be used to make this determination. In addition, QA staff are attending regular meetings of environmental monitoring personnel to emphasize the need for documenting problems and to answer any questions that may arise.

Twenty-three of the 53 problems reported in 2002 were due to problems with analytical laboratories; 13 were due to documentation, procedural, or sampling errors. The remaining 17 issues were related to equipment malfunction.

LLNL addresses analytical laboratory problems with the appropriate laboratory as they arise. Many of the documented problems related to analytical laboratories concerned minor documentation or paperwork errors, which were corrected soon after they were identified. Other problems—such as missed holding times, late analytical results, and typographical errors on data reports—accounted for the remaining analytical laboratory issues. These problems were corrected by reanalysis, resampling, reissued reports, or corrected paperwork, and associated sample results were not affected.

LLNL addresses internal documentation, training, and procedural errors by conducting formal and informal training. These errors generally do not result in lost samples, but may require extra work on the part of sampling and data management personnel to resolve or compensate for the errors.

QA staff also track and report planned environmental monitoring samples that are not collected for any reason. A summary of these lost samples appears in **Table 14-1**.

Analytical Laboratories

LLNL continued to operate under the Blanket Service Agreements (BSAs) put into place with seven analytical laboratories in March 1999. LLNL continues to work closely with these analytical laboratories to minimize the occurrence of problems.

Table 14-1. Sampling completeness in 2002 for the Livermore site and Site 300

Environmental medium	Number of analyses planned	Number of analyses completed	Complete-ness (%)	Reason(s) for lost samples
Air particulate				
Radiological parameters (Livermore site)	1188	1175	99	Power off/GFI tripped (8), possible leak (2), unit replaced (1), wind blew unit over (1), no access (1)
Beryllium (Livermore site)	96	96	100	
Radiological parameters (Site 300)	728	722	99	Power off (4), no access (2)
Beryllium (Site 300)	48	48	100	
Air tritium				
Livermore site	520	500	96	Insufficient flow (13), broken flask (6), broken pump (1)
Site 300	26	25	96	Broken flask (1)
Soil and Sediment				
Livermore site	42	42	100	
Site 300	30	28	93	Area inaccessible for programmatic reasons (2)
Arroyo sediment (Livermore site only)	43	43	100	
Vegetation and Foodstuffs				
Livermore site and vicinity	64	64	100	
Site 300	20	20	100	
Wine	25	25	100	
Thermoluminescent dosimeters (TLDs)				
Livermore site perimeter	76	76	100	
Livermore Valley	100	97	97	TLD missing at pick up (3)
Site 300	72	68	94	TLD missing at pick up (3); no access (1)
Rain				
Livermore site	68	66	97	Bucket on ground (2)
Site 300	12	8	67	Buckets found on ground (3), bucket missing (1)

Table 14-1. Sampling completeness in 2002 for the Livermore site and Site 300 (continued)

Environmental medium	Number of analyses planned	Number of analyses completed	Complete-ness (%)	Reason(s) for lost samples
Storm water runoff				
Livermore site	397	387	97	One location not sampled at the discretion of the analyst (10)
Site 300	188	145	77	No flow (28), could not access area (15)
Drainage Retention Basin				
Field measurements	896	856	96	Meter problems (34), interference from vegetation (6)
Samples	82	81	99	Analytical lab error (1)
Releases	63	63	100	
Groundwater				
Livermore site	352	340	97	Two wells had insufficient water for sampling during third quarter (12).
Livermore Valley	29	27	93	These wells are sampled at the discretion of the local water agencies. Some wells go dry, some are exchanged for new wells. (2)
Site 300				
Building 829 network	186	182	98	Pump line obstruction (4)
Barcads	65	44	68	Three barcads inoperable (21)
Elk Ravine	122	95	78	Staff shortage (20), well dry (7)
Pit 1	335	335	100	
Pit 6	378	378	100	
Pit 7	342	342	100	
Pit 8	32	5	16	Staff shortage (19), electrical hazard (8)
Pit 9	32	32	100	
Offsite surveillance (annual)	61	61	100	
Offsite surveillance (quarterly)	153	153	100	
Sewage				
B196	910	906	99.6	Technologist error (2), clogged flow line (2)

Table 14-1. Sampling completeness in 2002 for the Livermore site and Site 300 (continued)

