Chapter 10

QUALITY ASSURANCE PROGRAM

Responsibility for quality at BNL starts with the Laboratory Director and permeates down through the entire organization, with individuals at each level assuming their appropriate share. The BNL Quality Management (QM) Office, headed by the QM Manager, coordinates and evaluates QA implementation at the Laboratory, and provides professional assistance and guidance to the Departments and Divisions. The ES&HS Division appointed a Quality Representative and Quality Management Team (QMT) to assist, assess, advise, and improve implementation of the Division-wide QA program.

10.1 Environmental Surveillance Program

The QA Program developed by BNL to achieve Laboratory objectives provides policies, responsibilities, and guidance procedures for the Divisions and Departments based on DOE Order 5700.6C. The ES&HS Division has adopted or adapted these program elements into the ES&HS Division Management System Manual (BNL, 1994) and has established responsibilities, methods, and controls for conducting its operations. The Environmental Protection Office and Analytical Services Laboratory (ASL) integrated both these elements and the additional environmental QA requirements of DOE Order 5400.1 into their sampling, analysis, and data handling activities. The implementing procedures on Environmental Monitoring, Radiation Measurements, Analytical Chemistry, and Regulatory Programs, in conjunction with the ES&HS Division Management System Manual (BNL, 1994) and the ES&HS QA Procedures, comprise the QA Program for the environmental surveillance and effluent monitoring programs.

The objectives of the Environmental Protection QA Program are to ensure that management provides planning, organization, direction, control, and support to achieve the objectives of the environmental program; line managers achieve quality in their product or services; and overall performance is reviewed and evaluated using a rigorous assessment process. This program was developed to ensure compliance with QA requirements established by DOE in Orders 5700.6C, Quality Assurance, and 5400.1, General Environmental Protection Program.

The ES&HS Division is responsible for establishing a program of internal assessments and external audits to verify the effectiveness of the environmental sampling, analysis, and database activities and their adherence to the QA program. Annual self-assessments of activities by the respective managers identify areas needing attention. Furthermore, the ASL participates in inter-laboratory performance evaluation programs organized by DOE, EPA, and NYSDOH. Contract laboratories that augment the capabilities of the in-house Laboratory are required to maintain a comprehensive QA program and are subject to audits by ES&HS Division personnel to ensure its implementation. In addition, the BNL QM Office, DOE-CH, regulatory agencies, and other independent groups periodically audit the environmental programs.

A major activity for the Environmental Protection Office and the ASL is ensuring that environmental media are sampled and analyzed in a way that provides representative, defensible data. The QA program supports this activity by incorporating QA elements, such as field sampling designs, documented procedures, chain of custody, a calibration/standardization program, acceptance criteria, statistical data analyses, software QA, and data processing systems, in the environmental surveillance and effluent monitoring programs. Standard Operating Procedures are established to calibrate instruments, analyze samples, and check quality control. Depending on the analytical method, quality control checks include analysis of blanks or background concentrations, use of Amersham or National Institute for Standards and Technology (NIST) traceable standards, and analysis of reference standards, spiked samples, and duplicate samples. The Labo-

ratory supervisors review all analytical and quality control results before the data are reported and incorporated into the database. The ASL is certified by the NYSDOH, Environmental Laboratory Approval Program (ELAP) for specific analytes identified below. The offsite contractor laboratories that perform radiological and chemical analyses to augment the onsite analytical capabilities also are required to incorporate these QA elements into their operation.

10.1.1 Radiological Analyses

The ES&HS Division ASL performs radiological analysis of both environmental and facility samples for gross alpha, gross beta, gamma, tritium, and strontium-90. The Laboratory participates in the DOE Environmental Measurements Laboratory (EML) QA Program and the EPA National Exposure Research Laboratory, Characterization Research Division, Las Vegas (NERL-LV) Performance Evaluation Study. In 1996, NYSDOH ELAP certified the Laboratory for potable and nonpotable analysis of gross alpha and beta and photon emitters (gamma). In addition it was certified to perform potable water analysis for tritium. During 1997, the ASL analyzed samples using an alternative analytical method for determining strontium-90 that was not approved by NYSDOH (see Appendix C). The ASL analyzes proficiency samples as part of the ELAP certification program. The results of these three intercomparison programs are shown in Tables 10-1 through 10-3, respectively.

Overall, the ASL performance in the EML intercomparison study was acceptable in 94% of the analyses performed on 4 matrices. Twenty-five of forty-eight EML analyses were within established acceptance limits, thirteen of forty-eight were within upper and lower limits (warning); ten analyses fell outside the acceptance limits. Many of the March and September air filter test results were reported in the warning and unacceptable range, but a review of the QC data for the unacceptable cobalt-57 and manganese-54 analyses on the air filter matrix showed no problem associated with the sample preparation, analytical process, or data calculations. However, the EML test filter is not the same geometry used to calibrate the gamma spectrometer used in the BNL EM air-monitoring program, which would account for a positive bias. These results imply that the environmental air sampling data presented in this report may be overestimated.

Overall, the ASL performance in the NERL intercomparison study was acceptable in 72% of the water analyses. The NERL-LV comparisons resulted in excellent agreement for seven of the eighteen analyses (within 1σ of the known value), and good agreement for six analyses (within 2σ of the known. The five remaining sample analyses were unacceptable because the results were outside the $\pm 3\sigma$ control limit.

Review of the QC data for the unacceptable results found no problem associated with the sample preparation nor data calculations. The gross alpha and beta results of April and July reported to NERL-LV were unacceptable because the instrument required maintenance that occurred in the latter quarter of 1997. To reduce the number of unacceptable results, a geometry correction factor will be used to account for the slight difference in the way the ASL counts its samples (which is dependent on the instrument) as opposed to the way they are counted at the Labs where the samples are prepared.

Lastly, the radiological results from the ELAP proficiency test for gross alpha and beta showed acceptable agreement for all four analyses performed. BNL did not receive two alpha/beta samples in October 1997 and, therefore, results were not reported. Because of this, the ASL lost alpha/beta certification in potable water analyses for 4 months. Certification was reinstated in calendar year 1998.

Figures 10-1 through 10-3 summarize the internal quality control program for the radiological instruments. Figure 10-1 shows the annual mean and 99% confidence interval for the efficiency of the alpha, beta, tritium, and strontium-90 analyzers, as determined by a daily calibration standard. All analyzers were stable. Figure 10-2 summarizes the daily variation in background counts from each of these instruments in 1997. An investigation into the wide range of the 99% confidence interval for H-3 revealed that the liquid scintillator experienced increased variability in

Table 10-1
BNL Site Environmental Report for Calendar Year 1997
BNL Quality Assessment Program Results
Environmental Measurements Laboratory

Matrix	Units	Isotope	Date	EML	BNL	Ratio	Comments
Air Filter	Bq/Filter	Alpha	Mar-97	0.9	0.96	0.94	
			Sep-97	1.39	1.49	0.93	
		Am241	Mar-97	0.4	0.152	2.63	Not Acceptable
			Sep-97	0.57	0.21	2.71	Not Acceptable
		Beta	Mar-97	0.44	0.45	0.98	
			Sep-97	2.87	3	0.96	
		Ce144	Mar-97	20.4	15.7	1.30	Not Acceptable
			Sep-97	22.7	19.12	1.19	Warning
		Co57	Mar-97	14.7	10.8	1.36	Not Acceptable
			Sep-97	16.05	12.64	1.27	Warning
		Co60	Mar-97	5.2	5.01	1.04	
			Sep-97	9.99	10.7	0.93	
		Cs134	Mar-97	10.8	10.88	0.99	
			Sep-97	24.9	28.17	0.88	
		Cs137	Mar-97	11.9	8.7	1.37	Not Acceptable
			Sep-97	9.32	7.31	1.27	Warning
		Mn54	Mar-97	10.4	7.6	1.37	Not Acceptable
			Sep-97	8.7	6.72	1.29	Warning
		Sb125	Mar-97	17.6	12.33	1.43	Not Acceptable
			Sep-97	23.14	16.1	1.44	Not Acceptable
Soil	Bq/g	Am241	Mar-97	9.1	5.68	1.60	Warning
			Sep-97	13.83	6.04	2.29	Warning
		Co60	Mar-97	1.1	1.06	1.04	
			Sep-97	1.51	1.5	1.01	
		Cs137	Mar-97	846.1	825.5	1.02	
			Sep-97	775.53	810	0.96	
		K40	Mar-97	295.6	334.25	0.88	
			Sep-97	261	315	0.83	Warning
Vegetation	Bq/g	Co60	Mar-97	13	12.5	1.04	
			Sep-97	23.61	32.4	0.73	Warning
		Cs137	Mar-97	241.6	189.2	1.28	Warning
			Sep-97	595	624	0.95	
		K40	Mar-97	888.1	811.5	1.09	
			Sep-97	931.3	1130	0.82	Warning
Water	Bq/L	Alpha	Mar-97	1153.3	1130.3	1.02	
			Sep-97	492.3	557	0.88	
		Beta	Mar-97	639.9	744	0.86	
			Sep-97	812.5	712	1.14	
		Co60	Mar-97	98.4	90.85	1.08	
			Sep-97	23.5	23.3	1.01	
		Cs137	Mar-97	91	69.7	1.31	Not Acceptable
			Sep-97	41.5	34.3	1.21	Warning
		H3	Mar-97	255.7	250.3	1.02	
			Sep-97	117.22	115	1.02	
		Mn54	Mar-97	26.5	20.85	1.27	Not Acceptable
			Sep-97	45.6	37.8	1.21	Warning
		Sr90	Mar-97	20.3	23.2	0.88	Warning
			Sep-97	3	2.94	1.02	

Note: Comment column provides EML evaluation of analytical performance which is based on conrol limits established from percentiles of historic data disributions. No comment indicates that the performance was still within acceptable limits. A warning means that the results were just within the 2 sigma “window” of acceptable results.

