Quality Assurance

QA 14

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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 2001 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 30 Nonconformance Reports (NCRs) and 20 Analytical Lab Problem Reporting Forms related to environmental monitoring in 2001. These 50 reported problems can be compared to 76 in 2000 and 111 in 1999. The primary reason for the decrease in reported problems in 2001 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.

Thirty-four of the 50 problems reported in 2001 were due to problems with analytical laboratories. Thirteen were due to documentation or procedural errors. Of the remaining 3 issues, 2 were related to equipment malfunction and the other was related to questionable results.

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 2001 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)	1188	1154	97	No power at location (22), power off at arrival/GFI tripped (5), unacceptable flow rate (4), could not access location (2), motor problems (1)
Beryllium (Livermore)	96	96	100	
Radiological parameters (Site 300)	728	727	99.9	Could not access location (1)
Beryllium (Site 300)	72	72	100	
Air tritium				
Livermore site	499	467	94	Insufficient flow (13), no power at location (9), broken flask (6), outliers (4)
Site 300	26	25	96	Outlier (1)
Soil and Sediment				
Livermore	42	42	100	
Site 300	30	30	100	
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	77	87	TLD missing (13)
Site 300	82	79	96	TLD missing (3)
Rain				
Livermore site	76	75	99	Insufficient sample volume (1)
Site 300	20	20	100	

Table 14-1. Sampling completeness in 2001 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	903	809	90	Insufficient rainfall to produce runoff (43), sampling error (34), no time to sample (15), sampler oversight (1), broke in transit to lab (1)
Site 300	338	138	41	Insufficient rainfall to produce runoff (193), sampling error (4), analytical lab error (3)
Drainage Retention Basin				
Field measurements	822	781	95	Equipment malfunction (24), sampler oversight (17)
Samples	87	86	99	Analytical lab error (1)
Releases	81	81	100	
Groundwater				
Livermore site	369	358	97	Well did not produce enough water for sampling (11)
Livermore Valley wells	29	26	90	No sample provided (2), well out of order (1)
Site 300				
Building 829 network	297	225	76	Wells dry (72)
Barcads	101	56	55	Barcads inoperable (45)
Elk Ravine	180	166	92	Well dry (14)
Pit 1	427	419	98	Sampler error (8)
Pit 6	498	454	91	Well dry (44)
Pit 7	423	403	95	Pump inoperable (11), sampler error (7), well sampling problem (2)
Pit 8	34	26	76	Well inaccessible due to construction (8)
Pit 9	419	49	100	
Offsite surveillance (annual)	64	64	100	
Offsite surveillance (quarterly)	196	168	86	Well inaccessible (23), lab error (5)

Table 14-1. Sampling completeness in 2001 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
Sewage				
B196	924	924	100	
C196	324	324	100	
LWRP[a] effluent	128	128	100	
Digester sludge	80	80	100	
WDR-96-248				
Surface impoundment wastewater	68	68	100	
Surface impoundment groundwater	155	155	100	
Sewage ponds wastewater	41	41	100	
Sewage ponds ground-water	88	88	100	
Miscellaneous aqueous samples				
Other surface water (Livermore only)	58	58	100	
Cooling towers (Site 300 only)	26	26	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 38 of 41 results reported by CES and 8 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 2001. Nineteen of nineteen analytes reported fell within acceptable limits.

Although contract laboratories are also required to participate in laboratory intercomparison programs, permission to publish their results for comparison purposes was not granted for 2001.

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 one of the results in a pair is a nondetection, then the other result should be less than two times the detection limit. **Table 14-4** identifies the

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]	63	28.4	0.991	0.81	3.95×10^{-6} Bq/m^3
	Gross beta	103	13.7	0.973	0.92	2.83×10^{-5} Bq/m^3
	Beryllium	18	14.8	0.849	0.85	1.76 pg/m^3
	Tritium	25	32.3	0.703	0.95	0.0427 Bq/m^3
Groundwater	Gross beta[d]	22	34.6	3.51	0.04	–0.0262 Bq/L
	Arsenic	16	10.9	1.01	0.98	0.00104 mg/L
	Bicarbonate alk (as $CaCO_3$)	9	4.01	0.875	0.92	31.5 mg/L
	Nickel[d]	9	23.6	0.41	0.78	0.00603 mg/L
	Nitrate (as NO_3)	20	1.98	1.04	0.92	0.907 mg/L
	pH	9	0.37	0.941	0.95	0.49 Units
	Potassium	29	1.61	0.968	1.0	0.23 mg/L
	Uranium-234+233	19	9.33	0.954	1.0	0.00265 Bq/L
	Uranium-235+236[d]	15	36.7	1.3	0.94	–0.000443 Bq/L
	Uranium-238	19	7.55	0.948	1.0	0.00186 Bq/L
Runoff (from rain)	Barium[d]	9	6.15	0.855	0.59	0.0218 mg/L
	Boron	9	8.32	1.22	1.0	–0.0835 mg/L
	Chromium[d]	9	3.63	1.1	0.78	0.000417 mg/L
	Copper[e]	9	12.9	0.655	0.64	0.00245 mg/L
	Iron[d]	9	37.8	1.07	0.42	0.73 mg/L
	Nickel[e]	9	23.6	0.964	0.51	0.002 mg/L
	pH	10	1.56	0.84	0.83	1.34 Units
Sewer	Gross beta	51	6.93	0.912	0.81	8.34×10^{-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 or r^2 because of outliers

