Quality Assurance

9

Quality assurance is an integral part of every activity at Brookhaven National Laboratory. BNL's Quality Assurance Program ensures that all environmental monitoring data meet quality assurance and quality control requirements. Samples are collected and analyzed in accordance with standard operating procedures that are designed to ensure samples are representative and data are reliable and defensible. Quality control in the analytical laboratories is maintained through daily instrument calibration, efficiency and background checks, and testing for precision and accuracy. Data are verified and validated as required by project-specific quality objectives before they are used to support decision making.

BNL uses the on-site Analytical Services Laboratory and four off-site contractor laboratories to analyze environmental samples. All analytical laboratories are certified by New York State for the tests they perform for BNL and are subject to oversight that includes state and national performance evaluation testing, review of quality assurance programs, and audits.

The three primary laboratories reporting radiological analytical data (BNL and two off-site laboratories) each scored 90 percent or better in state and federal performance evaluation programs. BNL's overall satisfactory score in radiological testing was 97 percent, an improvement over 2001. In nonradiological performance evaluation testing under the New York State Environmental Laboratory Approval Program (potable and nonpotable water), BNL received a satisfactory rating of 96.8 percent; the two off-site contractor laboratories scored 96.8 percent and 98.7 percent.

BNL's combined score of 96.2 percent "overall satisfactory" for the 573 radiological and nonradiological performance evaluation tests carried out in 2002 is considered excellent. The multilayered components of quality assurance monitored at BNL ensure that all analytical data reported for the Site Environmental Report 2002 are reliable and of high quality.

9.1 QUALITY PROGRAM ELEMENTS

As required by DOE Order 5400.1 (1988), *General Environmental Protection Program*, BNL has established a Quality Assurance/Quality Control (QA/QC) Program to ensure that the accuracy, precision, and reliability of environmental monitoring data are consistent with the requirements of 10 CFR 830 Subpart A, "Quality Assurance Requirements," and DOE Order 414.1A (2001), "*Quality Assurance.*" Responsibility for quality at BNL starts with the Laboratory director and extends throughout the entire organization. The purpose of the BNL Quality Management (QM) System is to implement QM methodology throughout the various BNL management systems and associated processes to:

- Plan and perform BNL operations in a reliable and effective manner to minimize the impact on the environment, safety, and health of the public and staff

- Standardize processes and support continued improvement in all aspects of BNL operations
- Enable the delivery of products and services that meet or exceed our customers' requirements and expectations.

For environmental monitoring, QA is defined as an integrated system of management activities that includes planning, implementation, control, reporting, assessment, and continual improvement. Quality Control activities measure each process or service against the QA standards. QA/QC practices and procedures are documented in detail in manuals, plans, and a comprehensive set of environmental monitoring standard operating procedures, or EM-SOPs (BNL 2002). Staff who must follow these procedures and plans are required either to sign off on the SOPs or receive training.

The ultimate goal of the environmental monitoring and analysis QA/QC program is to ensure that results are representative and defensible and that data are of the type and quality needed to verify protection of the Laboratory and community environment, as well as the public and BNL employees. Figure 9-1 depicts the flow of the QA/QC elements of BNL's Environmental Monitoring Program and indicates the sections of this chapter that discuss each element in more detail.

First, BNL environmental scientists and engineers determine sampling requirements using the U.S. Environmental Protection Agency (EPA) Data Quality Objectives (or equivalent) process. During this process, the team project manager determines the type, amount, and quality of data needed to support decision making, legal requirements, stakeholder concerns, and technical information. Next, the team of scientists and engineers prepares an environmental monitoring plan or project-specific sampling plan that specifies the location, frequency, type of sample, analytical methods to be used, and a sampling schedule. These plans or the standard operating procedures also specify data acceptance criteria. Contracts with off-site analytical laboratories are established as necessary. Detailed SOPs direct sampling technicians on proper sample collection, preservation, and handling requirements. Field quality control samples are prepared as necessary. Samples are analyzed in the field or at certified laboratories in accordance with SOPs. The results are then validated or verified in accordance with published procedures. Finally, data are reviewed and evaluated by environmental professionals and management in the context of expected results, related monitoring results, historical data, and applicable regulatory requirements (e.g., drinking water standards, permit limits, etc.). Data are then used to support decision making. Data are also reported and summarized in this annual Site Environmental Report, as required. Most of the data contained in this report are condensed and summarized from a separate document, *Year 2002 ASL Quality Assurance Report* (Scarpitta and Heotis 2003).

9.2 SAMPLE COLLECTION AND HANDLING

In 2002, environmental monitoring samples were collected as specified by SOPs, the *BNL Environmental Monitoring Plan, CY 2002 Update* (BNL 2002a), and project-specific work plans, as applicable. For example, the *BNL Groundwater Monitoring Program Quality Assurance Project Plan* (BNL 1999a) describes the QA program and QC requirements followed for groundwater monitoring. This plan documents organizational structure, documentation requirements, sampling requirements, field QA/QC sample collection, acceptance criteria, sample custody requirements, data validation procedures, and general data handling/database procedures. (Since almost half of all environmental monitoring samples collected for BNL are of groundwater, this chapter uses groundwater procedures for many of the examples.)

BNL has prepared sampling SOPs for all environmental media, including groundwater, surface water, soil, sediment, air, flora, and fauna (BNL 2002b). These procedures contain detailed information on how to prepare for sample collection; what type of field equipment to use and how to calibrate it; how to properly collect, handle, and preserve samples; and how to manage any wastes generated during sampling. The procedures ensure consistency between samples collected by BNL employees or outside contractors, whether those samples are collected under the environmental restoration or environmental surveillance programs.

