Quality Assurance

CHAPTER 9

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Introduction

Quality assurance (QA) is a system of activities and processes put in place to ensure that products or services meet or exceed customer specifications. Quality control (QC) consists of activities used to verify that deliverables are of acceptable quality and meet criteria established in the quality planning process. Lawrence Livermore National Laboratory conducted environmental monitoring activities during 2005 in accordance with the Environmental Protection Department Quality Assurance Management Plan (Revision 4), which is based on DOE Order 414.1A. This order sets forth policy, requirements, and responsibilities for the establishment and maintenance of plans and actions that assure quality in DOE programs using 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.

LLNL and commercial laboratories analyze environmental monitoring samples using U.S. Environmental Protection Agency (EPA) standard methods when available (see, for example, Appendix A). When EPA standard methods are not available, custom analytical procedures, usually developed at LLNL, are used. 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. The radiochemical methods used by LLNL laboratories are described in procedures created and maintained by the laboratory performing the analyses.

Quality Assurance Activities

Nonconformance reporting and tracking is a formal process used for ensuring that problems are identified, resolved, and prevented from recurring. EPD reports and tracks problems using Nonconformance Reports (NCRs). NCRs are initiated when items or activities are identified that do not comply with procedures or other documents that specify requirements for Environmental Protection Department (EPD) operations or that cast doubt on the quality of EPD reports, sample integrity, or data *and* that are not covered by other reporting or tracking mechanisms. Many sampling or data problems are resolved without an NCR being generated.

LLNL averts sampling problems by requiring formal and informal training on sampling procedures. Errors that occur during sampling generally do not result in lost samples, but may require extra work on the part of sampling and data management personnel to correct the errors.

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

The LLNL EPD generated 12 NCRs related to environmental monitoring in 2005. Four of the NCRs were related to problems with analytical laboratories, seven documented minor equipment malfunctions that did not result in lost samples, and the remaining one documented an error made by a sampling technologist.

QA staff also track and report planned environmental monitoring samples that are not collected. A summary of sample completeness appears in **Table 9-1**.

Analytical Laboratories

LLNL awarded Blanket Service Agreements (BSAs) to eight analytical laboratories in 2005. LLNL works closely with these analytical laboratories to minimize the occurrence of problems.

Table 9-1. Sampling completeness in 2005 for the Livermore site and Site 300

Environmental medium	Number of analyses planned	Number of analyses completed	Completeness (%)	Reason(s) for lost samples
Air particulate				
Radiological parameters (Livermore site)	1208	1188	98	GFI tripped (11), motor problems (5), no access (3), low flow (1)
Beryllium (Livermore site)	95	95	100	
Radiological parameters (Site 300)	740	726	98	No access (10), no power (2), GFI tripped (1), unsafe conditions (1)
Beryllium (Site 300)	52	52	100	
Air tritium				
Livermore site and vicinity	526	520	99	Insufficient flow (6)
Site 300	30	30	100	
Soil and Sediment				
Livermore site	42	42	100	
Site 300	30	30	100	
Arroyo sediment (Livermore site only)	31	31	100	
Vegetation and Foodstuffs				
Livermore site and vicinity	56	56	100	
Site 300	20	20	100	
Wine	12	12	100	
Thermoluminescent dosimeters (TLDs)				
Livermore site perimeter	98	97	99	Missing (1)
Livermore Valley	102	97	95	TLD found burned (5)
Site 300	65	53	82	Missing (7), no access (5)
Rain				
Livermore site	34	34	100	
Site 300	6	6	100	
Storm water runoff				
Livermore site	103	103	100	
Site 300	97	71	73	No flow at location (26)

Table 9-1. Sampling completeness in 2005 for the Livermore site and Site 300 (continued)

Environmental medium	Number of analyses planned	Number of analyses completed	Completeness (%)	Reason(s) for lost samples
Drainage Retention Basin				
Field measurements	208	206	99	Samples not collected, no explanation (2)
Samples	72	71	99	Samples not collected, no explanation (1)
Releases	51	50	98	Fish toxicity samples not taken due to holiday schedule (1)
Livermore site wastewater				
B196	950	946	99	Unit malfunction (4)
C196	305	305	100	
LWRP[a] effluent	48	48	100	
Digester sludge	135	105	78	Digester #1 closed May & June (4), #2 closed January, February, May & October (12), #3 closed July–October (14)
WDR 96-248				
Surface impoundment wastewater	17	17	100	
Surface impoundment groundwater	190	190	100	
Sewage ponds wastewater	42	42	100	
Sewage ponds groundwater	157	157	100	
Miscellaneous aqueous samples				
Other surface water (Livermore Valley only)	46	46	100	
Cooling towers (Site 300 only)	24	16	67	Samples not collected because 836 shut down April 2005 (8)

[a] LWRP = Livermore Water Reclamation Plant

Analytical Laboratory Intercomparison Studies

LLNL uses the results of intercomparison program data to identify and monitor trends in performance and to draw attention to the need to improve laboratory performances. 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.