Environmental medium	Number of analyses planned	Number of analyses completed	Complete-ness (%)	Reason(s) for lost samples
C196	340	340	100	
LWRP[a] effluent	48	48	100	
Digester sludge	80	80	100	
WDR-96-248				
Surface impoundment wastewater	34	34	100	
Surface impoundment groundwater	116	116	100	
Sewage ponds wastewater	55	55	100	
Sewage ponds ground-water	72	64	89	Well was dry (4), well had bad equip-ment that was later replaced (4)
Miscellaneous aqueous samples				
Other surface water (Livermore Valley only)	58	58	100	
Cooling towers (Site 300 only)	24	24	100	

a LWRP = Livermore Water Reclamation Plant

Participation in Laboratory Intercomparison Studies

The LLNL Chemistry and Materials Science Environmental Services' (CES) Environmental Monitoring Radiation Laboratory (EMRL) and the Hazards Control Department's Analytical Laboratory (HCAL) participated in the DOE Environmental Monitoring Laboratory (EML) intercomparison studies program. A review of the EML studies indicates that 23 of 28 results reported by EMRL and 10 of 10 results reported by HCAL fell within the established acceptance control limits. Further discussion of unacceptable results and corrective actions taken is presented in the Data Supplement.

CES EMRL participated in two DOE Mixed Analyte Performance Evaluation Program (MAPEP) studies in 2002. Fourteen of 22 analytes reported fell within acceptable limits. Further discussion of unacceptable results and corrective actions taken is presented in the Data Supplement.

Although contract laboratories are also required to participate in laboratory intercomparison programs, permission to publish their results for comparison purposes was not granted for 2002.

LLNL uses the results of intercomparison program data to identify and monitor trends in performance and to solicit corrective action responses for unacceptable results. If a laboratory performs

unacceptably for a particular test in two consecutive performance evaluation studies, LLNL may choose to select another laboratory to perform the affected analyses until the original laboratory can demonstrate that the problem has been corrected.

If an off-site laboratory continues to perform unacceptably or fails to prepare and implement acceptable corrective action responses, the LLNL Procurement Department will formally notify the laboratory of its unsatisfactory performance. If the problem persists, the off-site laboratory's BSA could be terminated. If an on-site laboratory continues to perform unacceptably, use of that laboratory could be suspended until the problem is corrected.

Duplicate Analyses

Duplicate or collocated samples are distinct samples of the same matrix collected as closely to the same point in space and time as possible. Collocated samples processed and analyzed *by the same laboratory* provide intralaboratory information about the precision of the entire measurement system, including sample acquisition, homogeneity, handling, shipping, storage, preparation, and analysis. Collocated samples processed and analyzed *by different laboratories* provide interlaboratory information about the precision of the entire measurement system (U.S. EPA 1987). Collocated samples may also be used to identify errors such as mislabeled samples or data entry errors.

Table 14-2, **Table 14-3**, and **Table 14-4** present statistical data for collocated sample pairs, grouped by sample matrix and analyte. Samples from both the Livermore site and Site 300 are included. **Table 14-2** and **Table 14-3** are based on data pairs in which both values are detections (see "Summary Statistics"). **Table 14-4** is based on data pairs in which either or both values are nondetections.

Precision is measured by the percent relative standard deviation (%RSD); see the *EPA's Data Quality Objectives for Remedial Response Activities: Development Process,* Section 4.6 (U.S. EPA 1987). Acceptable values for %RSD vary greatly with matrix, analyte, and analytical method; however, lower values represent better precision. The results for %RSD given in **Table 14-2** 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 a slope equal to 1 and an intercept equal to 0, as illustrated in **Figure 14-1**. 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 greater than 0.8. These criteria apply to pairs in which both results are above the detection limit.

When there were more than eight data pairs with both results in each pair considered detections, precision and regression analyses were performed; those results are presented in **Table 14-2**. When there were eight or fewer data pairs with both results above the detection limit, the ratios of the individual duplicate sample pairs were averaged; the mean, minimum, and maximum ratios for selected analytes are given in **Table 14-3**. The mean ratio should be between 0.7 and 1.3. When either of the results in a pair is a nondetection, then the other result should be a nondetection or less than two times the detection limit. **Table 14-4** identifies the sample media and analytes for which at least one pair failed this criterion. Media and analytes with fewer than four pairs are omitted from the table.