e Outside acceptable range of slope of r^2 because of variability

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

Matrix	Analyte	N	Mean ratio	Minimum ratio	Maximum ratio
Air	Uranium-234+233	3	1.2	0.65	1.8
	Uranium-238	3	1.5	0.89	2.1
Aqueous	Gross beta	6	1.2	0.72	2.1
	Tritium	6	0.99	0.62	1.6
Groundwater	Gross alpha	7	0.89	0.54	1.2
	Tritium	8	1.2	0.74	3
	Radium-226	6	0.94	0.65	1.4
Rain	Tritium	1	1.5	1.5	1.5
Runoff (from rain)	Gross alpha	1	1.3	1.3	1.3
	Gross beta	3	2.4	0.98	5.1
	Tritium	2	1.1	0.68	1.6
	Uranium-234+233	3	1.1	0.94	1.4
	Uranium-235+236	2	1.1	0.84	1.4
	Uranium-238	3	1.1	0.92	1.4
Soil	Gross alpha	1	0.59	0.59	0.59
	Gross beta	1	0.45	0.45	0.45
	Cesium-137	3	0.99	0.92	1.1
	Tritium	1	1	1	1
	Tritium	1	0.79	0.79	0.79
	Potassium-40	4	1	0.91	1.2
	Plutonium-238	1	1.7	1.7	1.7
	Plutonium-239+240	3	6.3	0.054	18
	Radium-226	4	1.1	0.96	1.1
	Radium-228	4	1	0.91	1.1
	Thorium-228	4	1	0.94	1.1
	Uranium-235	4	1	0.78	1.3
	Uranium-238	4	1	0.78	1.3
Sewer	Gross alpha	7	0.83	0.41	1.2
	Tritium	2	1	0.99	1
Vegetation	Tritium	5	1.5	0.71	3.6

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	Uranium-234+233	1	9	11
	Uranium-235+236	2	24	8.3
	Uranium-238	2	9	22
Groundwater	Gross alpha	1	16	6.2
	Bis(2-ethylhexyl)phthalate	1	13	7.7
	Copper	1	18	5.6
	Nitrate (as NO_3)	1	5	20
	Trichloroethene	1	18	5.6
Runoff (from rain)	Oil and grease	1	8	12
Sewer	Gross alpha	1	45	2.2
	Benzyl alcohol	1	4	25

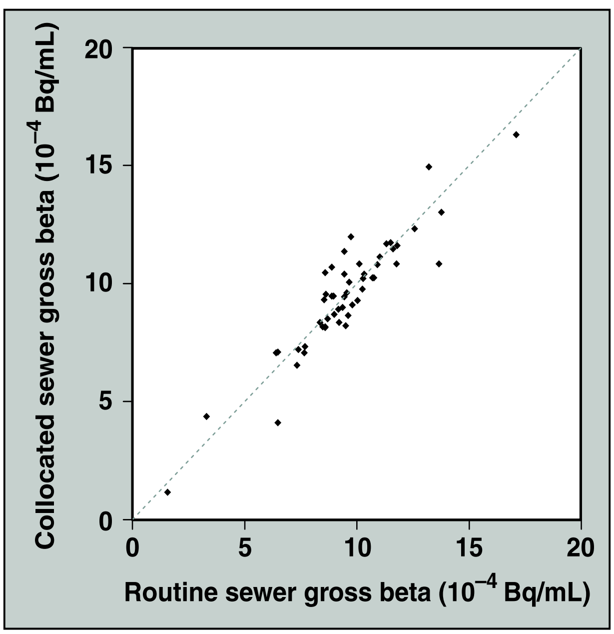

Figure 14-1. Gross beta concentrations from collocated samples. These samples lie close to a line with slope equal to 1 and intercept equal to 0.

sample media and analytes for which at least one pair failed this criterion. 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 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 in LLNL environmental monitoring sampling. Different criteria are sometimes used in special studies when more than one agency is involved.