Two laboratories at Lawrence Livermore National Laboratory participated in the Mixed Analyte Performance Evaluation Program (MAPEP) sponsored by the U.S. Department of Energy (DOE) during 2005. The two LLNL laboratories that participated in MAPEP are the Environmental Monitoring Radiological Laboratory (EMRL) and the Hazards Control Department's Analytical Laboratory (HCAL).

The results of EMRL's participation in the studies are presented in **Table 9-2**. According to the results, 33 of 38 reported results were determined to be acceptable, 2 results were acceptable with warning, and 3 results were unacceptable, based on established control limits.

Unacceptable results for gross alpha and gross beta in the 05-GrF13 and 05-GrW13 studies were the result of reporting results in units of pCi/L, rather than the requested units of Bq/L. As a corrective action, computer software controls will be implemented that will warn the user when specified limits are exceeded. The unacceptable result for gross beta in the 05-GrW14 study was the result of an incorrect hand calculation, which will be corrected by the use of computerized calculation methods. The unacceptable result for Cesium-137 was determined to be a result of sample geometry and position, and has been corrected by a new protocol for sample positioning in the analytical instrument.

The results of HCAL's participation in the 2005 MAPEP studies (see **Table 9-3**) indicate that ten of ten sample results fell within the acceptance control limits.

Table 9-2. EMRL performance in the MAPEP Intercomparison Program Studies for 2005

Study	Analyte	Result	Ref Value	Flag[(a)]	Acceptance Range[(b)]	Uncertainty Value
Air filter (Bq/sample)						
MAPEP-05-GrF13	Gross alpha	2.16	0.232	N	0.000 – 0.464	0.0101
	Gross beta	9.51	0.297	N	0.148 – 0.446	0.0250
MAPER-05-RdF13	Cesium-134	3.76	3.51	A	2.46 – 4.56	0.225
	Cesium-137	2.94	2.26	N	1.58 – 2.94	0.351
	Cobalt-57	5.85	4.92	A	3.44 – 6.40	0.487
	Cobalt-60	3.38	3.03	A	2.12 – 3.94	0.228
	Manganese-54	4.01	3.33	W	2.33 – 4.33	0.413
	Plutonium-238	0.199	0.195	A	0.14 – 0.25	0.0228
	Plutonium-239/240	0.161	0.165	A	0.12 – 0.21	0.0186
	Zinc-65	4.26	3.14	N	2.20 – 4.08	0.733
MAPEP-05-GrF14	Gross alpha	0.239	0.482	A	>0.0 – 0.96	0.000499
	Gross beta	0.893	0.827	A	0.41 – 1.24	0.00119
MAPEP-05-RdF14	Cesium-134	3.43	3.85	A	2.69 – 5.01	0.172
	Cesium-137	2.94	3.23	A	2.26 – 4.20	0.363
	Cobalt-57	6.19	6.20	A	4.34 – 8.06	0.367
	Cobalt-60	2.74	2.85	A	1.99 – 3.70	0.231
	Manganese-54	4.10	4.37	A	3.06 – 5.68	0.427
	Plutonium-238	0.0902	0.0969	A	0.07 – 0.13	0.0149
	Plutonium-239/240	0.0835	0.0898	A	0.06 – 0.12	0.0138
	Zinc-65	4.32	4.33	A	3.03 – 5.63	0.790
Aqueous (Bq/L)						
MAPEP-05-MaW13	Cesium-134	109	127	A	88.90 – 165.10	7.61
	Cesium-137	324	332	A	232.40 – 431.60	34.0
	Cobalt-57	241	227	A	158.90 – 295.10	19.9
	Cobalt-60	253	251	A	175.70 – 326.30	14.3
	Manganese-54	328	331	A	231.70 – 430.30	35.0
	Plutonium-238	0.0156	0.018	A	(c)	0.00406
	Plutonium-239/240	2.60	2.4	A	1.68 – 3.12	0.209
	Zinc-65	534	496	A	347.20 – 644.80	47.9
MAPEP-05-GrW13	Gross alpha	3.56	0.525	N	0.000 – 1.050	0.0406
	Gross beta	37.7	1.67	N	0.835 – 2.505	2.44
MAPEP-05-MaW14	Cesium-134	153	167	A	116.90 – 217.10	7.76
	Cesium-137	313	333	A	233.10 – 432.90	23.8
	Cobalt-57	267	272	A	190.40 – 353.60	16.0
	Cobalt-60	249	261	A	182.70 – 339.30	15.1