Table 10-2
BNL Site Environmental Report for Calendar Year 1997
BNL Quality Assessment Program Results
National Exposure Research Laboratory (NERL-LV)

Matrix	Units	Isotope	Date	NERL	BNL	Ratio	Comments
Water	Bq/L	Alpha	Oct-97	14.70	8.95	0.61	Not Acceptable
			Jul-97	3.10	6.63	2.14	Not Acceptable
			Jan-97	5.20	5.60	1.08	
		Beta	Oct-97	48.90	45.60	0.93	
			Jul-97	15.10	230.60	15.27	Not Acceptable (a)
			Jan-97	14.70	17.83	1.21	
		H3	Mar-97	7900.00	7270.00	0.92	
			Aug-97	11010.00	9790.00	0.89	
		Sr-90	Jan-97	25.00	23.00	0.92	
			Jul-97	16.00	20.00	1.25	
		Co60	Jun-97	27.00	32.30	1.20	
			Nov-97	44.00	47.90	1.09	
		Cs134	Jun-97	22.00	29.00	1.32	
			Nov-97	10.00	12.70	1.27	
		Cs137	Jun-97	49.00	67.70	1.38	Not Acceptable
			Nov-97	74.00	132.70	1.79	Not Acceptable
		Zn65	Jun-97	100.00	104.30	1.04	
			Nov-97	75.00	82.30	1.10	

[a] = Result was not acceptable because of transcription error in reporting.
Note: Comment column provides NERL evaluation of analytical performance which is based on 2 and 3 normalized standard deviations about the known value. Results outside these control limits are deemed not acceptable or a statistical outlier. No comment indicates that the performance was within acceptable limits.

Table 10-3
BNL Site Environmental Report for Calendar Year 1997
BNL Potable Water Radiochemistry Proficiency Test Results
Environmental Laboratory Approval Program

Analyte	Date	ELAP (pCi/L)	BNL (pCi/L)	Ratio	Comment
Alpha	Apr-97	18	12.7	0.71	Warning
	Apr-97	79	84.4	1.07	
	Oct-97	15.7	NR		[a]
	Oct-97	56.5	NR		[a]
Beta	Apr-97	13	15.7	1.21	
	Apr-97	76	87.6	1.15	
	Oct-97	14.7	NR		[a]
	Oct-97	52.1	NR		[a]

[a] = Data was not reported (NR) for Oct 1997 because the sample was not received by BNL.
Note: Comment column provides ELAP evaluation of analytical performance which is based on 95 and 99% confidence interval about the target value. No comment indicates that the performance was within acceptable limits.

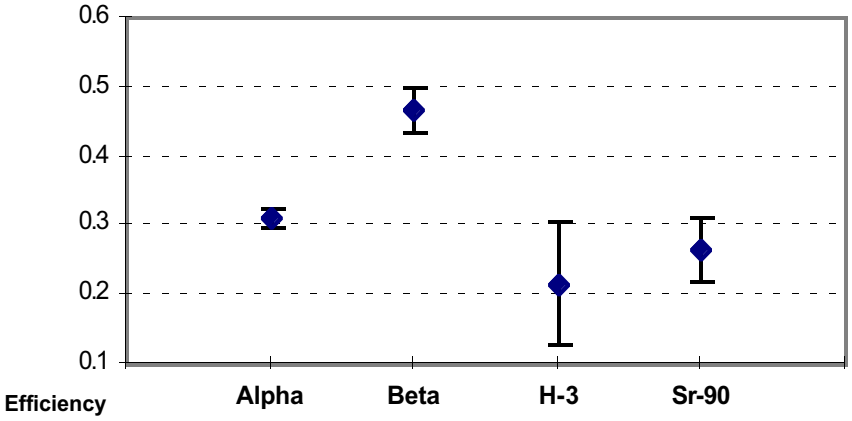

Figure 10-1. Instrument Efficiency Summary for 1997

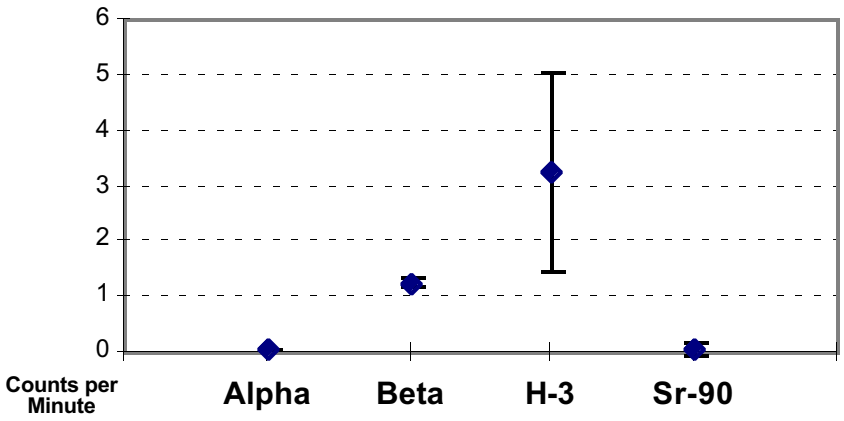

Figure 10-2. Instrument Background Summary for 1997

the first quarter of 1997 during the HFBR Tritium Plume Investigation and required preventative maintenance. Figure 10-3 compares the mean and 99% confidence intervals of the cesium-137 energy calibration for each gamma detector, as measured by a daily calibration standard. The 661.65 keV cesium-137 gamma energy line is illustrated on the graph as the center dashed line and the acceptance band of ± 1 keV is shown as the upper and lower dashed lines. As can be seen, all gamma detectors operated within the acceptance limit during 1997.

The ASL used an alternative strontium-90 method developed at the DOE Argonne National Laboratory (described in Appendix C). Figure 10-4 compares the mean and 99% confidence interval of the deviation of each detector's response from the calibration value. The plot shows that the mean percent deviation from the calibration standards was within ±2%. Each of the daily efficiency checks performed on all detectors were within the ±5% acceptance band, except two measurements on detectors 5 and 10. Excess variability in the daily responses of detectors 5 and 10 caused the 99% confidence interval to exceed the acceptance band even though the daily checks did not. The unit was subsequently sent offsite for repair. Quality control samples spiked with strontium-90 yielded mean recoveries of 94% ±8%, which is comparable to results reported the previous year.

Peconic River water samples were processed using the ASL's Sr-90 Water Method (RM-SOP-60). This method is a slight modification of the American Society for Testing and Materials (ASTM) Standard Method for Sr-90 in Water (ASTM-D5811-95) which is intended for environment water samples (i.e., non-process and effluent waters). All of the the Peconic River water samples were found to contain significant amounts of soluble salts that interfered with the strontium yield