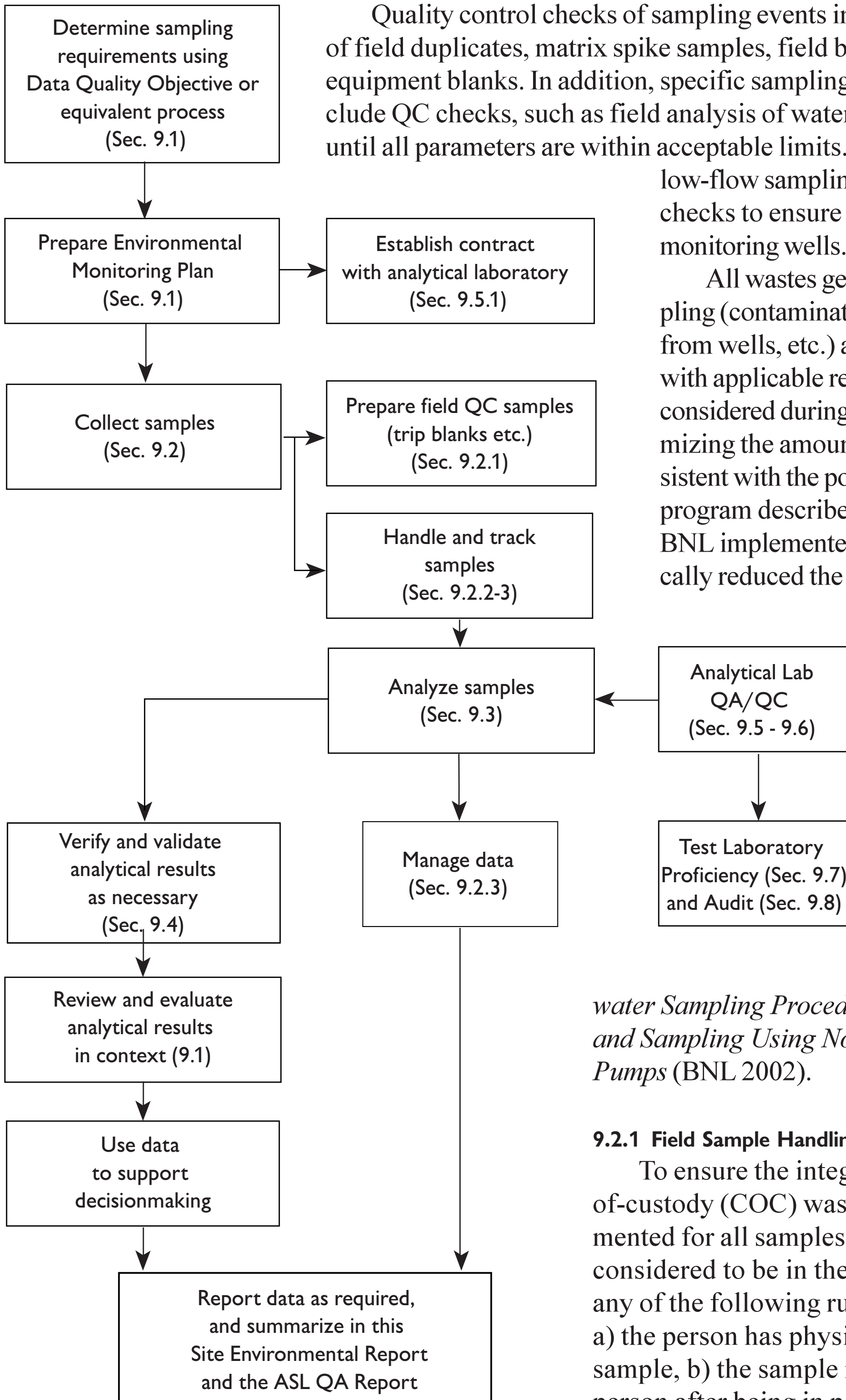

Figure 9-1. Flow of Environmental Monitoring QA/QC Program Elements.

Quality control checks of sampling events include the collection of field duplicates, matrix spike samples, field blanks, trip blanks, and equipment blanks. In addition, specific sampling methodologies include QC checks, such as field analysis of water quality parameters until all parameters are within acceptable limits. As an example, the low-flow sampling technique includes checks to ensure proper purging of the monitoring wells.

All wastes generated during sampling (contaminated equipment, purge water from wells, etc.) are managed in accordance with applicable requirements. One factor considered during sample collection is minimizing the amount of waste generated, consistent with the pollution prevention program described in Chapter 2. In the past, BNL implemented procedures that dramatically reduced the volume of wastewater that is generated when groundwater wells are sampled. These new procedures were EM-SOP-302, *Groundwater Sampling Procedure – Low Flow Purging and Sampling Using Dedicated Bladder Pumps*, and EM-SOP-307, *Groundwater Sampling Procedure – Low Flow Purging and Sampling Using Non-Dedicated Electrical Pumps* (BNL 2002).

9.2.1 Field Sample Handling

To ensure the integrity of samples, chain-of-custody (COC) was maintained and documented for all samples collected. A sample is considered to be in the custody of a person if any of the following rules of custody are met: a) the person has physical possession of the sample, b) the sample remains in view of the person after being in possession, c) the sample is placed in a secure location by the custody holder, or d) the sample is in a designated secure area. These procedures are outlined in EM-SOP-109, *Chain-of-Custody Procedure* (BNL 2002b). All environmental monitoring samples for 2002 maintained a valid COC from the time of sample collection through sample disposal.

9.2.1.1 Custody and Documentation

The field sampling team leader was responsible for the care and custody of samples until they were transferred to a receiving group or analytical laboratory. Samples requiring refrigeration were placed immediately into a refrigerator or a cooler with cooling media, and kept under custody rules. The team member who maintained custody of the samples signed the COC form when relinquishing custody. The laboratory or group receiving the samples signed the COC form when accepting custody.

The sampling team is also required to maintain field logsheets and a bound, weatherproof logbook that records sample ID, collection time, description, and collection method, as well as notes on daily weather conditions, field measurements, and other appropriate site-specific observations.

9.2.1.2 Preservation and Shipment

Samples shipped to off-site laboratories were managed as follows. Before sample collection, the team prepared all bottle labels and put them on the appropriate containers, as defined in the QA Program Plan or applicable EM-SOPs. Appropriate preservatives were added to the containers before or immediately after collection; in appropriate cases, samples were refrigerated.

Sample preservation was maintained as required throughout shipping. If samples were sent via commercial carrier, a bill-of-lading was used. COC seals were placed on the shipping containers; their intact status indicated that custody was maintained during shipment.