Collocated sample comparisons are more variable when the members of the pair are analyzed by different methods or with different criteria for

Table 14-2. Quality assurance collocated sampling. Summary statistics for analytes with more than eight pairs in which both results were above the detection limit

Matrix	Analyte	N[a]	%RSD[b]	Slope	r^2[c]	Intercept
Air	Gross alpha [d]	11	34.3	0.784	0.68	6.24×10^{-6} Bq/m^3
	Gross beta	95	23.4	0.91	0.90	2.95×10^{-5} Bq/m^3
	Tritium	18	15.6	0.9	0.98	0.0225 Bq/m^3
Dose	Radiological dose, raw[e]	31	2.55	0.805	0.79	3.02 mR
	90-day radiological dose	31	2.75	0.87	0.84	2.02 mrem
Groundwater	Gross alpha[e]	9	29	0.676	0.76	0.0204 Bq/L
	Gross beta[e]	22	22.6	0.268	0.47	0.143 Bq/L
	Arsenic	17	17.7	1.08	0.96	0.000495 mg/L
	Barium	9	3.58	1.01	1.00	–0.00201 mg/L
	Nitrate (as NO_3)	19	5.31	0.987	0.99	0.992 mg/L
	Potassium	27	2.61	0.929	0.99	0.35 mg/L
	Trichloroethene[e]	12	7.77	1.78	0.87	–9.17 μg/L
	Tritium	14	14	0.977	1.00	2.13 Bq/L
	Uranium-234+233	19	11.7	0.965	0.98	–0.00176 Bq/L
	Uranium-235+236	15	23.5	1.05	0.89	–0.000208 Bq/L
	Uranium-238	19	16.6	0.963	0.99	–0.00161 Bq/L
Sewer	Gross alpha[d]	28	38.4	0.108	0.007	0.000227 Bq/mL
	Gross beta	52	8.14	0.968	0.89	2.75×10^{-5} Bq/mL

a Number of collocated pairs included in regression analysis

b 75th percentile of percent relative standard deviations (%RSD) where $\%RSD = \left(\frac{200}{\sqrt{2}}\right)\frac{|x_1 - x_2|}{x_1 + x_2}$ 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 of r^2 because of scatter

e Outside acceptable range of slope or r^2 because of outliers

analytical precision. For example, radiological analyses using different counting times or different laboratory aliquot sizes will have different amounts of variability. Different criteria are rarely, if ever, used with collocated sample pairs in LLNL environmental monitoring sampling. Different criteria are sometimes used in special studies when more than one agency is involved.

Routine and collocated sample results show reasonably good agreement: 90% of the pairs have a precision of 33% or better. Data sets not meeting our precision criteria 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 the 18 data sets reported in **Table 14-2**, four did not meet the

Table 14-3. Quality assurance collocated sampling. Summary statistics for selected analytes with eight or fewer pairs in which both results were above the detection limit

Media	Analyte	N[a]	Mean ratio	Minimum ratio	Maximum ratio
Air	Uranium-234+233 (pCi/m^3)[b]	5	0.99	0.83	1.1
	Uranium-235 (μg/m^3)[b]	7	0.98	0.76	1.1
	Uranium-235+236 (pCi/m^3)[b]	4	0.82	0.7	0.95
	Uranium-238 (pCi/m^3)[b]	5	1.1	0.91	1.2
	Uranium-238 (μg/m^3)[b]	7	0.97	0.73	1.1
Aqueous	Gross alpha	1	0.62	0.62	0.62
	Gross beta	2	0.96	0.72	1.2
	Tritium	1	3.1	3.1	3.1
Groundwater	Radium 226	5	0.72	0.35	0.92
Runoff (from rain)	Gross alpha	3	2.3	1.1	3.9
	Gross beta	3	1.2	0.9	1.4
	Uranium-234+233	2	0.82	0.75	0.9
	Uranium-235+236	1	0.36	0.36	0.36
	Uranium-238	2	0.9	0.71	1.1
Soil	Cesium 137	2	1.1	1	1.1
	Potassium-40	3	1	0.98	1.1
	Plutonium-238	3	0.67	0.2	1.1
	Plutonium-239+240	3	0.83	0.72	1
	Radium 226	3	1	0.93	1.1
	Radium 228	3	1	0.93	1.1
	Thorium 228	3	0.96	0.88	1.1
	Uranium-235	3	1	0.8	1.3
	Uranium-238	3	1.2	0.82	1.6
Sewer	Tritium	2	1	0.95	1.1
Vegetation	Tritium	7	1	0.11	2.3
Wine	Tritium	3	0.87	0.82	0.98

a Number of samples

b The analytical method changed during 2002, so results in units of pCi/m^3 are listed separately from the results in μg/m^3.

Table 14-4. Quality assurance collocated sampling. Summary statistics for analytes with at least four pairs in which one or both results were below the detection limit.