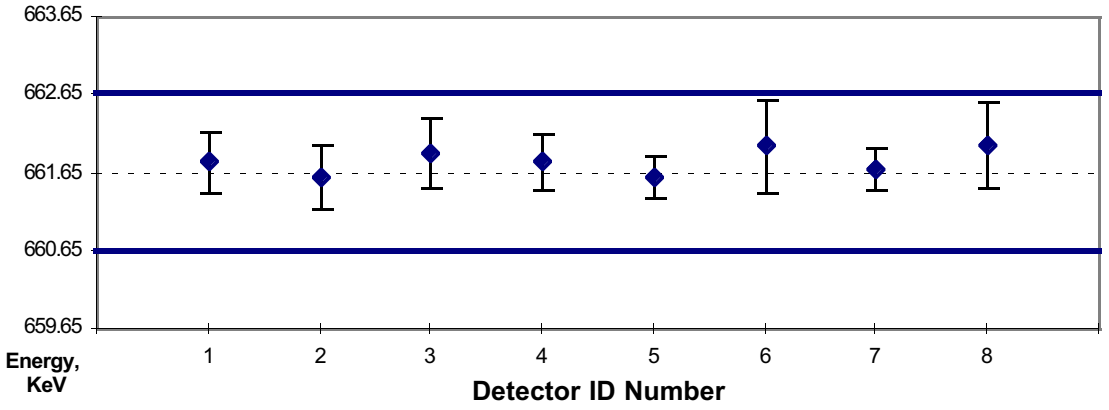

Figure 10-3. Cesium-137 Energy Calibration Summary for 1997

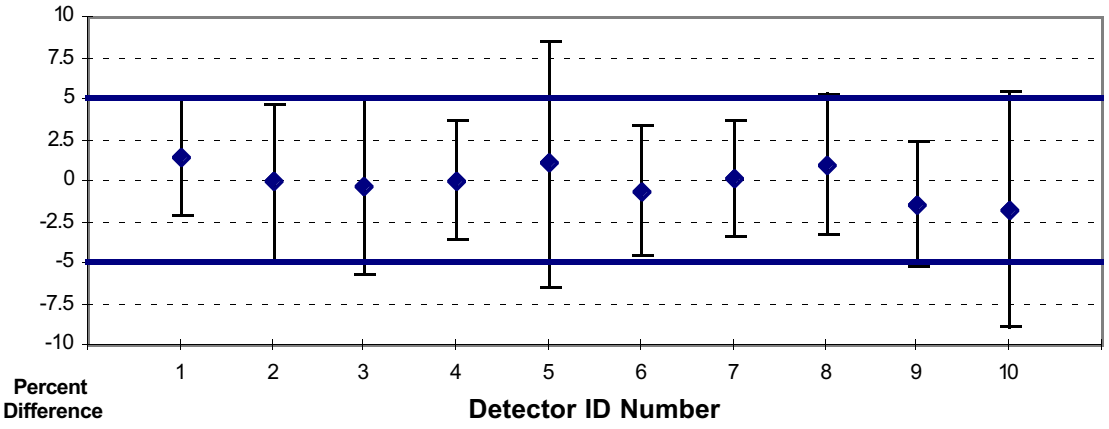

Figure 10-4. Strontium-90 Instrument Efficiency Summary for 1997

determinations. Because the strontium yields in the Peconic samples were below the ASL's acceptance criteria, the data were rejected and footnoted with the statement "sample results invalidated during QA review".

During the first quarter of 1997, there was an onsite audit of the radiological analytical processes conducted by NYSDOH ELAP. In addition, DOE's Office of Environmental Management made two appraisals of the ASL's radiological laboratory. In the April 1997 'Gilbert-Hill' audit of the ASL, corrective action plans for the findings and recommendations were developed and their implementation is virtually complete.

10.1.2 Analytical Chemistry

The ES&HS ASL is certified by NYSDOH ELAP for analyzing metals and anions under the environmental potable water category, and for specific purgeable organic compounds under the environmental analyses of nonpotable water. The analytes for which the ASL holds potable water certification are silver, cadmium, chromium, copper, iron, mercury, manganese, sodium, lead, zinc, chloride, nitrate (as nitrogen), and sulfate. The compounds which it holds certification in nonpotable water are benzene, toluene, xylene, ethylbenzene, chloroform, 1,1-Dichloroethylene (DCE), 1,1-Dichloroethane (DCA), 1,1,1-Trichloroethane (TCA), Trichloroethylene (TCE), and Tetrachloroethylene (PCE).

Table 10-4 shows the results of organic and inorganic proficiency samples analyzed for this certification program. Sixty-seven percent of all organic analyses of proficiency samples performed

for NYSDOH in January and July of 1997 were within acceptance limits. There was good agreement, within ±20%, in eight of twelve organic analyses. The remaining four tests (in July of 1997 only) were slightly greater than ±20% of the known value and were not acceptable. These results confirm the accuracy of the data presented in this report.

Similarly, the inorganic NYSDOH proficiency test results were acceptable in 94% of the analyses as shown in Table 10-5. Results showed excellent agreement, within ±10%, in forty-eight of the fifty-four analyses, with thirty-nine analyses being within ±5% of the known value, again confirming the accuracy of the data presented in this report. The remaining three were unacceptable; an investigation revealed that a transcription error occurred in reporting mercury. The April 1997 nitrate result just exceeded its acceptance criteria of ±15%. Table 10-5 gives the corrected results in the case of the mercury data processing error.

The ASL also participated in the EPA Environmental Monitoring Systems Laboratory (EMSL-CI) water pollution and water supply performance evaluation studies. Tables 10-6 and 10-7, respectively, give the results of these studies. Overall, the ASL performance in the EMSL-CI water pollution intercomparison study (WP037, Table 10-6) was acceptable in 89% of the analyses. The performance was excellent for sixteen of eighteen organic analyses. One of the paired TSS and residual chlorine results was acceptable. An investigation revealed that the analytical data were transcribed incorrectly onto the report form by not applying a factor of 2 dilution. Table 10-7 shows the results from using the WS038/039 EMSL-CI water supply samples for an internal blind QC study. Excellent performance was measured in twenty-one of twenty-three comparisons. The two unacceptable results in September 1997 were due to an error in the total xylene and chloroform algorithms, which has been corrected.

Corrective actions included reprocessing all the xylene and chloroform data, requesting funding to automate data processing, and requesting the manufacturer to adjust the GC/MS settings.

Figures 10-5 and 10-6 summarize the internal quality control program for the ion chromatography and atomic absorption methods used for inorganic analyses. Figure 10-5 presents the annual mean and 99% confidence interval for reference check and calibration check sample recoveries analyzed in each metal or anion sample batch. Both anions and metals were ±15 of the target values, except chromium, which was ±18%. Figure 10-6 gives the mean and 99% confidence interval of spike recoveries performed for all analyses. Each daily spike sample measured its recovery within the ±25% acceptance limit. These data attest to the accuracy of the data presented in this report.

Figures 10-7 through 10-9 show the 1997 results of the internal quality control program of the ASL for the gas chromatography/mass spectroscopy method used for organic analyses. Mean recoveries and 99% confidence intervals for all ten analytes were within their target ranges; that is, ±30% for mercury and ±20% for the remaining nine analytes. These results are a marked improvement from the previous year. In 1996, corrective actions by the manufacturer resulted in instrument upgrades and extension of the warranty period.

Figure 10-7 summarizes the recoveries of the 10 organic reference check samples by presenting the mean and 99% confidence interval for each of the primary volatile organic compounds. Variability was within the internally established control limit, ±20% of the known concentration, for each analyte except DCE (±42%) and toluene (±24%). The acceptance limit established by the EPA National Functional Guideline for this type of QC sample is ±40%. Increased variability of the DCE response was due to poor resolution of this chromatographic peak, which elutes in the region of the chromatogram immediately following the solvent peak. The manufacturer was contacted to make the appropriate adjustments to prevent recurrence of the problem.

Figure 10-8 shows the 99% confidence intervals of surrogate and spike recoveries for the organic analyses. The method's performance for each of the two surrogate analyses was ±11% and ±20% of the target value (fluorobenzene [Flbenz] and 4-Bromofluorobenzene [BFB], re-

Table 10-4
BNL Site Environmental Report for Calendar Year 1997
BNL Non-Potable Water Chemistry Proficiency Test Results
Environmental Laboratory Approval Program

Analyte	Date	ELAP (ug/L)	BNL (ug/L)	Ratio	Comment
1,1,1-Trichloroethane	Jan-97	20.10	NR		(a)
	Jan-97	59.60	NR		(a)
	Jul-97	29.80	34.60	1.16	
	Jul-97	39.80	47.00	1.18	
Benzene	Jan-97	21.20	NR		(a)
	Jan-97	52.60	NR		(a)
	Jul-97	29.00	35.70	1.23	
	Jul-97	63.50	81.20	1.28	Not Acceptable
Ethyl benzene	Jan-97	25.20	NR		(a)
	Jan-97	57.30	NR		(a)
	Jul-97	18.40	22.00	1.20	
	Jul-97	44.10	52.20	1.18	
Toluene	Jan-97	21.20	NR		(a)
	Jan-97	42.50	NR		(a)
	Jul-97	30.40	38.00	1.25	
	Jul-97	61.80	78.20	1.27	Not Acceptable
Total Xylene	Jan-97	20.30	NR		(a)
	Jan-97	51.90	NR		(a)
	Jul-97	38.00	28.00	0.74	Not Acceptable
	Jul-97	41.40	53.00	1.28	Not Acceptable
Chloroform	Jan-97	28.20	NR		(a)
	Jan-97	49.60	NR		(a)
	Jul-97	20.70	24.00	1.16	
	Jul-97	35.20	42.00	1.19	

(a) = Data not reported (NR) because samples were not received by BNL.
Note: Comment column provides ELAP evaluation of analytical performance which is based on 95 and 99% confidence interval about the target value. No comment indicates that the performance was within acceptable limits.

spectively) exceeding the acceptance limit of ±15% in the BFB case. The matrix spike recoveries ranged between ±20 - 26%, all within the acceptance band of ±25% except TCA. This variability was due to instrument problems including malfunctions in the autosampler valve and leaks in the concentrator. Data review and validation resulted in TCA samples being qualified, which means that they were estimates because the surrogate recoveries exceeded EPA limits.