9.2.2 Field Quality Control Samples

Field QC samples collected for the environmental monitoring program include equipment blanks, trip blanks, field blanks, field duplicate samples, and matrix spike and matrix spike duplicate samples. The rationale for selecting specific field QC samples and minimum requirements for their use in the environmental monitoring program are provided in EM-SOP-200, *Collection and Frequency of Field Quality Control Samples* (BNL 2002b). Equipment (rinsate) blanks and trip blanks were generally collected for all media except air, soil, and flora and fauna.

An *equipment blank* is a volume of solution (in this case, laboratory-grade water) that is used to rinse a sampling tool before sample collection. The rinsate is collected to demonstrate that the sampling tool was not contaminated. Equipment blank samples were collected, as needed, to verify the effectiveness of the decontamination procedures on nondedicated or reusable sampling equipment. For the groundwater monitoring program, equipment blanks were collected from the final rinse water that was generated during decontamination.

A *trip blank* is collected with each sampling event for samples being analyzed for volatile organic compounds (VOCs). Analysis of trip blanks shows whether sample bottles were contaminated during shipment from the factory, while in bottle storage during sample collection in shipment to the laboratory, or during analysis at a lab. For the groundwater monitoring program, trip blanks consist of an aliquot of reagent-grade water sealed in a sample bottle, prepared either by the analytical laboratory prior to shipping the sample bottles to BNL or by field sampling personnel. Under the groundwater monitoring program, trip blanks were included with all shipments of aqueous samples for VOC analysis.

Field blanks were collected to check for radiological and nonradiological cross-contamination that might occur during sample collection. For the groundwater monitoring program, one field blank was collected for every twenty samples or one per sampling round, whichever was more frequent. The field blanks are analyzed for the same parameters as the groundwater samples.

Contaminants in trip, field, and equipment blanks included methylene chloride, acetone, toluene, and phthalate esters. When these contaminants were detected, validation and/or verification procedures were used, where applicable, to qualify the associated data as "nondetected," as described in procedures EM-SOP-203 through 212 (see Section 9.4). The results from blank samples collected during 2002 did not indicate any significant impact to the quality of environmental data. Typically, the only compounds detected in the blanks were toluene, chloroform, methylene chloride, and acetone. These compounds are commonly detected in blanks and do not pose significant problems with the interpretation of the analytical results because EPA has defined these analytes as common laboratory contaminants.

Field duplicate samples were analyzed to check the reproducibility of sampling and analysis. For the groundwater monitoring program, duplicates were collected for 5 percent of the total number of samples collected for a project per sampling round. There were 161 field duplicate samples collected during 2002 groundwater sampling that were all acceptable for input into the Environmental Information Management System (EIMS) database (BNL 2003). Field duplicate acceptability was based on EPA Region II guidelines (EPA 1996).

The relative percent difference between the sample and the duplicate for concentrations above the contract reporting limit is required to be below 20 percent (see Section 9.6.3 for more information on the relative percent difference statistic). Although there were several instances where individual compounds did not meet the 20 percent relative percent difference limit, the majority of parameters analyzed for those samples did meet the 20 percent requirement. This indicated that the field sampling personnel and the laboratories were performing the sample collection and analyses at a consistently high level of quality, meeting the data quality objectives.

Matrix spike and *matrix spike duplicate* analyses were performed to determine whether the sample matrix adversely affected the sample analysis. Matrix spikes are used to evaluate the effect of the sample matrix on the accuracy and precision of a specific analysis. They were performed at a rate of approximately one per 20 samples collected or per project requirements. For groundwater samples, no significant matrix effects were observed.

9.2.3 Tracking and Data Management

9.2.3.1 Sample Tracking

Environmental Monitoring Program samples and analytical results were tracked in the EIMS. Tracking began when a sample was recorded on a COC. Copies of the COC form and supplemental forms were provided to the project manager or the sample coordinator and forwarded to the data coordinator to be entered into the EIMS. Each analytical laboratory also maintains its own internal sample tracking system.

9.2.3.2 Data Management

Data management procedures are in place to govern tracking, validation, verification, and distribution of the analytical data. When samples were shipped to an analytical laboratory, COC information was entered into the EIMS. Following sample analysis, the laboratory provided the results to the project manager or designee and, when applicable, to the validation subcontractor in accordance with that laboratory's contract.

9.2.3.3 Distribution of Analytical Data

Once data were entered into the EIMS, reports were generated by one of two means. Project personnel and DOE-Brookhaven Area Office staff have a data query tool that allows access to all analytical sample results and printed reports. If a project required a special report format, the data management group was contacted to design and print it.

9.3 SAMPLE ANALYSIS

Environmental samples were analyzed either by the on-site BNL Analytical Services Laboratory (ASL) or by one of four contractors whose selection is discussed in Section 9.3.2.

All samples were analyzed according to EPA-approved methods, where such methods exist. Where no EPA-approved methods exist, standard industry methods were approved by BNL personnel. In addition, sampling technicians performed field analyses for parameters such as temperature, conductivity, pH, dissolved oxygen, and turbidity.

Samples sent off site for radiological analyses were those requiring methods (either EPA or DOE) that ASL does not perform, such as actinide analyses in soil, vegetation, animal tissue, and water. Most samples used to verify compliance with permitting requirements were sent off site, as were samples requiring semivolatile organic analysis or the toxicity characteristic leachate procedure (TCLP). In addition, when demand exceeded ASL capacity, some samples to be tested for strontium-90, metals, and polychlorinated byphenyls (PCBs) were sent to a contractor laboratory.

9.3.1 ASL Qualifications

BNL's ASL performs approximately 5,000 radiological and nonradiological (organic/inorganic) analyses per year on environmental samples to support both environmental monitoring and facility operations. The ASL is certified by the New York State Department of Health (NYSDOH) and the EPA National Environmental Laboratory Accreditation Program (NELAP) for tritium, gross alpha/beta, and gamma in potable and nonpotable water analysis in several matrices, all of which are approved EPA methods. Additional qualifications are discussed in Section 9.6.

