APPENDIX E
SAMPLE COLLECTION, TRACKING, AND QA/QC RESULTS

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1.0 GROUNDWATER SAMPLING

This section describes the tracking system, quality assurance, and quality control (QA/QC) for samples collected for the CERCLA and Facility Monitoring (FM) Groundwater Monitoring Programs, and contains the procedures used to collect groundwater samples from monitoring wells. QA/QC issues and the procedures for collecting groundwater samples were formalized during 1999 into BNL Standard Operating Procedures (SOPs). The SOPs are updated on a 5 year schedule. These SOPs will be discussed in the appropriate sections below.

1.1 Sample Collection

Groundwater samples were collected during CY 2016 by the BNL Field Sampling Team for the Facility Monitoring (FM) program and treatment system samples and by R&C Formation, LTD for the Groundwater Protection Group (GPG) groundwater sampling program.

Monitoring well groundwater samples are collected from dedicated bladder pumps using a low flow purge technique. BNL EM-SOP-302, Low Purge Sampling of Monitoring Wells Using Dedicated Pumps, was followed by field personnel collecting groundwater samples from wells with dedicated pumps installed. A minimum of two times the volume of the sample pump and tubing are purged prior to the sampling of the well. Samples are collected once water quality parameters (pH, specific conductance and dissolved oxygen) stabilize or when an amount of groundwater equal to 25 percent of a casing volume has been purged. Depending on the parameter, purge flow rates are adjusted to approximately 100 milliliters per minute for sample collection. A typical low flow sampling produces 1.5 to 5 gallons of purge water waste per sampling event as compared to 25 to 200 gallons of purge water waste using the three purge volume technique.

The collection of groundwater samples from temporary wells is dependent on the drilling method used. When using an auger rig, hollow stem augers are advanced to the deepest sampling interval. A stainless steel well screen is connected to two-inch diameter steel well pipe and lowered through the center of the augers to the required sampling depth. The augers are then withdrawn above the well screen. A submersible pump is lowered to the well screen and three well volumes of groundwater are purged prior to sampling. Groundwater samples are collected from the operating pump discharge tubing into laboratory-supplied bottles and preserved

according to analysis requirements. This procedure is repeated at each depth interval required by the work plan.

When collecting groundwater samples via a Geoprobe , a screen is placed inside a sampler sheath and a expendable drive point is attached to the bottom of the sheath and then threaded onto a steel rod. . The probe is advanced to the deepest sample collection level and the screen is released using a trip rod. A length of Zelite™ (or equivalent) tubing sized to fit inside the probe rods is attached to a check valve. The check valve and tubing are sent down the probe rod until they reach the bottom of the screen, and then withdrawn 12 inches. An inertial pump (e.g., Waterra) is used to purge the Geoprobe well. Three casing volumes of groundwater are typically removed prior to sampling. Samples are collected with the inertial pump running continuously.

Purge water from groundwater samples is disposed of by one of three methods as described in BNL EM-SOP-802, Well Development, Purge and Decontamination Water Handling Procedure. If the groundwater does not contain any analytes above action levels, NYSDEC and Federal drinking water standards and DOE groundwater screening levels, the purge water is discharged to the ground surface approximately 20 feet down gradient from the wellhead. If the groundwater contains chemical analytes above action levels but no radiological parameters above action levels, the purge water is run through activated carbon and discharged at least 20 feet downgradient of the wellhead. Purge water which contains radiological parameters above action levels is containerized and disposed of off-site in accordance with all local, state, and federal regulations.

1.1.1 Decontamination

All groundwater sampling equipment is dedicated to each well, and was decontaminated by the manufacturer. No additional decontamination is required.

1.2 Sample Tracking System

Samples are tracked using the Environmental Information Management System (EIMS). Tracking is started when a sample is recorded on a chain-of-custody form. Sampling personnel submit these forms to the sampling coordinator, and the information is entered into the EIMS.

1.2.1 Sample Identification

Samples were identified using a code consisting of the chain-of-custody (COC) number and the unique ID number. This ID is written on the sampling logs along with the BNL well ID. BNL well IDs also were placed on the COC forms in the Site ID column. QA/QC samples are identified in the same manner as environmental samples. The blind duplicate samples were recorded as BD in the sample ID column of the COC. Supplemental forms are used by field sampling personnel to distinguish information about the QC samples, such as blind duplicate IDs and associated field and trip blanks. BNL EM-SOP-102 details BNL's Chain of Custody Procedure. COC records are filed at BNL and are available for review.