Lastly, the precision of the method was measured by analyzing duplicate samples; Figure 10-9 presents the results as relative percent difference. All duplicate analyses showed agreement within the EPA acceptance limit of ±25%, however they exceeded the internal control limits of ±10%. Irregularities in the injection of internal standards were noted. The percent variation in the internal standards corresponded with the change in spike recoveries, indicating that the variation resulted from inconsistencies in the autosampler mechanical injections.

During 1997, there was an onsite audit of the analytical chemistry processes conducted by NYSDOH ELAP. In addition, an appraisal of the Analytical Services Laboratory was conducted by an independent organization as part of the BNL Tier III Assessment Program. In both cases, correc-

Table 10-5
BNL Environmental Report for Calendar Year 1997
BNL Potable Water Chemistry Proficiency Test Results
Environmental Laboratory Approval Program

Analyte	Date	ELAP (ug/L)	BNL (ug/L)	Ratio	Comment
Cadmium	Apr-97	3.75	3.90	1.04	
	Apr-97	7.50	8.00	1.07	
	Oct-97	2.50	2.46	0.98	
	Oct-97	6.67	6.80	1.02	
Chloride	Apr-97	19.10	19.50	1.02	
	Apr-97	156.00	153.00	0.98	
	Oct-97	35.20	35.20	1.00	
	Oct-97	104.00	106.00	1.02	
Chromium	Apr-97	25.00	24.50	0.98	
	Apr-97	87.50	92.00	1.05	
	Oct-97	33.30	36.20	1.09	
	Oct-97	83.30	90.70	1.09	
Copper	Apr-97	75.00	75.00	1.00	
	Apr-97	735.00	757.00	1.03	
	Oct-97	100.00	104.00	1.04	
	Oct-97	1000.00	1027.00	1.03	
Iron	Apr-97	100.00	101.00	1.01	
	Apr-97	308.00	314.00	1.02	
	Oct-97	150.00	156.00	1.04	
	Oct-97	389.00	405.00	1.04	
Lead	Apr-97	12.50	13.20	1.06	
	Apr-97	50.00	57.80	1.16	
	Oct-97	16.70	17.40	1.04	
	Oct-97	33.30	36.00	1.08	
Manganese	Apr-97	99.10	102.00	1.03	
	Apr-97	246.00	258.00	1.05	
	Oct-97	83.10	86.00	1.03	
	Oct-97	213.00	223.00	1.05	
Mercury	Apr-97	1.69	1.25	0.74	[a]
	Apr-97	6.25	5.48	0.88	[a]
	Oct-97	3.33	3.01	0.90	
	Oct-97	10.00	9.97	1.00	
Nitrate (as N)	Apr-97	1.29	1.49	1.16	Not Acceptable
	Apr-97	6.92	6.91	1.00	
	Oct-97	0.76	0.73	0.96	
	Oct-97	9.23	8.86	0.96	
Silver	Apr-97	15.70	14.20	0.90	
	Apr-97	31.90	32.80	1.03	
	Oct-97	33.70	35.00	1.04	
	Oct-97	41.60	44.00	1.06	
Sodium	Apr-97	99.10	103.00	1.04	
	Apr-97	234.00	239.00	1.02	
	Oct-97	74.80	75.00	1.00	
	Oct-97	178.00	180.00	1.01	
Sulfate (as SO4)	Apr-97	37.80	38.70	1.02	
	Apr-97	176.00	174.00	0.99	
	Oct-97	79.40	80.00	1.01	
	Oct-97	149.00	149.00	1.00	
Zinc	Apr-97	88.10	98.00	1.11	
	Apr-97	1540.00	1610.00	1.05	
	Oct-97	200.00	196.00	0.98	
	Oct-97	987.00	995.00	1.01	

[a] = B21 BNL values were reversed in data transmissin; corrected BNL results are shown and were acceptable.

Note: Comment column provides ELAP evaluation of analytical performance which is based on 95 and 99% confidence interval about the target value.
No comment indicates that the performance was within acceptable limits.

Table 10-6
BNL Site Environmental Report for Calendar Year 1997
BNL Water Pollution Performance Evaluation Studies - WP037
USEPA Environmental Monitoring Systems Laboratory - Cincinnati

Analyte	Units	Date	BNL	EMSL-CI	Ratio	Comments
Chloroform	ug/l	May-97	57.60	59.40	0.97	
	ug/l	Nov-97	49.90	46.40	1.08	
1,1,1 Trichloroethane	ug/l	May-97	57.00	54.20	1.05	
	ug/l	Nov-97	40.60	38.70	1.05	
Trichloroethene	ug/l	May-97	61.60	64.20	0.96	
	ug/l	Nov-97	37.70	33.60	1.12	
Tetrachloroethene	ug/l	May-97	41.70	44.30	0.94	
	ug/l	Nov-97	43.20	43.70	0.99	
Benzene	ug/l	May-97	79.50	72.60	1.10	
	ug/l	Nov-97	14.60	13.30	1.10	
Ethylbenzene	ug/l	May-97	60.80	63.30	0.96	
	ug/l	Nov-97	10.50	10.40	1.01	
Toluene	ug/l	May-97	56.20	56.10	1.00	
	ug/l	Nov-97	13.80	12.70	1.09	
TSS	mg/l	May-97	115.00	226.00	0.51	Not Acceptable
	mg/l	Nov-97	48.20	56.00	0.86	
Total Residual Cl	mg/l	May-97	59.50	118	0.50	Not Acceptable
	mg/l	Nov-97	3.18	2.80	1.32	

Note: Comment column provides EMSL-CI evaluation of analytical performance which is based on 95 and 99% prediction interval calculated from samples analyzed by EPA and State Laboratories No comment indicates that the performance was within acceptable limits.

Table 10-7
BNL Site Environmental Report for Calendar Year 1997
BNL Water Supply Performance Evaluation Studies - WS038 and WS039
USEPA Environmental Monitoring Systems Laboratory - Cincinnati

Analyte	Units	Date	BNL	EMSL-CI	Ratio	Comments
Cd	ug/l	Sep-97	27.00	28.50	0.95	
Cr	ug/l	Sep-97	23.70	23.90	0.99	
Cu	ug/l	Sep-97	506.00	490.00	1.03	
Hg	ug/l	Sep-97	3.46	3.80	0.91	
Mn	ug/l	Sep-97	86.00	82.00	1.05	
Zn	ug/l	Sep-97	779.00	760.00	1.03	
NO3 - N	mg/l	Sep-97	9.58	9.50	1.01	
SO4	mg/l	Sep-97	472.00	490.00	0.96	
Chloroform	ug/l	Mar-97	34.50	36.50	0.95	
		Sep-97	25.30	16.20	1.56	Not Acceptable
TCA	ug/l	Mar-97	17.00	17.20	0.99	
		Sep-97	12.70	11.20	1.13	
TCE	ug/l	Mar-97	12.80	12.40	1.03	
		Sep-97	18.80	16.40	1.15	
Benzene	ug/l	Mar-97	13.60	12.50	1.09	
		Sep-97	11.20	9.39	1.19	
PCE	ug/l	Mar-97	14.70	14.10	1.04	
		Sep-97	7.85	7.60	1.03	
Toluene	ug/l	Mar-97	18.70	16.20	1.15	
		Sep-97	8.09	7.31	1.11	
Ethylbenzene	ug/l	Mar-97	15.80	15.70	1.01	
		Sep-97	12.50	11.60	1.08	
Total Xylenes	ug/l	Mar-97	12.20	22.90	0.53	Not Acceptable

NA = Not analyzed
Note: Comment column provides EMSL-CI evaluation of analytical performance which is based on 40CFR141 analyte-specific acceptance limits. No comment indicates that the performance was within acceptable limits.