9.3.2 Contractor Lab Qualifications

BNL procured and maintained contracts with the following off-site laboratories:

- General Engineering Lab (GEL) in Charleston, South Carolina, for radiological and nonradiological analytes
- H2M Lab in Melville, New York, for nonradiological analytes
- Severn-Trent Lab (STL) in Newburgh, New York, Connecticut, and St. Louis, Missouri, for radiological and nonradiological analytes
- Chemtex Lab in Port Arthur, Texas, for select nonradiological analytes.

The process of selecting contractor laboratories involves a number of factors: 1) their record on proficiency evaluation (PE) tests, 2) pre-selection bidding, 3) post-selection auditing, and 4) their adherence to their own QA/QC programs. Once a contract has been awarded, the laboratory must follow the QA requirements and analytical and QC requirements in the BNL Statement of Work. Routine QC procedures that labs must follow, as discussed in Section 9.5, include daily instrument calibrations, efficiency and background checks, and standard tests for precision and accuracy. All the analytical labs that BNL uses are certified by NYSDOH for the relevant analytes. The laboratories also are subject to PE testing (Section 9.7) and audits.

9.4 VERIFICATION AND VALIDATION OF ANALYTICAL RESULTS

Environmental monitoring data are subject either to data verification or data validation performed in accordance with established procedures, when the data quality objectives of the project require this step. The data verification process involves checking for common errors associated with analytical data. The following criteria cause data to be rejected during the data verification process:

- *Holding time missed* - The analysis was not initiated or the sample was not extracted within the time frame required by EPA or by the contract.
- *Incorrect test method* - The analysis was not performed according to a method required by the contract.
- *Poor recovery* - The analyte or radioisotopes added to the sample prior to laboratory processing were not recovered at the recovery ratio required by the contract.
- *Insufficient QA/QC data* - Supporting data received from the analytical laboratory were insufficient to allow validation of results.
- *Incorrect minimum detection limit (MDL)* - The laboratory reported extremely low levels of analytes as "less than minimum detectable," but the contractually required limit was not used.
- *Invalid COC* - There was a failure to maintain proper custody of samples, as documented on chain-of-custody forms.
- *Instrument failure* - The instrument did not perform correctly or was broken.
- *Preservation requirements not met* - The requirements identified by the specific analytical method were not met or properly documented.
- *Contamination of samples from outside sources* – These possible sources include sampling equipment and personnel.
- *Matrix interference* – Analysis was affected by dissolved inorganic /organic materials in the matrix.

- *Incomplete data package or report* –Some information was missing.

Data *validation* is a more exhaustive process that includes all the verification checks as well as checks for less common errors, including calibration that was not conducted as required, internal standard errors, transcription errors, and calculation errors.

The amount of data that is checked varies, depending on the environmental media and on the data quality objectives for each project. Data for some projects, such as long-term groundwater monitoring, may be verified only, not validated. Data from initial investigations receive the more rigorous validation testing, performed on 20 percent to 100 percent of the analytical results. The results of the verification and validation process are entered into the EIMS.

9.4.1 Verifying and Validating ASL Results

For samples analyzed by BNL's ASL in 2002, the QA officer or group leader verified that all analytical batches fulfilled internal QA/QC acceptance criteria. These criteria, which include precision, accuracy, recovery, instrument background checks, and stable instrument efficiency performance, are fully described in ASL's *QA Program Plan* (BNL 1999b). All QA/QC data were reviewed before ASL results were reported.

9.4.2 Verifying and Validating Off-Site Results

A subject matter expert in either radiological analyses or analytical chemistry reviewed a percentage of the 2002 results from off-site labs depending on project-specific data quality objectives. Nonradiological data analyzed off site were verified and validated using EPA Contract Laboratory Program guidelines (EPA 1992, 1996). Radiological packages were verified and validated using BNL and DOE guidance documents (BNL 1997, DOE 1994).

9.5 ANALYTICAL LABORATORY QA/QC

Sample results for environmental restoration and environmental surveillance were analyzed by the on-site ASL, or by one of the off-site contract labs: STL, GEL, Chemtex, or H2M.

For ASL analyses, procedures for calibrating instruments, analyzing samples, and assessing quality control (Appendix D) are consistent with EPA methodology. QC checks that were performed include analyzing blanks and instrument background; using Amersham Radiopharmaceutical Company or National Institute for Standards and Technology (NIST) traceable standards; and analyzing reference standards, spiked samples, and duplicate samples. The ASL supervisor, QA officer, or group leaders reviewed all ASL analytical and QA results before data were reported. More details of the ASL QA program are in Section 9.6.

Off-site contractor laboratories that perform radiological and chemical analyses for BNL also are required to maintain stringent QA programs. Their contracts specify analytes, methods, required detection limits, and deliverables—which include standard batch QA/QC performance checks. As part of the contract lab selection process, contract labs were required to provide BNL with copies of their QA/QC manuals, as well as their QA program plans.

A nonconformance report was generated when discrepancies were found in field sampling designs, documented procedures, COC, data analyses, data processing systems, QA software, or when failures in PE testing occurred. Following an investigation into the root cause, corrective actions were made and tracked to closure.

9.6 ASL INTERNAL QUALITY ASSURANCE PROGRAM

This section further describes the QA requirements for analytical activities conducted as part of the 2002 BNL Environmental Monitoring Program and the results of QA checks. ASL's nonradiological chemical group is certified by the NYSDOH Environmental Laboratory Approval Program (ELAP) to perform analyses utilizing EPA Methods 524 and 624 for volatile organic analytes, in potable and wastewaters, respectively. Thirty-seven VOCs are currently provided for analysis with Method 624 (for ground and wastewaters), an additional 26 new analytes since 1998. EPA Method 524 (for potable water) includes 63 organic analytes and was a new addition to ASL's capabilities. Metals are analyzed utilizing both atomic absorption spectroscopy and inductively coupled plasma/

mass spectroscopy by EPA methods. ASL is certified for analyses of 17 metals (the entire ELAP list) in potable water as well as 21 metals in wastewater. Certification for three anions has been established for potable and wastewaters using EPA Method 300.