Media	Analyte	Number of inconsistent pairs	Number of pairs	Percent of inconsistent pairs
Air	Gross alpha	2	92	2.2
	Gross beta	4	8	50
	Plutonium-238	1	7	14
	Plutonium-239+240	1	12	8.3
Groundwater	2-Amino-4,6-dinitrotoluene	3	6	50
	Perchlorate	1	11	9.1
Sewer	Gross alpha	4	24	17
	m- and p-Cresol	1	4	25
	o-Cresol	1	6	17
Vegetation	Tritium	1	5	20

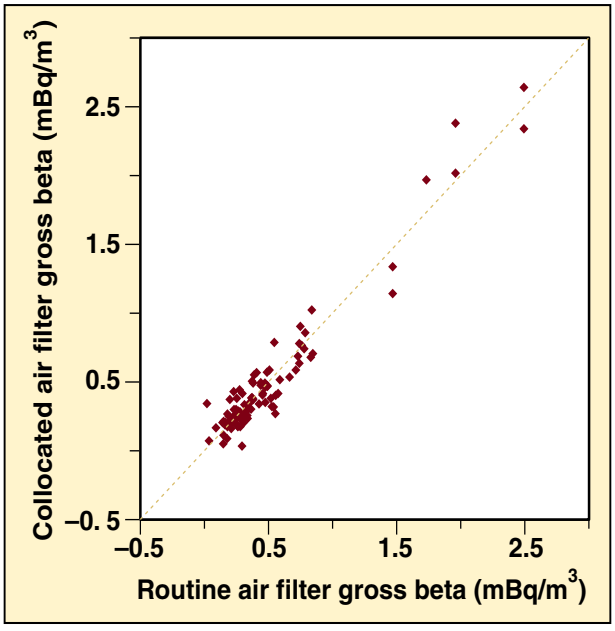

Figure 14-1. Example of data points that lie close to a line with slope equal to 1 and intercept equal to 0 using air filter gross beta concentrations from collocated samples

criterion for acceptability because of outliers. Figure 14-2 illustrates a set of collocated pairs with one outlier.

The second category are data sets that do not meet the criterion for acceptability because there is a lot of scatter. This tends to be typical of nondetections and measurements at extremely low concentrations, as illustrated in Figure 14-3. Low concentrations of radionuclides on particulates in air highlight this effect, because one or two radionuclide-containing particles on an air filter can significantly affect results. Other causes of high variability are sampling and analytical methodology. Analyses of total organic carbon and total organic halides in water are particularly difficult to control. Of the 18 data sets in Table 14-2, two show sufficient variability in results to make them fall outside the acceptable range.

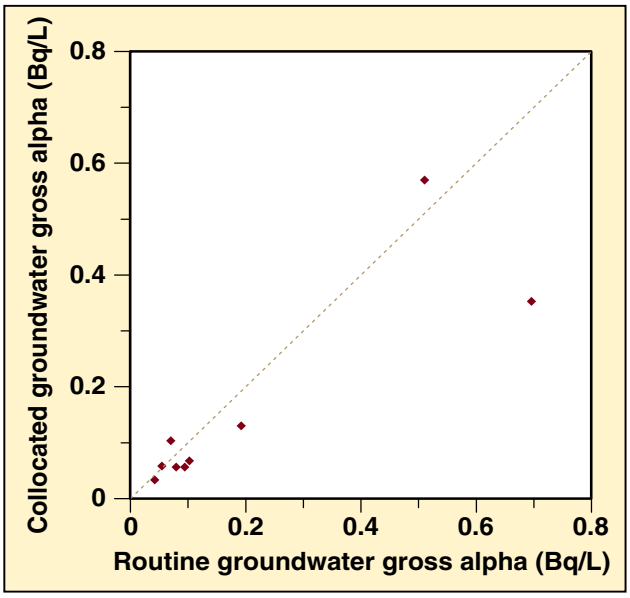

Figure 14-2. Example of data outliers using groundwater gross alpha concentrations from collocated samples