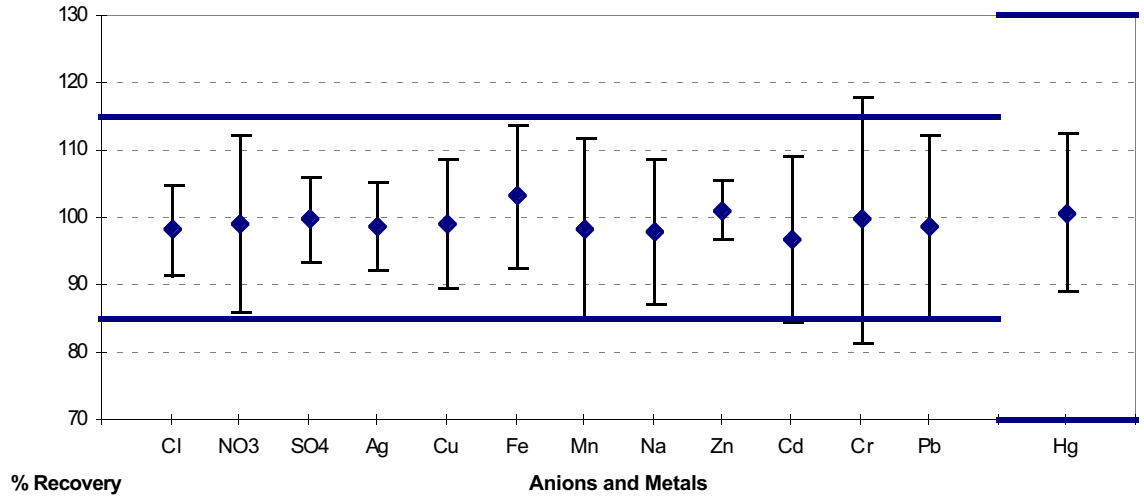

Figure 10-5. Reference Check Summary for 1997 Inorganic Analyses

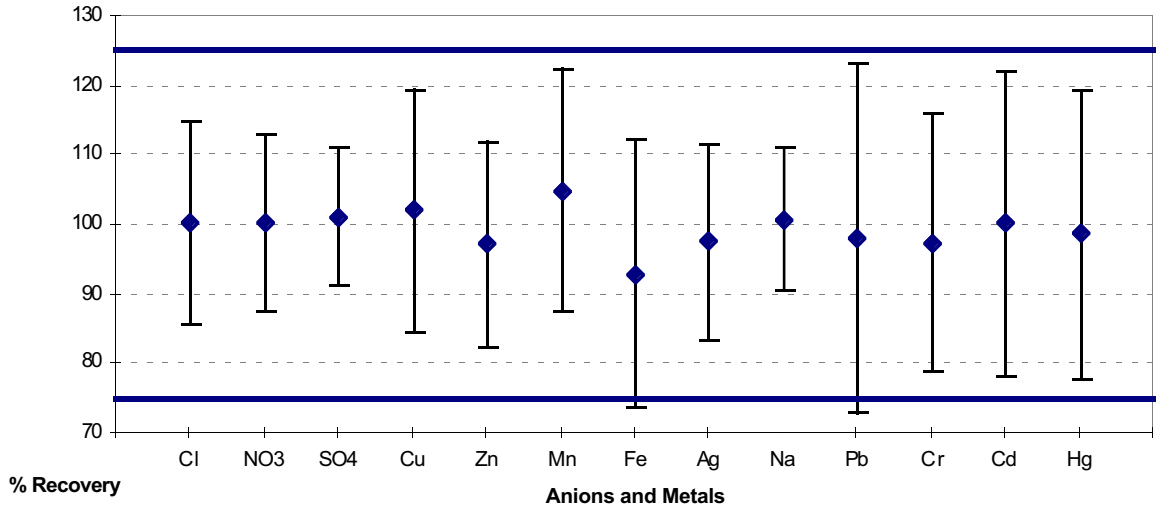

Figure 10-6. Summary of Spike Recoveries for 1997 Inorganic Analyses

tive action plans for the findings and recommendations were developed and implementation is ongoing.

10.1.3 Contractor Laboratories

Samples collected for regulatory compliance, such as SPDES discharge monitoring reports, Water Treatment Plant (WTP) monthly reports, and Central Steam Facility (CSF) semiannual reports are analyzed by offsite contractor laboratories. Contractor laboratories were used when the ASL could not perform a specific analysis, such as strontium-90 or Toxicity Characteristic Leachate Procedure (TCLP) by EPA methods. The laboratory has a person dedicated to specifying contract and technical requirements, including applicable certifications for each analytical method, and evaluating the contractor's performance. The incoming data packages are reviewed to ensure that