Table 9-2. EMRL performance in the MAPEP Intercomparison Program Studies for 2005 (continued)

Study	Analyte	Result	Ref Value	Flag(a)	Acceptance Range(b)	Uncertainty Value
	Hydrogen-3	601	527	A	368.90 – 685.10	6.69
	Manganese-54	399	418	A	292.60 – 543.40	30.2
	Plutonium-238	1.68	1.67	A	1.34 – 2.48	0.269
	Plutonium-239/240	2.41	2.45	A	1.92 – 3.58	0.269
	Zinc-65	341	330	A	231.00 – 429.00	24.5
MAPEP-05-GrW14	Gross alpha	0.252	0.790	A	0.21 – 1.38	0.0958
	Gross beta	0.782	1.350	N	0.85 – 1.92	0.475
Soil (Bq/kg)						
MAPEP-05-MaS13	Cesium-134	644	759	A	531.30 – 986.70	30.1
	Cesium-137	311	315	A	220.50 – 409.50	31.5
	Cobalt-57	250	242	A	169.40 – 314.60	18.9
	Cobalt-60	212	212	A	148.40 – 275.60	14.0
	Manganese-54	511	485	A	339.50 – 630.50	50.8
	Plutonium-238	0.452	0.48	A	(c)	0.0672
	Plutonium-239/240	90.9	89.5	A	62.65 – 116.35	5.15
	Potassium-40	641	604	A	422.80 – 785.20	103
	Zinc-65	886	810	A	567.00 – 1053.00	79
MAPEP-05-MaS14	Cesium-134	500	568	A	397.60 – 738.40	19.9
	Cesium-137	456	439	A	307.30 – 570.70	49.9
	Cobalt-57	551	524	A	366.80 – 681.20	45.3
	Cobalt-60	294	287	A	200.90 – 373.10	16.1
	Manganese-54	464	439	A	307.30 – 570.70	55.5
	Plutonium-238	61.5	60.8	A	42.56 – 79.04	9.89
	Potassium-40	625	604	A	422.80 – 785.20	56.8
	Zinc-65	919	823	A	576.10 – 1069.09	80.9

a Gross alpha flags:
A = Result acceptable. Bias ≤ ±100% with a statistically positive result at two standard deviations.
N = Result not acceptable. Bias > ±100% or the reported result is not statistically positive at two standard deviations.

Gross beta flags:
A = Result acceptable. Bias ≤ ±50% with a statistically positive result at two standard deviations.
N = Result not acceptable. Bias > ±50% or the reported result is not statistically positive at two standard deviations.

All other flags:
A = Result acceptable. Bias ≤20%.
W = Result acceptable with warning. Bias >20% and bias ≤30%.
N = Result not acceptable. Bias >30%

b Significant figures shown are those of the MAPEP program.

c Acceptance range not provided for this analysis.

Table 9-3. HCAL performance in the MAPEP Intercomparison Program Studies for 2005

Study	Analyte	Result	Ref Value	Flag[a]	Acceptance Range	Uncertainty Value
Air filter (Bq/sample)						
MAPEP-05-GrF13	Gross alpha	0.116	0.232	A	0.000 – 0.464	0.013
	Gross beta	0.38	0.297	A	0.148 – 0.446	0.02
MAPEP-05-GrF14	Gross alpha	0.27	0.482	A	>0.0 – 0.96	0.04
	Gross beta	1.01	0.827	A	0.41 – 1.24	0.07
Aqueous (Bq/L)						
MAPEP-05-GrW13	Gross alpha	0.32	0.525	A	0.000 – 1.050	0.04
	Gross beta	1.60	1.67	A	0.835 – 2.505	0.09
MAPEP-05-MaW13	Hydrogen-3	285	280	A	196.00 – 364.00	15
MAPEP-05-GrW14	Gross alpha	0.803	0.790	A	0.21 – 1.38	0.090
	Gross beta	1.33	1.350	A	>0.0 – 0.96	0.08
MAPEP-05-MaW14	Hydrogen-3	543	527	A	0.41 – 1.24	29

a Gross alpha flags:
A = Result acceptable. Bias ≤ ±100% with a statistically positive result at two standard deviations.
N = Result not acceptable. Bias > ±100% or the reported result is not statistically positive at two standard deviations.