In May 1999, ASL issued its own *QA Program Plan* (BNL 1999b) following EPA Region II guidelines (EPA 1998). Twenty-five internal operating procedures maintained by ASL were revised in 2001 and four were added in 2002. The QA procedures followed at ASL include daily instrument calibrations, efficiency and background checks, and routine tests for precision and accuracy. A detailed description of these activities can be found in the document titled *Year 2002 Quality Assurance Report of the Analytical Services Laboratory* (Scarpitta and Heotis 2003). A brief summary of that report is given below.

9.6.1 Radiological Instrument Calibrations

ASL operates eight high-purity germanium gamma detectors. Each detector was calibrated daily for energy and instrument efficiency using a NIST-traceable cesium-137 standard. Geometry efficiency calibrations were performed annually. Efficiency is the measure by which radiological decaying events are converted into observable counts (counts per minute). During 2002, all eight gamma detectors performed well within the EPA acceptance limit of 1 keV of the 662 keV centroid peak. One gamma detector was out of service for repair during the month of July.

ASL operates two gross alpha/beta (GAB) detectors and two liquid scintillation spectrometers for tritium analysis. Instrument background and count-time were used to determine the "minimum detection limit" (MDL) of a radiological analyte. In 2002, there was no unusual drift or variability in instrument background for alpha, beta, and tritium, based on the mean background count-rates (and one standard deviation) values. Instrument efficiencies were determined daily, using a calibration standard, and averaged for the calendar year.

9.6.2 Upgrades

In 2002, ASL made the following six upgrades and repairs:

- New Tennelec alpha/beta counter plus software upgrade - April
- Tennelec LB 5140 electronic board repair - May
- Preventative Maintenance of Liquid Scintillation Analyzer, Unit 4 - May
- Purchased Dell Optiplex GX260 WIN 2000 Pro Computer for Gamma System
- Canberra GC8021 HPGe Detector (s/n 2007029) restored - August
- GC/MS Agilent system brought on-line.

9.6.3 Accuracy and Precision

Accuracy is the percent difference between a measured value and its known (expected) value. Precision is the percent difference between two measured values. The measure of batch precision is the "relative percent difference" statistic. This is defined as the absolute difference between two results, divided by the average of both results, multiplied by 100. Typically, a radioactive tracer solution (i.e., "spike") is added to either a routine sample or tap water sample as a means of determining both precision and accuracy. In the case of nonradiological analyses, the spike is a known amount of a given analyte added to a sample and the accuracy is stated as "percent recovery": the ratio of the measured amount, divided by the known (spiked) amount, multiplied by 100.

9.6.3.1 Gross Alpha/Beta

For gross alpha/beta, the relative percent difference was determined for each batch of analyses performed. Tap water was spiked with known amounts of americium-241 (for alpha) and strontium/yttrium-90 (for beta) in order to determine batch precision. The acceptance criterion for batch precision is a relative percent difference less than 20 percent (for activity concentrations that are five times greater than the method MDL). During 2002, gross alpha/beta batch precision for all 534 batches tested was within the acceptable range; no batches were rejected.

9.6.3.2 Tritium

Tritium precision was determined for 267 batches processed in 2002. ASL utilizes three sampling protocols for differing sample volumes (i.e., 7 mL distilled, 7 mL undistilled, and 1 mL undistilled). Blind proficiency evaluation test scores for tritium were satisfactory. Two batches were rejected for tritium in 2002, corresponding to a rejection rate of 0.7 percent.

9.6.3.3 Strontium-90

The eight batches of strontium-90 processed in 2002 all met standard precision and accuracy requirements. There were two rejected batches of the eight processed, after which the batches were repeated and found acceptable.

9.6.3.4 Nonradiological Organic and Inorganic Analyses

Method precision was determined for 14 VOCs, three anions (discussed below), and 21 metals processed by ASL in 2002. With the exception of two metals, all analytes had relative percent differences within ASL's internal acceptance limit of ± 20 percent. The three standard deviation uncertainties were also within the EPA acceptance criteria.

ASL has an internal QC program for the ion chromatography, Inductively Coupled Plasma Mass Spectroscopy (ICP/MS), and atomic absorption methods used for inorganic analyses. Several QC checks were performed for each batch of metals and anions. For the 21 certified metals analyzed by ASL, beryllium and aluminum exceeded the three standard deviation EPA acceptance criteria for recovery. For these two metals, this was attributable to a single daily excursion that resulted in an overall three-sigma standard deviation value that was higher than acceptable. For this reason, analytical data for aluminum and beryllium from the months in question were "qualified" but still usable.

The ASL has an internal QC program for the gas chromatography/mass spectroscopy method used for 14 primary VOCs. Recoveries and 99 percent confidence intervals were determined for approximately 74 independent VOC batches. Average recoveries for all of the 14 analytes were within their target ranges of ± 25 percent for both EPA 524.0 and EPA 624.0 methods.

The 99 percent confidence intervals for surrogate recoveries were also determined for four analytes in 2002. The recovery for 4-bromofluorobenzene, toluene, and dibromofluoromethane were within three-sigma acceptance criteria. All surrogate recoveries were within EPA acceptance limits.

9.7 PROFICIENCY EVALUATION TESTING

As in prior years, ASL and three contractor laboratories (GEL, STL, and H2M) participated in several national and state proficiency evaluation (PE) testing programs. Results of those PE tests provide information on the quality of a laboratory's analytical capabilities.

During 2002, ASL, GEL, STL, and H2M participated in either the NYSDOH ELAP (for radiological and nonradiological PE testing) or the DOE Environmental Measurements Laboratory (EML) Quality Assessment Program (for radiological PE testing only). Both H2M and STL also participated in the Analytical Products Group (APG) PE Testing program. All laboratories participated in at least one proficiency evaluation program, although several labs participated in multiple programs. The results from these blind, independent tests are discussed in Section 9.7.1.

Effective December 21, 1998, EPA terminated its PE programs for both radiological and nonradiological analytes. To replace that program, ASL, GEL and STL chose Environmental Resource Associates (ERA) private, independent PE programs. H2M participates in both the ERA and APG programs.