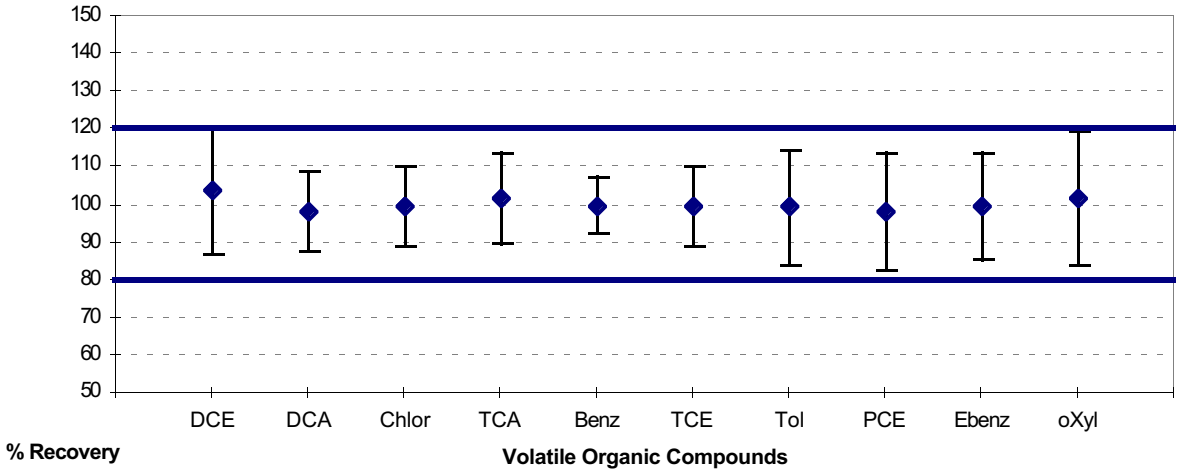

Figure 10-7. Reference Check Summary for Organic Analyses in 1997

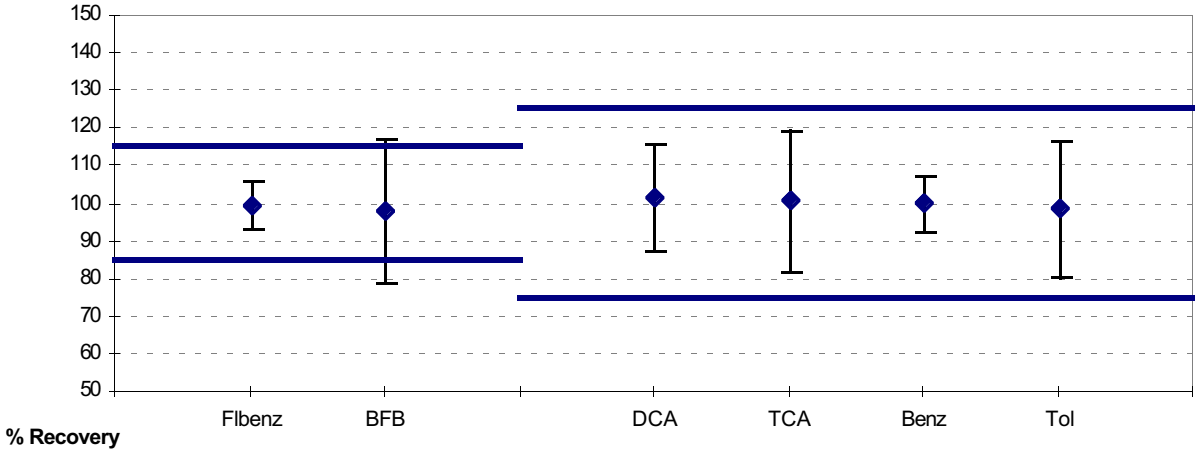

Figure 10-8. Surrogate and Spike Recovery Summaries for Organic Analyses

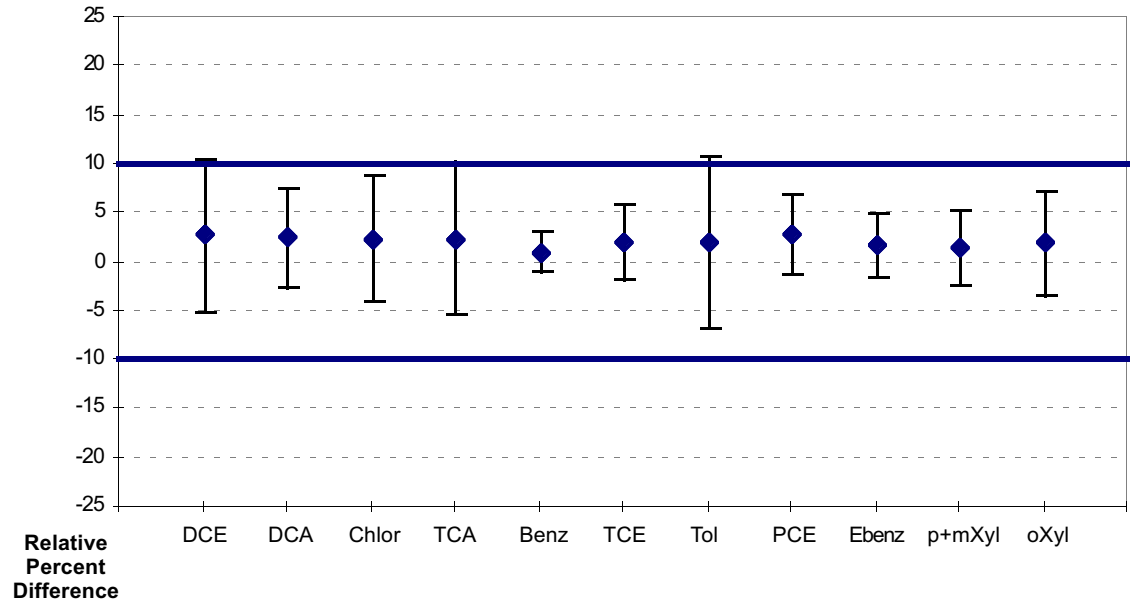

Figure 10-9. Matrix Spike Duplicate Summary for Organic Analyses in 1997

they comply with the contract specification before the data is reported. The commercial laboratories are audited periodically by the supervisor and QA Officer to verify competence in analytical methodology and implementation of a comprehensive QA program.

The contract laboratories responsible for analyzing the BNL SPDES samples are required to participate in the NPDES Performance Evaluation Study; these results are presented in Table 10-8. Twenty-four of the twenty-four analyses showed acceptable agreement which is an improvement from the performances of the previous years two contractor labs.

A contractor laboratory participated in the EMSL-CI Water Pollution Performance Evaluation Study (WP038 and WP039) in May and November of 1997. The results given in Table 10-9 for the same SPDES parameters show acceptable agreement for twenty-six of twenty-eight analyses. However, one sample in May 1997 for Oil and Grease was outside the acceptance limit. Overall, this contractor laboratory performed acceptably in 97% of the comparisons. A dilution error

Table 10-8
BNL Site Environmental Report for Calendar Year 1997
BNL Contractor Laboratory Performance Evaluation Study
BNL National Pollution Discharge Elimination System (NPDES) - DMR QA 17

Analyte	Units	Date	Reported	NPDES	Ratio	Comments
Cu	mg/L	Jan-98	289.000	277.000	1.04	
Fe	mg/L	Jan-98	1996.000	0.95		
Pb	mg/L	Jan-98	429.000	430.000	1.00	
Ni	mg/L	Jan-98	185.000	188.000	0.98	
Zn	mg/L	Jan-98	1564.000	1551.000	1.01	
Cr	mg/L	Jan-98	418.000	420.000	1.00	
Mn	mg/L	Jan-98	1101.000	1100.000	1.00	
Cd	mg/L	Jan-98	65.800	69.000	0.95	
pH		Jan-98	6.530	6.580	0.99	
TSS	mg/L	Jan-98	40.200	46.000	0.87	
Oil and Grease	mg/L	Jan-98	8.500	12.200	0.70	
Ammonia - N	mg/L	Jan-98	2.970	2.800	1.06	
NO3 - N	mg/L	Jan-98	31.500	31.000	1.02	
Kjeldahl - N	mg/L	Jan-98	23.000	24.000	0.96	
	mg/L					
5 Day BOD	mg/L	Jan-98	46.000	50.300	0.91	
Total Cyanide	mg/L	Jan-98	0.162	0.190	0.85	
Total Phenolics	mg/L	Jan-98	0.124	0.113	1.10	
Total Residual Cl	mg/L	Jan-98	1.430	1.390	1.03	
Fathead Minnow						
Chronic Data -						
Survival, NOEC	%	Jan-98	25.000	25.000	1.00	
Growth, IC25	%	Jan-98	24.200	37.700	0.64	
Growth, NOEC	%	Jan-98	12.500	25.000	0.50	
Cerlodaphnia						
Chronic Data						
Survival, NOEC	%	Jan-98	12.500	25.000	0.50	
Growth, IC25	%	Jan-98	12.700	15.700	0.81	
Growth, NOEC	%	Jan-98	12.500	12.500	1.00	

Note: Comment column provides evaluation of analytical performance which is based on 95 and 99% prediction interval calculated from samples analyzed by EPA and State laboratories. No comment indicates that the performance was within acceptable limits.

Table 10-9
BNL Site Environmental Report for Calendar Year 1997
BNL Contractor Laboratory (H2M) Water Pollution Performance Evaluation Studies
USEPA Environmental Monitoring Systems Laboratory - Cincinnati

Analyte	Units	Date	Contractor	EMSL-CI	Ratio	Comments
Cu	ug/l	Nov-97	289.000	277.000	1.04	
		May-97	118.000	115.000	1.03	
Fe	ug/l	Nov-97	1996.000	2100.000	0.95	
		May-97	402.000	393.000	1.02	
Pb	ug/l	Nov-97	429.000	430.000	1.00	
		May-97	126.000	130.000	0.97	
Ni	ug/l	Nov-97	185.000	188.000	0.98	
		May-97	426.000	417.000	1.02	
Zn	ug/l	Nov-97	1561.000	1551.000	1.01	
		May-97	304.000	296.000	1.03	
pH		Nov-97	6.680	6.580	1.02	
		May-97	9.300	9.300	1.00	
TSS	mg/l	Nov-97	596.000	512.000	1.16	
		May-97	710.000	685.000	1.04	
Oil and Grease	mg/l	Nov-97	8.500	12.200	0.70	Warning
		May-97	15.500	32.000	0.48	Not Acceptable
Ammonia - N	mg/l	Nov-97	2.970	2.800	1.06	
		May-97	0.250	0.261	0.96	
NO3 - N	mg/l	Nov-97	31.500	31.000	1.02	
		May-97	0.611	0.620	0.99	
Kjeldahl - N	mg/l	Nov-97	23.000	24.000	0.96	
		May-97	2.900	2.600	1.12	
5 Day BOD	mg/l	Nov-97	46.000	50.300	0.91	
	mg/l	May-97	106.000	93.100	1.14	
Total Phenolics	mg/l	Nov-97	0.124	0.113	1.10	
		May-97	2.110	2.080	1.01	
Total Residual Chlorine	mg/l	Nov-97	1.630	1.390	1.17	
		May-97	2.750	2.630	1.05	

Note: Comment column provides evaluation of analytical performance which is based on 95 and 99% prediction interval calculated from samples analyzed by EPA and State laboratories. No comment indicates that the performance was within acceptable limits.

seems to be the most likely cause of this problem, but no attributable cause for the oil and grease data have been provided by the contractor laboratory.

10.2 The HFBR Tritium Plume Characterization Project

In December of 1996, groundwater samples taken from one of two recently installed permanent wells south of the BNL High Flux Beam Reactor (HFBR) had detectable levels of tritium (2,500

pCi/L). In January 1997, confirmatory samples from well 75-12 showed tritium at a concentration of 44,700 pCi/L, over twice the federal drinking water standard of 20,000 pCi/L. BNL implemented an intensive groundwater investigation to characterize the extent of tritium in groundwater downgradient of the HFBR. Beginning in mid-January of 1997, twenty-five temporary Geoprobe (GP) wells were installed close to the HFBR and groundwater samples taken at 5 different depths for tritium, strontium-90, gamma and gross alpha/beta analyses. The ES&HS Division's ASL performed all radiological analyses on the GP water samples, the analytical results are listed in the Operable Unit III Tritium Compilation Report (ITC, 1997).

During characterization, split groundwater samples from the 25 GP wells were sent to the USEPA's National Air and Radiation Environmental Laboratory (NAREL) in Montgomery, AL. The NAREL performed distilled tritium measurements on the GP water samples, as well as gamma analyses on select samples. The EPA measurements confirmed BNL's accuracy in performing distilled tritium analyses in groundwater using EPA Method 906.0. Figure 10-10 compares the results of 48 analyses performed at BNL's ASL with those from EPA's NAREL. Only results greater than the ASL's minimum detectable level (MDL) of 700 pCi/L are shown. Regression of the data show that the BNL tritium results were within 5% of the USEPA results, as demonstrated by the slope of 1.05. The correlation coefficient (R2) of the paired data was 0.9982. The ratios of the BNL tritium result to the EPA result were also calculated for each GP sample collected during Phase-I of the Tritium Plume Characterization Project. The mean ratio for the 48 comparisons was 0.97 $\pm$0.15, which demonstrates excellent agreement between the ASL and the U.S. EPA/NAREL. Eighty-three percent of the 48 "positive" BNL results shown in Figure 10-10 were within +20% of the U.S. USEPA measured values. This finding was noted in the February 1997 "Interim Report on the Office of Environment, Safety and Health Oversight of Groundwater Tritium Plume Recovery Activities at BNL" published by the U.S. DOE Office of Oversight.