Gross beta flags:
A = Result acceptable. Bias ≤ ±50% with a statistically positive result at two standard deviations.
N = Result not acceptable. Bias > ±50% or the reported result is not statistically positive at two standard deviations.

All other flags:
A = Result acceptable. Bias ≤20%.
W = Result acceptable with warning. Bias >20% and bias ≤30%.
N = Result not acceptable. Bias >30%

HCAL also participated in two Environmental Resource Associates (ERA) performance evaluation studies in 2005. The results of these studies are presented in **Table 9-4**. Fourteen of fifteen analytes reported by HCAL in these studies fell within acceptable limits. The unacceptable tritium result was caused by the improper entry of the 95% uncertainty value in place of the tritium value.

Although contract laboratories are also required to participate in laboratory intercomparison programs, permission to publish their results for comparison purposes was not granted for 2005. See the following website to obtain MAPEP reports that include the results from all participating laboratories: http://www.inl.gov/resl/mapep/reports.html

Table 9-4. HCAL performance in the ERA Intercomparison Program Studies for 2005

Study	Analyte	Reported Value	ERA Assigned Value	Control Limits	Warning Limits	Performance Evaluation
Radiological (pCi/L)						
RAD-60	Gross alpha	68.7	67.9	38.5 – 97.3	48.3 – 87.5	Acceptable
	Gross beta	60.6	51.1	33.8 – 68.4	39.6 – 62.6	Acceptable
	Tritium	494	30200	25000 – 35400	26700 – 33700	Not Acceptable
Nonradiological (µg/L)						
WP-121	Aluminum	1200	1120	955 – 1280	1010 – 1220	Acceptable
	Arsenic	703	750	631 – 877	672 – 836	Acceptable
	Beryllium	409	405	344 – 457	363 – 439	Acceptable
	Cadmium	160	168	143 – 192	151 – 184	Acceptable
	Chromium	571	552	481 – 625	505 – 601	Acceptable
	Copper	594	607	551 – 666	570 – 647	Acceptable
	Iron	485	432	379 – 492	398 – 473	Acceptable
	Lead	314	326	281 – 370	296 – 355	Acceptable
	Mercury	7.4	7.14	5.28 – 8.97	5.90 – 8.36	Acceptable
	Nickel	197	194	169 – 220	178 – 212	Acceptable
	Silver	149	150	128 – 172	136 – 165	Acceptable
	Zinc	1120	1120	993 – 1260	1040 – 1210	Acceptable

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 intra-laboratory 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.

Tables 9-5, **9-6**, and **9-7** present statistical data for collocated sample pairs, grouped by sample matrix and analyte. Samples from both the Livermore site and Site 300 are included. **Tables 9-5** and **9-6** are based on data pairs in which both values are detections (see "Data Presentation" in this chapter). **Table 9-7** is based on data pairs in which either or both values are nondetections.

Table 9-5. Quality assurance collocated sampling: Summary statistics for analytes with more than eight pairs in which both results were above the detection limit