Routine and collated sample results show good agreement: 90% of the pairs have a precision better than 20%. Data sets not meeting our precision criteria fall into one of two categories. The first category, outliers, can occur because of data transcription errors, measure-ment errors, or real but anomalous results. Of the 31 data sets reported in Table 14-2, 10 did not meet the criterion for acceptability because of outliers. Figure 14-2 illustrates a set of collocated pairs with one outlier.

Three other results do not meet the criterion for acceptability because they consist of data sets where there is a lot of scatter. This tends to be typical of nondetec-tions and measurements at extremely low concen-trations, as illustrated in Figure 14-3. Low concentrations of radionuclides on particulates in air highlight this effect, because one or two radio-nuclide-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 31 data sets in Table 14-2, three show sufficient variability in results to make them fall outside the acceptable range.

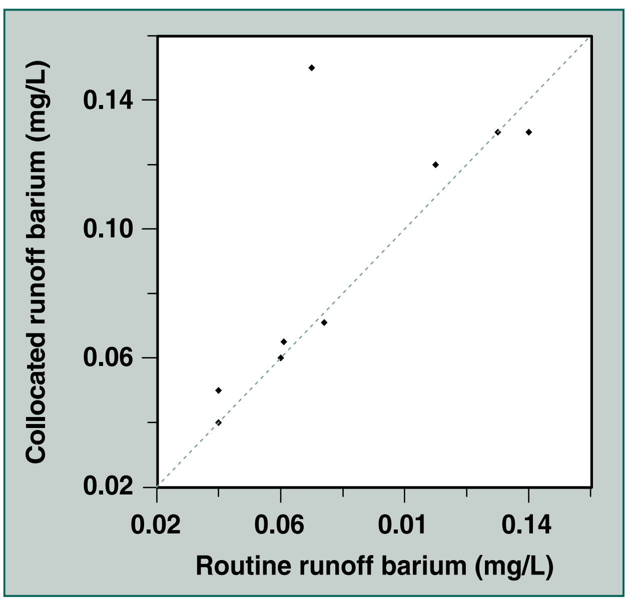

Figure 14-2. Runoff barium concentrations from collocated samples showing an outlier

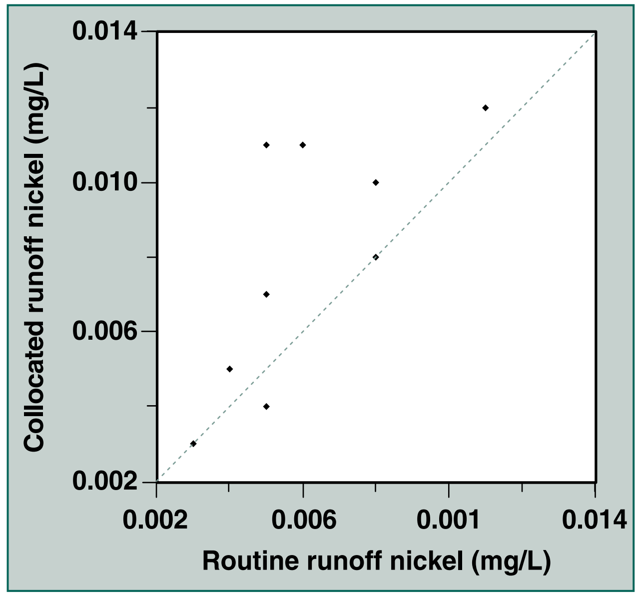

Figure 14-3. Runoff nickel concentrations from collocated samples showing a lot of scatter

Radiation Units

Data for 2001 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.

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

Radiological Data

The precision of radiological analytical results is displayed in the Data Supplement tables as the 2σ uncertainty. The uncertainties are not used in summary statistic calculations. Any radiological result exhibiting a 2σ uncertainty greater than or equal to 100% is considered to be a nondetection. The reported concentration is derived from the number of sample counts minus the number of background counts. 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 radioactivity limit-of-sensitivity values instead of a reported concentration when the radiological result is below the detection criterion. Such results are displayed in tables with a less-than symbol.

Nonradiological Data

Nonradiological data reported as being below the reporting limit are also 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, 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 with one or more, but 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.

Data Presentation

Analytical laboratory data, and values calculated from analytical laboratory data, are normally displayed with at most 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.

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 we used concentrated on the tables and figures in the report and enlisted authors, contributors, and technicians to check the accuracy of sections other than those they had authored or contributed to. In 2001, the illustrations and tables 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. This QA check resulted in the correction of data errors and omissions on 10% of the illustrations, 33% of the tables in the main volume, and 39% of the tables in the Data Supplement. Other corrections were made to footnotes, headings, titles in tables, graph axes, callouts, and captions in figures.