Beginning in early February of 1997, twenty-one additional GP wells were installed at locations north and south of the HFBR to further characterize the tritium plume. In total, 46 temporary GP wells were installed. As the investigation progressed, there was a need to install wells deeper than the 100 foot depth limitation of the Geoprobe. From late February through November 1997, 77 vertical profile (VP) wells were drilled. Groundwater samples were acquired for tritium, strontium-90, gross alpha/beta and gamma measurements at 10-foot intervals to a depth of 200 feet below grade.

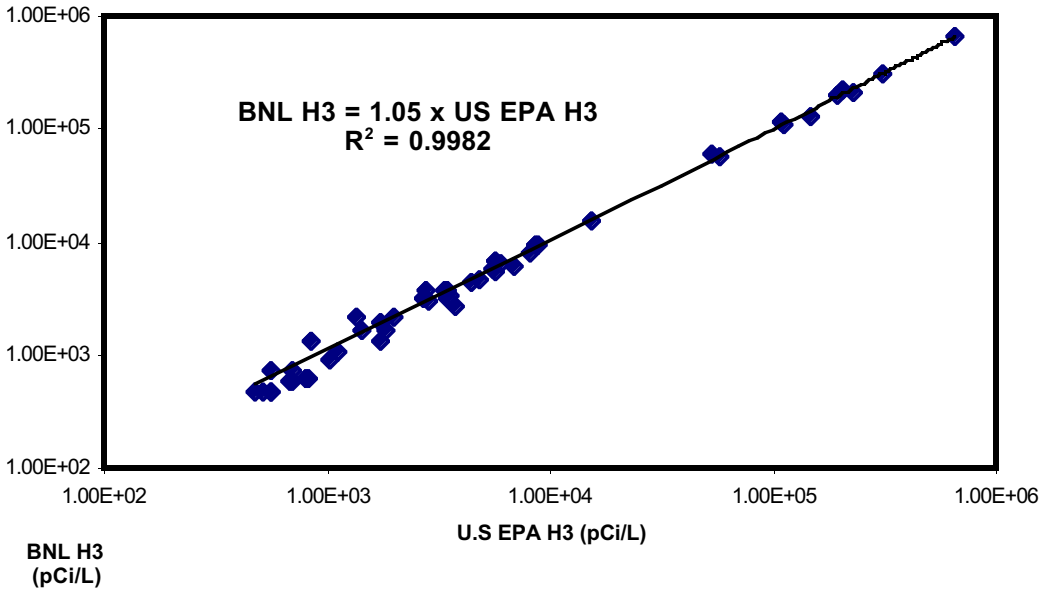

Figure 10-10. Comparison of BNL vs. U.S. EPA Tritium Results on 48 HFBR Geoprobe Water Samples: January 1997

Due to the large number of samples, ASL services were supplemented by four additional NYS Certified laboratories to perform tritium, strontium-90; gamma and gross alpha/beta analyses on the VP and GP groundwater samples, using approved USEPA methods. The laboratories were selected from their past performance in two national radiological assessment programs: (a) DOE's Environmental Measurements Laboratory (EML) QAP; and (b) the USEPA/NERL-LV Radiological Program:

(1) Data Chem Labs (DCL), Salt Lake City, UT
(2) Environmental Physics Inc. (EPI), Charleston SC
(3) IEA, Inc., Carey, NC
(4) Quanterra Lab, St. Louis, MI.

In May 1997, each of the five participating laboratories received a set of "blind" water samples containing strontium-90, gamma and gross alpha/beta activity. These quality assurance (QA) samples were prepared by the ES&HS Division's ASL using National Institute of Standards and Technology (NIST) Certified radionuclides added to Long Island tap-water. This approach established each laboratory's accuracy for radiological analyses (other than tritium) that were performed during the HFBR Plume Investigation Project. Table 10-10 shows the results of the five laboratories that performed gross alpha/beta, gamma and strontium-90 analyses on the "blind" QA tap-waters using EPA Methods 900.0, 901.0 and 905.0, respectively. With the exception of Quanterra Lab, all 5 laboratories were able to measure strontium-90, Gamma and Gross alpha/beta activity to within $\pm$25% of known activity concentrations.

Contractor Lab Tritium Analysis Accuracy

Each contractor laboratory, including the ASL, received the complete sample set for a given GP or VP location to assure data uniformity. Two QA samples were always included in every BNL shipment to a contractor laboratory: 1) a double steam-distilled deep-well water sample (American Eagle Water Co, East Orange, NJ) that served as a 'Blank'; and 2) a BNL spiked tap-water sample that contained a known amount (200,000 pCi/L) of NIST traceable tritium.

With every 40-60 samples shipped to each contractor laboratory, a BNL groundwater sample of known tritium activity concentration was also sent. This BNL groundwater was one of the 48 GP samples that had been previously measured by both BNL and the U.S. EPA in January 1997 (Figure 10-10).

Each of the three QA samples (e.g., Blank, H3-spike and BNL/EPA measured GP sample) were used to assess the contractor labs' accuracy for every batch of samples they analyzed for tritium. Batch precision was determined using the reported results of field duplicates submitted to a laboratory in each batch of samples. Table 10-11 shows the mean ratio of reported to known tritium results for each of the 4 contractor laboratories during Phase-II of the HFBR Tritium Plume Investigation Project. These data show that each laboratory was able to measure tritium activity concentrations to within $\pm$15% of "known" tritium levels. With the exception of Data Chem Lab (DCL), all "blank" samples submitted for tritium analysis were reported as < MDL. The contract with Data Chem Labs was terminated in March 1997 when it was discovered that "blank" results of 1000 pCi/L were reported by the laboratory on four consecutive occasions. Tritium results >1000 pCi/L were also reported by Data Chem Labs at VP well 094, located at the BNL south-boundary. At the request of BNL, these samples were reanalyzed and subsequently found to be non-detectable (i.e., < MDL) for tritium. A letter of retraction, claiming that tritium results for VP-094 was biased high, was received by BNL from Data Chem Labs on March 27, 1997.

Audit of the ASL

Between April 2-4, 1997, an audit of the ASL was conducted by Charles Miller of Gilbert-Hill Associates and David Baldwin of Pacific Northwest National Laboratory. The audit was requested by DOE Headquarters to assess the tritium analytical data generated during Phases I and II of the HFBR plume characterization. The final report, issued on May 7, 1997, contained 29 corrective

Table 10-10
Results of BNL Prepared Blind QA Water Samples*
Analyzed by U.S. EPA Methods May 1997

LAB		Gross Alpha (216 pCi/L)	Gross Beta (304 pCi/L)	Gamma (^{137}Cs) (459 pCi/L)	Sr-90 (297 pCi/L)
IEA					
	Result	226.3 ± 6.0	301.2 ± 4.1	502.2 ± 29.7	310.2 ± 4.3
	Ratio	1.05	0.99	1.09	1.04
EPI					
	Result	264.0 ± 18.5	286 ± 15.0	487.0± 80.0	296.0 ± 7.5
	Ratio	1.22	0.99	1.06	1.00
DCL					
	Result	220.0 ± 4.7	340.0 ± 3.8	470.0 ± 70	NR
	Ratio	1.02	1.12	1.02	
Quanterra					
	Result	228.0 ± 24.7	238.0 ± 24.2	536.5 ± 66.9	198.1± 39.0
	Ratio	1.06	0.78	1.17	0.67
BNL/ASL					
	Result	228.0 ± 30	352.0 ± 40	579 ± 60	273.4 ± 8.4
	Ratio	1.06	1.16	1.25	0.92

*NIST Certified radionuclides added to acidified (HNO_3) DI-Water.
NR means not reported by contractor lab.