1.2.2 Sample Tracking

Copies of the COC forms are provided weekly to the sampling coordinator to enter into the EIMS. The status of each sample is updated when

1. The sample is assigned to a Sample Delivery Group (SDG) and the analytical laboratory communicates this information to the Sampling Coordinator;

2. The Project Manager receives and approves the hard copy with the results of the sample analysis;

3. The Electronic Data Deliverable (EDD) analytical results are received and entered into the EIMS;

4. The Project Manager receives and approves of the hard copy of the data validation package (when applicable);

5. The results of the EDD data-validation results are received and entered (when applicable) into the EIMS.

1.2.3 Sample Packaging and Shipping

Samples that are shipped to external contractor laboratories are packaged by placing each sample bottle inside a plastic bag and sealing it. The bottles with VOC samples are placed in protective cans with foam inserts. Glass bottles are wrapped with protective packaging to protect against breakage during shipment. Plastic bags are filled with ice and sealed, or blue-ice containers are

placed inside each cooler with the samples to ensure that they arrive at the analytical laboratory at four degrees Celsius (plus or minus two degrees). A BNL chain-of-custody form completed by the sampling team accompanies the samples to the laboratory. The form is placed in a plastic bag, sealed, and put inside the cooler with the samples. The analytical samples are shipped to the analytical laboratory via an overnight mail carrier. Samples that are transported to the BNL ASL for analyses are treated in much the same way, except that the packaging requirements to protect against breakage during shipment are less critical.

1.2.4 Sample Documentation

The sample teams maintain field notebooks (bound weatherproof logbooks) that are filled out at the location where the sample is collected. They contain the sample's designation, collection time, description, collection method, and the weather conditions, field measurements, and other site-specific observations.

The sample teams also complete collection logs for every sample that is collected. The completed sample-collection logs are submitted to the sample coordinator each week.

1.3 Analytical Methods

The following sections describe the analytical methods used for the BNL Groundwater Monitoring Program.

1.3.1 Chemical Analytical Methods

The CERCLA and FM samples collected during CY 2016 were analyzed by organic, inorganic, and various wet-chemical methods. FM and CERCLA chemical analyses were performed by GEL Laboratories, and Test America. Table 1-5 summarizes the analytes and/or methods used for specific CERCLA monitoring programs and samples. Table 1-6 summarizes this information for the FM program.

The following inorganic, organic, and wet chemical methods were used: United States Environmental Protection Agency (USEPA) methods including 200 and 500 Series methods (40 Code of Federal Regulations (CFR) 141); 600 Series methods (40 CFR 136); and SW-846 methods (40 CFR 261). Other standard methods include those listed in *Standard Methods for the*

Analysis of Wastewater (latest edition) and those in the American Society for Testing and Materials (ASTM) publications (latest revision).

1.3.2 Radiological Analytical Methods

Unlike organic and inorganic chemical analytical methods, few standard methods are available for the radiological analysis of environmental samples. There are no standard established QA/QC requirements and acceptance criteria for environmental radiological methods; therefore, different USEPA, U.S. Department of Energy (DOE), and commercial laboratories may have different methods of preparing samples preparing and analytical techniques for specific radiological analytes. Hence, laboratory-reported detection limits may vary. Nonetheless, multi-laboratory validation studies and inter-laboratory comparisons have demonstrated that accurate, comparable, radiological data are obtainable even when different procedures are used.

Tables 1-5 and 1-6 provide the analytical parameters and/or methods used for specific monitoring programs and samples. Radiological analyses were undertaken for onsite and offsite locations. The radiological analyses enable BNL to monitor radiological water-quality status throughout the site.

1.4 Quality Assurance and Quality Control

This section describes the QA/QC requirements for field work conducted under the CERCLA and FM Groundwater Monitoring Programs. In general, the quality of the analytical results from groundwater samples collected during CY 2016 met data quality objectives.

1.4.1 Calibration and Preventive Maintenance of Field Instruments

Sampling team personnel are responsible for assuring that a master calibration/maintenance log is maintained for each field-measuring device (i.e., pH, conductivity, turbidity meters, etc.). The sample coordinator provides a calibration/maintenance logbook for equipment supplied to contracted sampling teams.

1.4.2 QA/QC Sample Collection

Guidance on collecting the QA/QC samples is given in *BNL EM-SOP-200 "Collection and Frequency of Field Quality Control Samples."* Sample-specific requirements are listed separately, below.

The collection of QA/QC samples is dependent on the data quality objectives of each project. The following is a general breakdown of the QA/QC samples collected by project type:

CERCLA Groundwater Monitoring: trip blanks, field blanks, equipment blanks, matrix spike/matrix spike duplicates (MS/MSDs), and blind duplicates.

Remediation Treatment System Sampling: trip blanks.

FM Groundwater Monitoring: trip blanks, field blanks, equipment blanks, and blind duplicates.

1.4.2.1 Equipment Blanks

Equipment blanks are collected to evaluate any potential cross-contamination of samples due to the sampling equipment. They are collected by pouring laboratory grade water over the sampling equipment which comes in contact to the groundwater sample. Equipment blanks are only collected for projects that require the use on non-dedicated sampling equipment. The frequency of collecting equipment blanks is one for every 20 groundwater samples shipped to the analytical laboratory. Since only dedicated sampling equipment was used during 2016, no equipment blanks were collected.