Media	Analyte	N[a]	%RSD[b]	Slope	$r^{2(c)}$	Intercept
Air	Gross alpha[d]	69	70.4	–0.482	0	4.64×10^{-5} (Bq/m^3)
	Gross beta[d]	99	19.8	0.841	0.45	8.55×10^{-5} (Bq/m^3)
	Beryllium[d]	11	19.8	0.606	0.83	2.09 (pg/m^3)
	Uranium-235[d]	11	10.2	0.385	0.82	7.58×10^{-8} ($\mu g/m^3$)
	Uranium-238[d]	11	13.1	0.221	0.73	1.46×10^{-5} ($\mu g/m^3$)
	Uranium-235/238[d]	12	4.95	0.318	0.36	0.00468 (ratio)
	Tritium	27	20.1	0.929	0.97	0.00388 (Bq/m^3)
Dose (TLD)	90-day radiological dose	27	2.38	1.07	0.9	–0.93 (mrem)
Groundwater	Gross alpha	10	30.6	0.928	0.9	0.00132 (Bq/L)
	Gross beta	34	26.7	1.07	0.81	–0.0339 (Bq/L)
	Arsenic	30	10.4	1.02	1	–0.000743 (mg/L)
	Barium	19	3.69	1.05	1	–0.0032 (mg/L)
	Bromide	9	6	0.912	0.97	0.0634 (mg/L)
	Chloride	9	0	1	1	6.8×10^{-14} (mg/L)
	Copper	9	29.8	0.776	0.86	0.00347 (mg/L)
	Molybdenum	11	2.62	1.02	1	–0.000149 (mg/L)
	Nitrate (as NO_3)	21	2.11	1.02	1	–0.695 (mg/L)
	Potassium	13	43.8	0.786	0.83	4.39 (mg/L)
	Sulfate	9	0	1	1	7.84×10^{-14} (mg/L)
	Tritium	14	6.42	1.01	1	1.78 (Bq/L)
	Uranium-234+233	18	8.2	1.03	0.99	–0.0028 (Bq/L)
	Uranium-235	13	16.8	0.765	0.95	0.000699 (Bq/L)
	Uranium-238	16	11	1.03	0.99	–0.00247 (Bq/L)
	Vanadium	9	1.35	1	1	-3.39×10^{-5} (mg/L)
	Zinc[d]	9	20.2	1.35	0.96	–0.0217 (mg/L)
Sewer	Gross beta[e]	52	15.3	0.681	0.36	0.000221 (Bq/mL)
	Chloroform[e]	9	15.7	1.08	0.59	–2.07 ($\mu g/L$)

a Number of collocated pairs included in regression analysis

b 75th percentile of percent relative standard deviations (%RSD) where

$$\%RSD = \left(\frac{200}{\sqrt{2}}\right)\frac{|x_1 \pm x_2|}{x_1 + x_2}$$ 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 or r^2 because of variability

Table 9-6. 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
Aqueous	Gross beta	2	0.83	0.71	0.95
Groundwater	Radium 226	3	0.86	0.52	1.2
	Radium 228	1	1.1	1.1	1.1
Rain	Tritium	1	0.69	0.69	0.69
Runoff (from rain)	Gross alpha	3	0.9	0.74	1
	Gross beta	3	0.9	0.85	0.98
	Uranium-234 and uranium-233	1	1	1	1
	Uranium-235 and uranium-236	1	0.85	0.85	0.85
	Uranium-238	1	0.97	0.97	0.97
Soil	Gross alpha	1	0.91	0.91	0.91
	Gross beta	1	1.2	1.2	1.2
	Cesium-137	3	1.1	0.83	1.2
	Tritium	1	0.95	0.95	0.95
	Tritium	1	1.2	1.2	1.2
	Potassium-40	4	0.97	0.85	1
	Plutonium-238	3	0.67	0.42	0.81
	Plutonium-239+240	3	0.99	0.91	1.1
	Radium-226	4	0.94	0.86	1
	Radium-228	4	0.97	0.87	1
	Thorium-228	4	0.98	0.89	1
	Uranium-235	4	0.99	0.88	1.1
	Uranium-238	3	1	0.96	1.1
Sewer	Gross alpha	2	0.74	0.7	0.78
	Tritium	1	0.94	0.94	0.94
Vegetation	Tritium	2	2.8	0.93	4.6

a Number of collocated pairs used in ratio calculations

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 9-5** 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 9-1**. 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.

Table 9-7. 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[(a)]
Air	Gross alpha	1	30	3.3
	Plutonium 239+240	2	24	8.3
	Plutonium 239+240	2	24	8.3
	Tritium	1	23	4.3
Groundwater	Copper	2	33	6.1
	Manganese	1	12	8.3
	Pentaerythritol tetranitrate	1	4	25
	Zinc	1	33	3
Runoff (from rain)	Cadmium	1	4	25
Vegetation	Tritium	1	10	10

a Inconsistent pairs are those for which one of the results is more than twice the reporting limit of the other.