PE test data are not presented in this report for the fourth contractor, Chemtex Laboratory, because there is no ERA or NYSDOH PE testing program for the specific analytes analyzed by this laboratory. Chemtex performed three chemical analyses for BNL on the following analytes: tolytriazole, polypropylene-glycol-monobutyl-ether, and 1,1-hydroxyethylidene-diphosphonic acid.

9.7.1 Summary of Test Results

Figures 9-2 and 9-3 summarize the 2002 scores of BNL's ASL and the three contractor laboratories that participated in the mandatory DOE EML program (for radiological analytes only) and the NYSDOH ELAP, as well as the voluntary ERA program. The bar graphs of

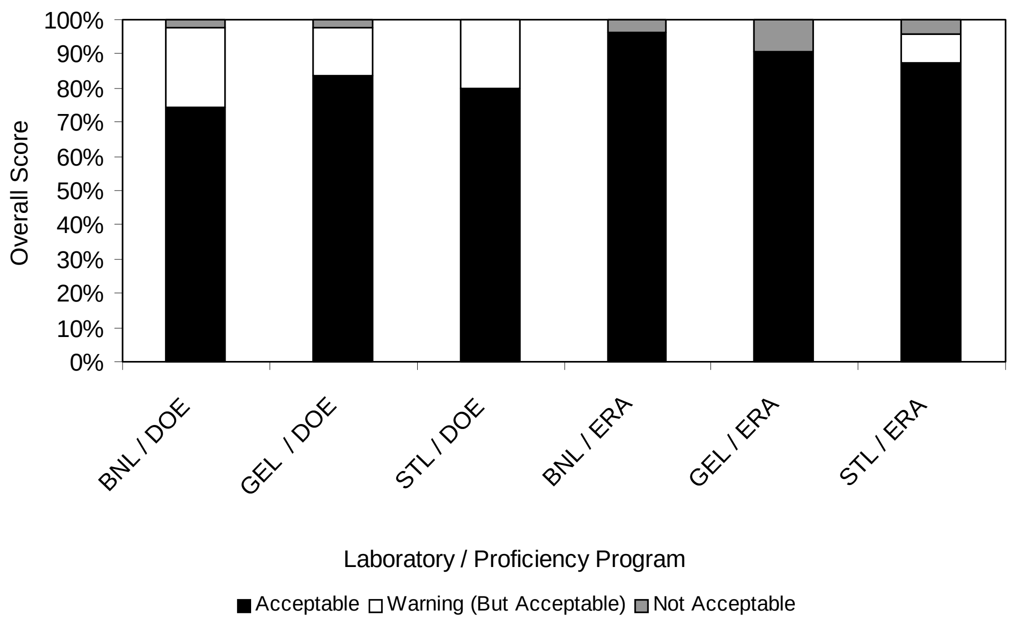

Figure 9-2. Radiological Proficiency Evaluation Scores in U.S. DOE and ERA Programs.

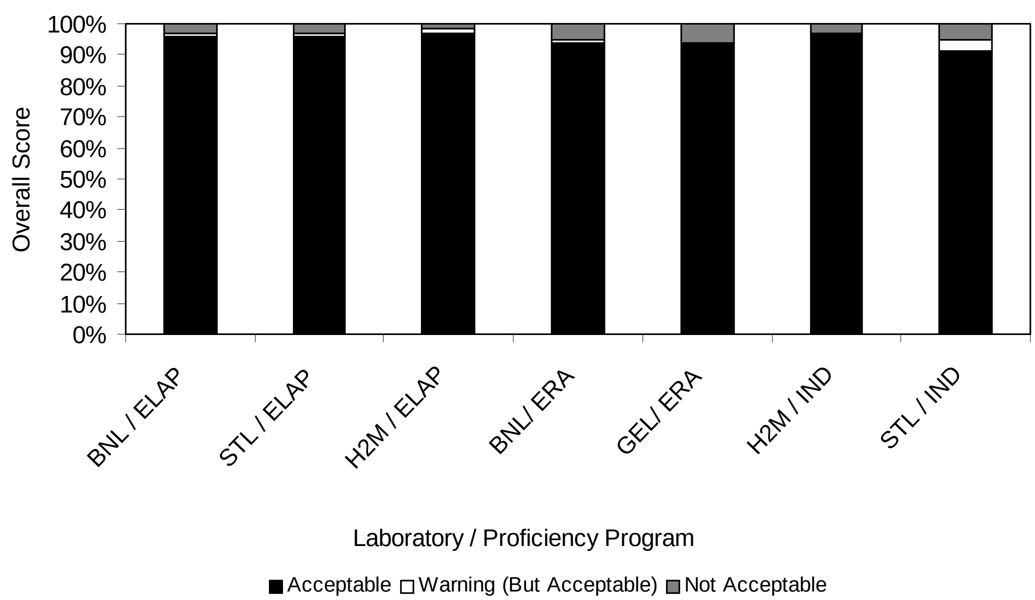

Figure 9-3. Nonradiological Proficiency Evaluation Scores in ELAP, ERA, and Independent Programs.

Figures 9-2 and 9-3 summarize all tabulated radiological and nonradiological results (as percentage scores) that were "Acceptable," "Warning (But Acceptable)," or "Not Acceptable," for each analytical laboratory, by PE test program. A Warning is considered "Satisfactory," being within two and three standard deviations of the target value. (An Overall Satisfactory score is the sum of results rated as Acceptable and those rated as Warning, divided by the total number of results reported.) A Not Acceptable rating reflects a result that is greater than three standard deviations of the target value. Tabulated results are presented in the ASL's *2002 Annual QA Report* (Scarpitta and Heotis, 2003).

During 2002, the NYSDOH ELAP did not provide radiological samples for PE testing. The ASL's Overall Satisfactory score on radiological

PE tests in ERA and mandatory DOE EML radiological program was 96.2 percent, whereas BNL's off-site contractor laboratories, GEL and STL, scored 97.8 percent and 100 percent, respectively. In the voluntary ERA radiological program, BNL, STL, and GEL achieved scores of 96.4 percent, 95.8 percent and 90.5 percent, respectively.

For nonradiological results, the Overall Satisfactory results ranged from 94.7 percent to 98.7 percent for BNL, H2M, GEL, and STL in the ERA, APG, and NYSDOH testing programs.