Table 10-11
Accuracy of Contractor Labs Performing Distilled Tritium Analyses
in Water During Phase-II of HFBR Plume Project

Contractor Laboratory	N	Mean Ratio (± 1__ of Reported Results to Known Values	Blank Results
EPI	16	1.15 ± 0.23	All Acceptable
IEA	24	1.10 ± 0.22	All Acceptable
Quanterra	13	0.96 ± 0.15	All Acceptable
Data Chem Lab	8	0.95 ± 0.13	4 Unacceptable

N = # of "Blind" QA samples analyzed (which include Tritium Spikes and GP samples of known tritium levels)

action recommendations to improve the quality of radiological data reported by the ASL. Approximately 90% of the recommendations were accepted and were subsequently incorporated into all radiological analyses performed by the ASL. Several of the corrective actions that the ASL implemented improved quality assurance by adding spikes and spiked duplicates into each analytical batch to determine precision. Figure 10-10 shows the Relative Percent Difference (RPD) for each of the 198 analytical batches of tritium analyses performed immediately after the Gilbert-Hill Audit of the ASL. The RPD statistic is the measure of batch precision and is defined as the

difference between two tritium results (performed on spiked tap water samples) divided by the average of the two results. The acceptance criteria for batch precision is an RPD statistic < 20% for activity concentrations five times greater than the method MDL. The data in Figure 10-11 show that tritium precision was consistent for all 198 analytical batches performed by the ASL after the audit.

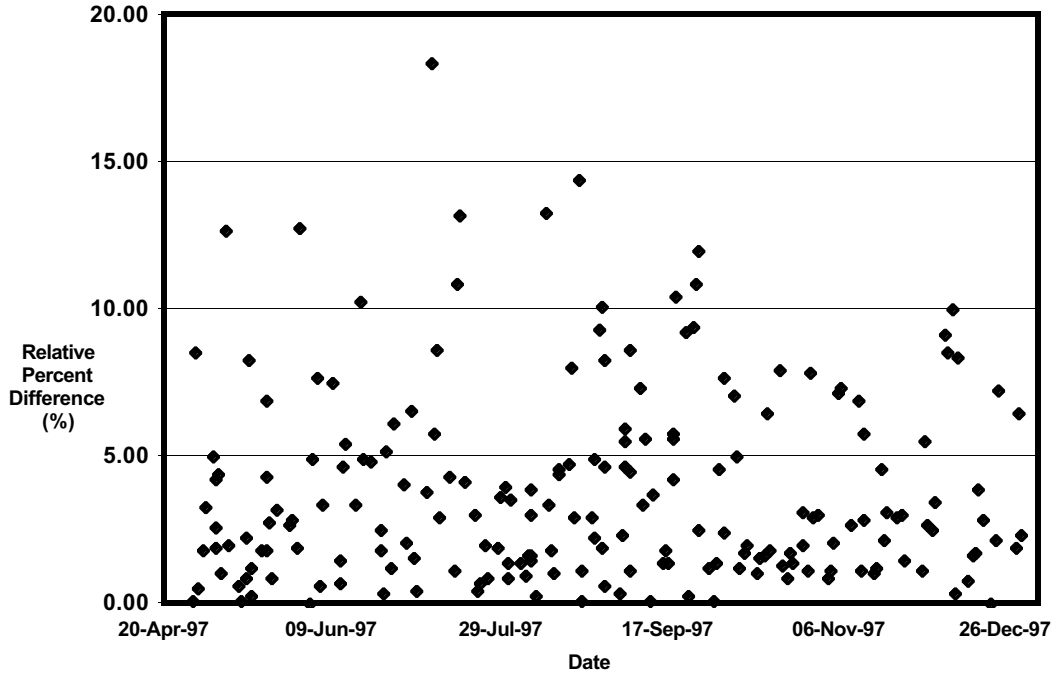

Figure 10-11. ASL Tritium Precision

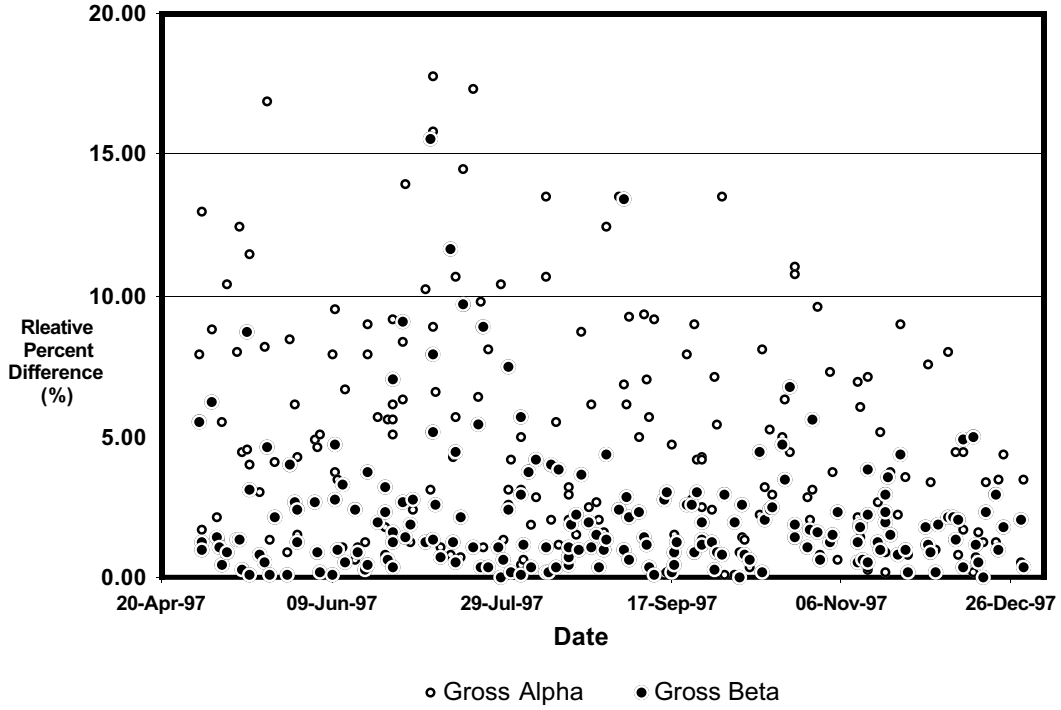

Figure 10-12. ASL Gross Alpha/Beta Precision

Gross Alpha/Beta Analyses

Figure 10-12 shows the RPD values for the 126 batches of gross alpha and beta analyses performed by the ASL after the ASL audit in April 1997. Precision was consistently below 20% during the calendar year for both ASL counting units.

In the first quarter of 1998, the ASL discovered that several carriers that hold the alpha/beta planchets in Unit 2 were slightly contaminated on the external surface. The contamination was removed and the empty carriers are each routinely background counted on a biweekly basis. The low levels of contamination would not have been discernable on the spike and spiked duplicate carrier locations used to determine gross alpha and beta precision shown in Figure 10-12. However, the low-level contamination might have affected certain environmental samples placed in contaminated carrier locations of Unit 2. A detailed review of all daily gross alpha/beta analyses performed on BNL potable water (i.e., FN and ZB) during 1997 showed a slight gradual increase in alpha/beta activity over time. Still, all FN and ZB results were below the EPA drinking water standard. Because no background checks were made on the empty carriers in 1997, some batches counted in Unit 2 might have been biased high by 20 to 25% by contamination of the planchet carriers.

In October 1997 one of the 2 Tennelec gross alpha/beta counters experienced electronic difficulties that caused a 15% drop in its efficiency. The instrument was serviced and a new power pack installed, after which the background and alpha/beta efficiencies were restored to their typical levels, as shown in Figures 10-1 and 10-2.

10.3 Quality Assurance Program for CERCLA Groundwater Monitoring Activities

This section describes the QA requirements for field activities that were conducted as part of the 1997 Environmental Restoration Division (ERD) Sitewide Groundwater Monitoring Program. The offsite contractor laboratories that perform the radiological and chemical analyses as part of this program are certified by the NYSDOH, Environmental Laboratory Approval Program (ELAP) and are required to perform all analytical work in accordance with the ERD Statement of Work for Hazardous Chemical and Radiochemical Analytical Services. In addition, contractor laboratories are audited periodically to verify their competence in analytical methodology and implementation of a comprehensive QA program.

Details for attaining QA objectives for environmental sampling and analysis programs include field quality control samples. Field blanks are collected for every 20 samples shipped to the laboratory and are used to evaluate potential cross contamination of samples due to sampling equipment. For projects with less than 20 monitoring wells, a minimum of one field blank is collected per project for each sampling event. A trip blank is also sent to the laboratory with each shipment to determine if any cross contamination occurs between aqueous samples during shipment. Blind duplicate samples are analyzed to check reproducibility of analytical data. At least five percent of the total number of samples are duplicated to evaluate the precision of the methods used. Matrix spike/matrix spike duplicates (MS/MSDs) for organic analysis are also performed.

The *Draft ERD Calendar Year 1998 Sitewide Groundwater Monitoring Program Quality Assurance Project Plan* describes the QA program and the QC requirements followed during the sitewide groundwater-sampling program. The project's organization structure, documentation requirements, sample custody requirements, acceptance criteria, and audit and corrective action provisions, and guidance on collecting of QA/QC samples are also described in this document.