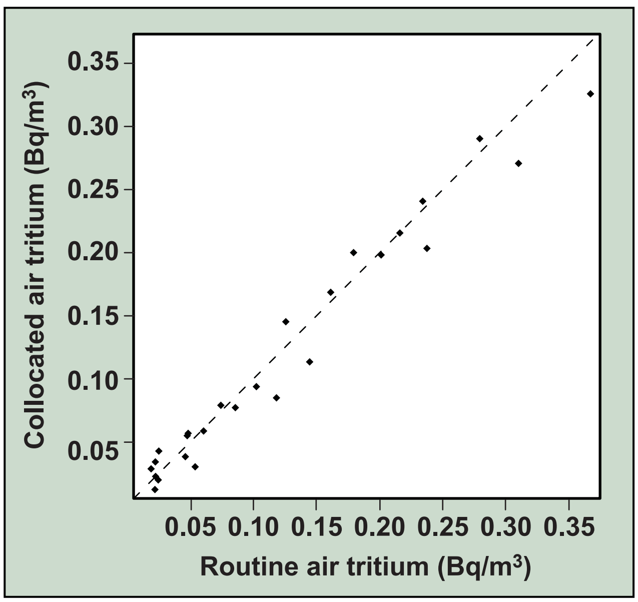

Figure 9-1. Example of data points that demonstrate good agreement between duplicate sample results using air tritium concentrations from collocated samples

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 9-5**. 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 9-6**. 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 9-7** 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 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 regulatory agency is involved.

Routine and collocated sample results show fairly good agreement: 90% of the pairs have a precision of 46% or better; 75% have a precision of 21% 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 27 data sets reported in **Table 9-5**, seven did not meet the criterion for acceptability because of outliers. **Figure 9-2** illustrates a set of collocated pairs with one outlier.

The second category is data sets that do not meet the criterion for acceptability because results are highly variable, as illustrated in **Figure 9-3**. This tends to be typical of measurements at extremely low concentrations. Low concentrations of radionuclides on particulates in air highlight this effect, because a small number or 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 27 data sets in **Table 9-5**, two show sufficient variability in results to make them fall outside the acceptable range.

Data Presentation

Data tables provided in the report CD were created using computer scripts that retrieve data from the database, convert to SI units when necessary, calculate summary statistics, format data as appropriate, lay out the table into the desired rows and columns, and present a draft table. Final tables are included after review by the responsible analyst. Analytical laboratory data, and values calculated from analytical laboratory data, are normally displayed with two or at most three significant digits. Significant trailing zeros may be omitted.

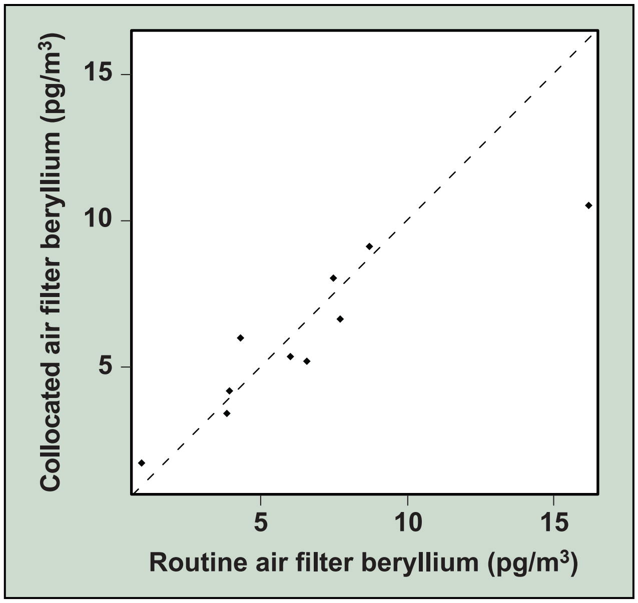

Figure 9-2. Example of data with an outlier using collocated air filter beryllium concentrations

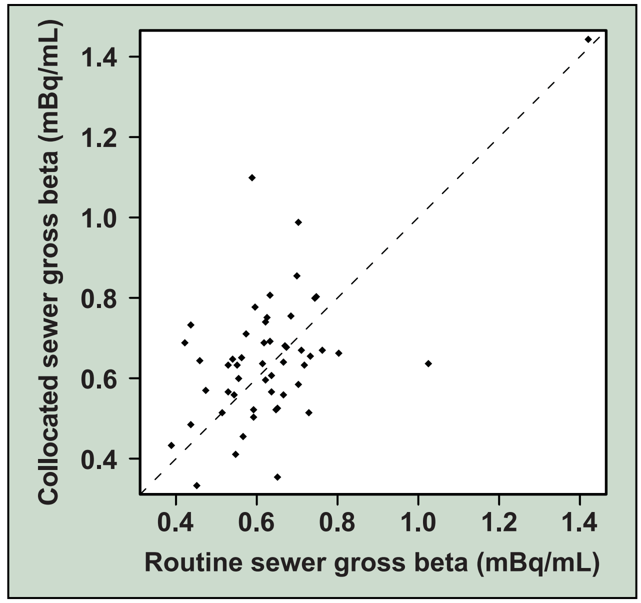

Figure 9-3. Example of variability using sewer gross beta concentrations from collocated samples