BNL's combined score of 96.2 percent Overall Satisfactory on the 573 radiological and nonradiological PE tests performed in 2002 is considered excellent.

9.7.2 Radiological Assessments

Both ASL and GEL participated in the DOE EML Quality Assessment Program and the ERA radiological program. Results are discussed below.

9.7.2.1 EML Radiological Results

Overall, ASL's performance in the EML program was Satisfactory in 97.7 percent of the analyses performed on four matrices (air, vegetation, water, and soil). Thirty-two of 43 analyses (74.4 percent) were within established DOE EML limits, showing acceptable agreement with the known value. Ten results (23.3 percent) were within warning limits, also earning Satisfactory status. One analysis (2.3 percent) exceeded the acceptance limits, as shown in Figure 9-2.

Figure 9-2 also presents GEL's performance, which was Satisfactory (acceptable or within warning limits) in 97.8 percent of the analyses performed on the four matrices (air, vegetation, water, and soil). Seventy-seven of 92 analyses (83.7 percent) were within EML's acceptance limit; 13 of 92 analyses (14.1 percent) were within upper and lower warning limits, demonstrating satisfactory agreement; two analyses exceeded the acceptance limits.

STL participated in the EML program, with 72 analyses of 90 found acceptable (80 percent) and 18 within warning limits (20 percent). This corresponds to an overall passing score of 100 percent.

9.7.2.2 ELAP Radiological Results

There were no samples provided by the NYSDOH ELAP for radiological testing in 2002.

9.7.2.3 ERA Radiological Results

ASL, STL, and GEL participated in the ERA radiological performance evaluation studies. ASL's overall score for the 28 results reported in 2002 was 96.4 percent, with one unacceptable gamma result (cesium-137). GEL's overall score in the ERA radiological PE studies was 90.5 percent, whereas STL's overall score was 95.8 percent.

9.7.3 Nonradiological Assessments

During 2002, ASL, GEL, STL, and H2M participated in the NYSDOH ELAP, which certifies laboratories that test for nonpotable water, potable water, and solid wastes. Note that STL has three labs: one in Missouri, one in Connecticut, and one in New York. Although participation in the ERA water supply and water pollution studies is not required for New York State certification, ASL and GEL also participated in the ERA evaluation. These results are summarized in Figure 9-3.

9.7.3.1 ELAP Nonpotable Water Results

Of the 121 results reported for ASL, there were five Not Acceptables, earning ASL an Overall Satisfactory score of 95.9 percent. GEL did not participate in ELAP because they are NELAP Certified. H2M reported 587 results, with eight Not Acceptables, scoring 99.5 percent. STL's three labs reported 1,315 results and scored 97.5 percent.

9.7.3.2 ELAP Solid and Hazardous Waste Chemistry

ASL scored 100 percent in this category for the 14 results reported for the NYSDOH ELAP Solid and Hazardous Waste Chemistry Proficiency Program.

9.7.3.3 ELAP Potable Water Results

In the potable water category of the NYSDOH ELAP, BNL's ASL reported 143 results with four Not Acceptables, earning an Overall Satisfactory score of 97.2 percent. H2M reported 256 results with seven Not

Acceptables, generating a score of 97.3 percent. STL's three labs reported 748 results with 31 Not Acceptables, earning a score of 95.9 percent.

9.7.3.4 Voluntary PE Studies

GEL and Brookhaven's ASL participated in the voluntary ERA water pollution and water supply performance evaluation studies. For these studies combined, ASL reported 224 results: 210 Acceptables, three within Warning limits, and 11 Not Acceptables. The Overall Satisfactory score for ASL in ERA's water supply and water pollution studies was 95.1 percent. GEL reported 735 results, with 687 Acceptables, two Check for Errors, and 46 Not Acceptables. GEL's score in these voluntary PE studies was 93.7 percent.

STL (St. Louis and Connecticut) and H2M Labs participated in the Analytical Products Group (APG) and ERA PE Testing programs. Results in these two independent programs are labeled as "IND" on the bar graph in Figure 9-3 for these two laboratories. STL's overall passing score was 94.7 percent, whereas H2M's overall passing score was 96.8 percent.

9.8 AUDITS

In addition to PE testing, BNL conducts a program of internal and external audits to verify the effectiveness of the environmental sampling, analysis, and database activities. Contractor laboratories are subject to audits by BNL personnel at the time of contract renewal. To verify competence in analytical methodology and implementation of a comprehensive QA program, the contractor laboratories are also audited periodically by the ASL, the Quality Programs and Services Office, or the Environmental Restoration Program staff. There were no audits performed for off-site laboratories that reported data in this SER, since they were still under the last year of a three-year contract.

9.9 BNL DEER INVESTIGATION

In April 2002, a positive bias was found in one of eight gamma detectors used to measure ^{137}Cs in deer meat. Details are presented in an ASL technical paper (ASL 2002) titled "*Positive Bias in One of Eight HPGe Detectors Used to Measure ^{137}Cs in Deer at Brookhaven National Laboratory.*" A summary is provided below.

One of eight BNL High Purity Germanium (HPGe) gamma detectors was found to give a factor of 2.5 (high) bias in cesium-137 measurements for a road-killed deer in the vicinity of the lab. The initial cesium-137 deer activity concentration was 21 pCi/g (wet weight), with an MDL of 0.03 pCi/g. Blind recounts of the original sample yielded the same result for two separate measurements made on the same detector. Results were reported to the Suffolk County Department of Health Services (SCDHS), NYSDEC, and EPA, and disseminated to the public.

Because the BNL-reported activity concentration exceeded the NYSDEC threshold for cesium-137 in deer (6.7 pCi/g wet weight), the NYSDOH then received and analyzed a portion of the same sample. Their results indicated a cesium-137 concentration of just 8.4 pCi/g (wet weight).