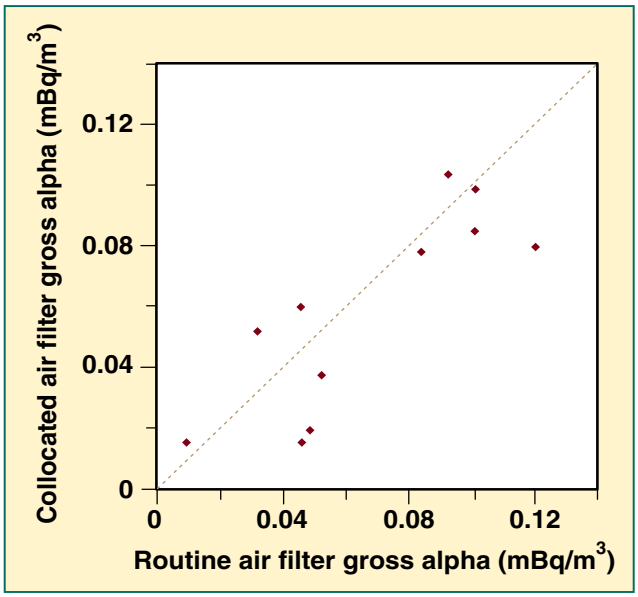

Figure 14-3. Example of scatter using air filter gross alpha concentrations from collocated samples

Radiation Units

Data for 2002 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 sieverts (Sv); equivalent values in curies (Ci) and rems (rem) are given in parentheses.

See Appendix D for a more detailed discussion of radiation units.

Radiological Data

Most of the Data Supplement tables display radiological data as a result plus-or-minus an associated 2σ uncertainty. The uncertainties are not used in summary statistic calculations. Any radiological result exhibiting a 2σ uncertainty greater than or equal to 100% of the result is considered to be a nondetection.

Radiological results are derived from the number of sample counts minus the number of background counts inside the measurement apparatus. Therefore, a sample with a low concentration may have a negative value; such results are reported in the tables and used in the calculation of summary statistics and statistical comparisons.

Some Data Supplement tables provide a limit-of-sensitivity value instead of an uncertainty when the radiological result is below the detection criterion. Such results are displayed with the limit-of-sensitivity value in parentheses.

Nonradiological Data

Nonradiological data reported as being below the reporting limit are displayed in tables with a less-than symbol. The reporting 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. 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. Instead, these uses 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. 1999). For data sets that do not contain values below the detection criterion, and radiological data sets that include reported 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. The IQR is calculated by subtracting the 25th percentile of the data set from the 75th percentile of the data set. When necessary, the percentiles are interpolated from the data. Software vendors may use slightly different formulas for calculating percentiles. Radiological data sets that include values less than zero may have an IQR greater than the median.

For data sets that include one or more values below the detection criterion, but do not include reported values below the detection criterion, the summary statistic calculations take into account the detection limit values. When fewer than one-half, of the 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. See Chapter 14 of the Data Supplement for additional discussion.

The median and the IQR are not calculated for data sets having no detections. The median is not calculated for data sets having fewer than four samples; the IQR is not calculated for data sets having fewer than six samples.

Table Preparation and Data Presentation

The process for creating data tables in the Data Supplement changed with this report. The new process incorporates a larger degree of automation to make the task of preparing data tables more efficient and less error-prone. For additional information see Chapter 14 of the Data Supplement.

Analytical laboratory data, and values calculated from analytical laboratory data, are normally displayed with at most two or three significant digits. Significant trailing zeros may be omitted.

Summary statistics are calculated from values that have already been rounded (if necessary), and are then rounded to an appropriate number of significant digits. See Chapter 14 in the Data Supplement for additional discussion of significant digits and uncertainty.

Quality Assurance Process for the Environmental Report

Unlike the preceding discussion, which focused on standards of accuracy and precision in data acquisition and reporting, a discussion of QA/QC procedures for a technical publication must deal with how to retain content accuracy through the publication process. Because publication of a large, data-rich document like this site annual environmental report involves many operations and many people, the chances of introducing errors are great. At the same time, ensuring quality is more difficult because a publication is less amenable to the statistical processes used in standard quality assurance methods.

The QA procedure used for this report concentrated on the tables and figures and enlisted authors, contributors, and technicians to check the accuracy of sections other than those they had authored or contributed to. In 2002, the tables and figures in the main volume and the tables in the Data Supplement were checked.

Checkers were assigned illustrations and tables and given a copy of each item they were to check along with a quality control form to fill out as they checked the item. Items to be checked included figure captions and table titles for clarity and accuracy, data accuracy and completeness, figure labels and table headings, units, significant digits, and consistency with text.

When checking numerical data, checkers randomly selected 10% of the data and compared it to values in the master database. If all 10% agreed with the database, further checking was considered unnecessary. If there was disagreement in the data, the checker compared another 10% of the data with the database values. If more errors were found, the entire table or illustration had to be checked against the data in the database.

A coordinator guided the process to ensure that forms were tracked and the proper approvals were obtained. Completed quality control forms and the corrected illustrations or tables were returned to the report editors, who were responsible for ensuring that changes, with the agreement of the original contributor, were made.