Radiological Data

Most of the data tables display radiological data as a result plus-or-minus an associated 2σ uncertainty. This measure of uncertainty represents intrinsic variation in the measurement process, most of which is due to the random nature of radioactive decay (see also the section "Reporting Uncertainty in Data Tables" in this chapter). 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.

Some 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 concentration at or near background 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 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 by the analytical laboratory 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 and Summary Statistics

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 are calculated according to the *Environmental Monitoring Plan* (Woods 2005). The usual summary statistics are the median, which is a measure of central tendency, and interquartile range (IQR), which is a measure of dispersion (variability). However, some tables may present other measures, at the discretion of the responsible analyst.

The median indicates the middle of the data set. That is, half of the measured results are above the median, and half are below. 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. Different 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. To calculate the median, at least four values are required; to calculate the IQR at least six values are needed.

Summary statistics are calculated from values that, if necessary, have already been rounded (such as when units have been converted from pCi to Bq) and are then rounded to an appropriate number of significant digits. The calculation of summary statistics is also affected by the presence of nondetections. A nondetection indicates that no specific measured value is available; instead, the best information available is that the actual value is less than the reporting limit. Adjustments to the calculation of the median and IQR for data sets that include nondetections are described below.

For data sets with all measurements above the reporting limit and radiological data sets that include reported values below the reporting limit, all reported values, including any below the reporting limit, are included in the calculation of summary statistics.

For data sets that include one or more values reported as “less than the reporting limit,” the reporting limit is used as an upper bound value in the calculation of summary statistics.

If the number of values is odd, the middle value (when sorted from smallest to largest) is the median. If the middle value and all larger values are detections then the middle value is reported as the median. Otherwise, the median is assigned a less-than (<) sign.

If the number of values is even, the median is halfway between the middle two values (i.e., the middle two when the values are sorted from smallest to largest). If both of the middle two values and all larger values are detections, then the median is reported. Otherwise, the median is assigned a less-than sign.

If any of the values used to calculate the 25th percentile is a nondetection, or any values larger than the 25th percentile are nondetections, then the IQR cannot be calculated and is not reported.

The median and the IQR are not calculated for data sets having no detections.

Reporting Uncertainty in Data Tables

The measurement uncertainties associated with results from analytical laboratories are represented in two ways. The first of these, significant digits, relates to the resolution of the measuring device. For example, if an ordinary household ruler with a metric scale is used to measure the length of an object in centimeters, and the ruler has tick marks every tenth centimeter, then the length can reliably and consistently be measured to the nearest tenth of a centimeter (i.e., to the nearest tick mark). However, an attempt to be more precise is not likely to yield reliable or reproducible results, because it requires a visual estimate of a distance between tick marks. The appropriate way to report such a measurement would be, for example, “2.1 cm.” This would indicate that the “true” length of the object is nearer to 2.1 cm than to 2.0 cm or 2.2 cm (i.e., between 2.05 and 2.15 cm). This result is said to have two significant digits. Although not explicitly stated, the uncertainty is considered to be ± 0.05 cm. A more precise measuring device might be able to measure an object to the nearest one-hundredth of a centimeter; in that case a value such as “2.12 cm” might be reported. This value would have three significant digits and the implied uncertainty would be ± 0.005 cm. A result reported as "3.0 cm" has two significant digits. That is, the trailing zero is significant, and implies that the true length is between 2.95 and 3.05 cm; closer to 3.0 than to 2.9 or 3.1 cm.

When performing calculations with measured values that have significant digits, all digits are used. The number of significant digits in the calculated result is the same as that of the measured value with the fewest number of significant digits.

Most unit conversion factors do not have significant digits. For example, the conversion from milligrams (mg) to micrograms (µg) requires multiplying by the fixed (constant) value of 1000. The value 1000 is exact; it has no uncertainty and therefore the concept of significant digits does not apply.