After a DOE Occurrence Report was filed, an internal assessment was conducted at BNL with the following findings (1 through 5) and recommendations (6 and 7) for enhancing the Deer Program:

1. BNL's on-site laboratory, the ASL, is NY State and US EPA NELAP Certified.
2. All SOPs were properly followed and samples were not routinely spiked.
3. Gamma Proficiency Testing Scores in the NYS DOH ELAP, U.S. DOE/EML QAP, and Environmental Resource Associates programs were excellent in 2001.
4. The suspect detector is a 10-year-old "top-looker" that differs from the other state-of-the-art detectors, which are "bottom lookers."
5. For solid matrices, the eight ASL gamma detectors were geometry-calibrated using standard 300 mL aluminum cans filled with either 100 or 200 grams of a NIST traceable *soil*-equivalent resin material following EML-HASL 300 procedures. For the suspect detector, the difference in density between the soil calibration matrix (1.2/pCi/g) and actual deer sample (0.7/pCi/g) caused a factor of 2.5 high bias because there was a 1-inch air space in the 300 mL soil calibration geometry can (half-filled with 200 gm

material), but not in the 300 mL deer sample can (fully packed with 200 gm of material). This air space was not a factor in cesium-137 results obtained after later counting the deer sample using the other ASL soil-calibrated detectors.

6. Program enhancements would include recalibrating the eight detectors using sealed 300 mL cans containing 100 and 200 grams of a commercially available NIST traceable *deer*-equivalent resin material spiked with cesium-137 (and other gamma-emitters).
7. Additional QA/QC would include using an Environmental Measurements Laboratory Quality Assurance Program vegetation sample, containing known amounts of cesium-137 and K-40, as a standard reference material. This sample would be counted weekly on all detectors to obtain estimates of precision and accuracy in lieu of spiking samples.

In summary, ASL internal QC checks on instrument performance indicated that all detectors were within EPA acceptance criteria for energy calibration. Blind PE testing scores in EML and ERA Programs in 2001 showed that ASL can accurately measure cesium-137 (and other gamma emitters) in a variety of matrices. The re-count of the suspect deer sample at BNL in July 2002, using all gamma detectors recalibrated with a deer-equivalent spiked resin material, showed statistically equivalent results compared to NYSDOH measurements performed in March 2002.

9.10 CONCLUSIONS

Detailed data on quality control results for all analyses conducted at BNL's ASL are presented in ASL's *Year 2002 QA Report* (Scarpitta and Heotis 2003). That report presents tables and figures depicting instrument calibration, efficiency, background checks, precision, and accuracy testing. Overall, QC checks were consistently within the EPA guidelines of ± 20 percent.

Detailed data on external performance evaluation testing for the ASL and the three BNL contractor laboratories are also presented in the *Year 2002 QA Report*. Overall, the three laboratories reporting radiological analytical data in the *Site Environmental Report 2002* (ASL, STL, and GEL) each had combined satisfactory results of 95 percent or better in both state and federal performance evaluation programs. For nonradiological performance evaluation testing, ASL and the three BNL contractor laboratories (H2M, GEL, and STL) all scored better than 95 percent in the NYSDOH ELAP evaluations. BNL's combined Overall Satisfactory score of 96.2 percent on the 573 radiological and nonradiological PE tests performed in 2002 is considered excellent.

Based on implementation and evaluation of the QA/QC program, it can be concluded that the analytical data reported in the *Site Environmental Report 2002* are reliable and of high quality.

REFERENCES AND BIBLIOGRAPHY

10 CFR 830 Subpart A. 2000. U.S. Department of Energy. "Quality Assurance Requirements." *U.S. Code of Federal Regulations.*

ASL 2002. *Positive Bias in One of Eight HPGe Detectors Used to Measure ^{137}Cs in Deer at Brookhaven National Laboratory*. Scarpitta, S.C., Gaschott, R. and P. Heotis, Brookhaven National Lab, Upton NY. ASL-2002 Tech Report, Rev. 02, June 2002.

BNL. 1997. *Radiochemical Data Validation Standard Operating Procedure*. Brookhaven National Laboratory, Upton, NY.

BNL. 1998. *Natural Attenuation Monitoring Work Plan for the HFBR Tritium Plume*. Brookhaven National Laboratory, Upton, NY. December 1998.

BNL. 1999a. *BNL Groundwater Monitoring Program Quality Assurance Project Plan (QAPP)*. Brookhaven National Laboratory, Upton, NY. August 31, 1999.

BNL. 1999b. *Quality Assurance Program Plan: Analysis of Radionuclides and Hazardous Chemicals at Brookhaven National Laboratory*. BNL-RCD/ASL-99-01. Radiological Control Division/ Analytical Services Laboratory, Brookhaven National Laboratory, Upton, NY.

BNL. 2002a. *Brookhaven National Laboratory Environmental Monitoring Plan, 2002 Update*. BNL-52584. Brookhaven National Laboratory, Upton, NY. January 2002.

BNL. 2002b. *Environmental Monitoring Standard Operating Procedures*. Brookhaven National Laboratory, Upton, NY.

BNL. 2003. *BNL 2002 Groundwater Status Report*. Brookhaven National Laboratory, Upton, NY. June 2003.

DOE. 1994. *RD-4 Guidance for Radiochemical Data Validation*. Draft. Report EM-73. U.S. Department of Energy, Washington, DC.

DOE Order 414.1A. 2001. *Quality Assurance*. U.S. Department of Energy, Washington, D.C. November 24, 1998.

DOE Order 5400.1. 1988. *General Environmental Protection Program*. U.S. Department of Energy, Washington, DC. Change 1: 6-29-90.

EPA. 1992. *Evaluation of Metals Data for the Contract Laboratory Program*. EPA Region-II SOP HW-2. U.S. Environmental Protection Agency, Washington, DC.

EPA. 1996. *CLP Organic Data Review and Preliminary Review.* EPA Region II, SOP HW-6. U.S. Environmental Protection Agency, Washington, DC.

EPA. 1998. *EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations.* Report QA/R-5. US Environmental Protection Agency, Washington, DC.

Scarpitta, S., and Heotis, P. 2002. *Year 2002 Quality Assurance Report of the Analytical Services Laboratory*. RCD-ASL-QA Report 2002, Rev-4. Radiation Control Division, Brookhaven National Laboratory, Upton, NY. May 2003.