The other method of representing uncertainty is based on random variation. For radiological measurements, there is variation due to the random nature of radioactive decay. As a sample is measured, the number of radioactive decay events is counted, and the reported result is calculated from the number of decay events that were observed. If the sample is recounted, the number of decay events will almost always be different—because radioactive decay events occur randomly. Uncertainties of this type are reported in this volume as 2σ uncertainties. A 2σ uncertainty represents the range of results expected to occur approximately 95% of the time, if a sample were to be recounted many times. A radiological result reported as, for example, "2.6 ± 1.2 Bq/g" would indicate that with approximately 95% confidence, the "true" value is in the range 1.4 to 3.8 Bq/g (i.e., 2.6 – 1.2 = 1.4 and 2.6 + 1.2 = 3.8).

The concept of significant digits applies to both the radiological result and its uncertainty. So, for example, in a result reported as "2.6 ± 1.2", both the measurement and its uncertainty have the same number of significant digits, that is, two. When expanding an interval reported in the "±" form, for example "2.4 ± 0.44", to a range of values, the rule described above for calculations involving significant digits must be followed. For example, 2.4 – 0.44 = 1.96. However, the measurements 2.4 and 0.44 each have two significant digits, so 1.96 must be rounded to two significant digits, i.e., to 2.0. Similarly, 2.4 + 0.44 = 2.84, and this must be rounded to 2.8. Therefore, a measurement reported as "2.4 ± 0.44 Bq/g" would represent an interval of 2.0 to 2.8 Bq/g.

When rounding a value having a final digit of "5", the software that prepared the tables follows the Institute of Electrical and Electronics Engineers (IEEE) Standard 754-1985, which is "go to the even digit". For example, 2.45 would round down to 2.4, and 2.55 would round up to 2.6.

Quality Assurance Process for the Environmental Report

Unlike the preceding sections, which focused on standards of accuracy and precision in data acquisition and reporting, the following discussion deals with actions to ensure that the content of this report is accurate and has not been corrupted during 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.

Up to and including the 2003 Environmental Report, the formal QA procedure concentrated on ensuring that the data presented in tables and figures was the same as that reported by the analytical laboratory. Authors, contributors, and technicians were enlisted to check the accuracy of sections other than those with which they were routinely involved. Members of the Data Management Team (DMT) were excluded from this process because they prepared the tables. When checking values in tables and figures, checkers randomly selected 10% of the numbers and compared them to values in the reports provided by the analytical laboratories. If these values agreed with the reports, further checking was considered unnecessary. If there was disagreement, the checker compared another 10% of the data with the analytical values. If more errors were found, the entire table or figure was checked against hard copies of the analytical data. Unit conversions (e.g., from English to SI units) and summary calculations (e.g., mean, interquartile range, fractions of various limits) for each table or figure were also checked as part of this process.

The above procedure was extremely time-consuming. By the time the 2004 Environmental Report was being prepared, advances had been made that eliminated most of the potential for errors in simple supplementary data tables, such as are found primarily on the report CD. One of the advances was that, rather than sending printed reports that had to be hand-entered into the electronic database, the analytical laboratories send reports electronically, which are loaded directly into the database. This practice should result in perfect agreement between the database and data in printed reports from the laboratories. In practice, however, laboratory reporting is not perfect, so the DMT carefully checks all incoming data throughout the year, to make sure that electronic and printed reports from the laboratories agree. This aspect of QC, while not formally part of the QA process for the preparation of this environmental report, is essential to this report's accuracy. Because of this ongoing QC of incoming data, data stored in the database and used to prepare the annual environmental report tables are unlikely to contain errors.

Another advance is that scripts were written to pull data from the DMT database directly into the format of the table, including unit conversion and summary statistic calculations. All data tables found on the CD are prepared in this manner. For these tables, it is the responsibility of the appropriate analyst to check each year that the table is up-to-date (e.g., new locations/analytes added, old ones removed), that the data agree with the data they have received from DMT, and that the summary calculations have been done correctly.

For the 2005 Environmental Report, LLNL staff checked tables and figures in the body of the report as described above. Forms to aid in the QC of tables and figures were distributed along with the appropriate figure, table, and text; a coordinator kept track of the process. 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. Completed QC forms and the corrected figures or tables were returned to the report editors, who, in collaboration with the contributor, ensured that corrections were made.