1.4.2.2 Field Blanks

Field blanks are obtained by pouring laboratory grade water into clean sample bottles containing preservatives. The field blanks are collected in the field and accompany field personnel to the sampling location. They are analyzed for the same parameters that the groundwater is being analyzed for on that day. The frequency of collecting equipment blanks is one for every 20 groundwater samples shipped to the analytical laboratory. For projects with less than 20 monitoring wells, a minimum of one field blank is collected per project for each sampling event. Field blank results are summarized on Table E-1. The most common constituent detected was chloroform which was detected in 5 of the 37 field blanks collected for VOCs. The highest concentration of any organic compound was di-n-butyl phthalate detected at 0.73 µg/L. Chloroform is often found as a byproduct of using hydrochloric acid as a preservative.

1.4.2.3 Trip Blanks

A trip blank is an aliquot of deionized water that is sealed in a sample bottle (glass vials (40 ml) with Teflon septa). It is used to determine if there is any cross-contamination between aqueous samples during shipment. Trip blanks are analyzed for aqueous VOCs only. A trip blank is shipped to the analytical laboratory with each set of samples submitted for VOC analyses. Upon arrival at BNL, the sealed trip blank bottles are placed in a cooler and brought to the field by the sampling team. If several coolers are required, each cooler must contain an individual trip blank. Trip blank detections are summarized on Table E-2. 107 trip blanks were collected in 2016. The constituent detected most frequently was chloroform which was detected in 23 times. The maximum concentration of chloroform was 0.25 µg/L. .

1.4.2.4 Duplicate Samples

Field duplicate samples are analyzed to check the reproducibility of the laboratory's analytical results. Duplicates are either blind (the laboratory doesn't know the identity of the sample location) or field (the laboratory is told the identity of the sampling location). The specific type of duplicate used on a project is dependent on the project data quality objectives. At least 5 percent (one out of every 20 samples) of the total number of collected groundwater samples are duplicated to evaluate the precision of the methods. For projects with less than 20 monitoring wells, a minimum of one blind duplicate sample is collected per project for each sampling event. USEPA Region II USEPA Region II data validation criteria were used for field duplicate interpretation. For detects above 5 times the contract required detection limit (CRDL), a relative percent difference (RPD) was calculated. An acceptable RPD was 50% or below. For detects below 5 times the CRDL, the QC requirement is that the difference between the duplicate results must be less than or equal to the CRDL. A total of 33 duplicate samples were collected for non-radiological analyses and 21 duplicates were collected for radiologic analyses. Not all parameters were analyzed in every duplicate. The parameters in each duplicate were consistent with those required for the specific program the duplicate was monitoring. Of the 2,047 parameters analyzed, only 13 (0.63%) of the non-radiologic analyses failed to meet QA criteria. For the radiologic parameters only 2 of the 98 parameters (2%) failed to meet QA criteria. The results are indicative of consistency with the laboratory and sampling team that is resulting in valid, reproducible data.

1.4.2.5 Requirements for Matrix Spike/Matrix Spike Duplicate Volumes

MS/MSDs for organic analysis are performed at a frequency of one MS/MSD for every 20 groundwater samples in an SDG. Reanalysis may be necessary in certain situations. To ensure that the laboratory has sufficient volume for MS/MSD analysis, triple the sample volume must be collected.

1.4.3 Data Verification

There are two stages of data verification. One stage consists of reviewing the latest data in comparison to historical data generated at the sampling site. All groundwater data collected at BNL undergoes this type of verification. The other stage is formal, documented, data verification. The procedures for the formal data verification are given in BNL EM-SOP-203, Chemical Data Verification and BNL EM-SOP-204, Radiochemical Data Verification. This is BNL's internal process to verify the accuracy and/or completeness of analytical data.

The decision to perform a formal verification is based on the data quality objectives of the specific projects. Data generated under of the CERCLA Groundwater Monitoring Program that were not validated underwent data verification. FM data and treatment system data do not undergo formal verification, but are compared to known baseline data. Therefore, the FM and treatment system analytical data only require a historical review. If the comparison of historical data to new data indicates an inconsistency with the expected results, a further review is conducted which may include, formal data verification, data validation, and/or a data usability review.

The formal data verification process is designed to detect the most common analytical problems that affect the quality of the results. To accomplish this task, QA/QC items such as the following are checked: holding times; matrix spikes; laboratory and field blanks; and, field logs. If items are detected that can affect the use of the data, they are either corrected, as in the case of unintelligible information on the field logs, or the data is qualified, as in the case of blank contamination or holding time violations.

1.4.4 Data Usability

Data usability is the process by which data that does not meet the expected results, but which has been deemed acceptable by a data validation or verification, is reviewed.

Determining the usability of chemical data is relatively straightforward. Laboratory analytical data are validated or verified, and validation qualifiers are assigned to them. Table E-3 defines the qualifiers placed on the data by the analytical laboratory and Table E-4 defines the data validation, verification, and usability qualifiers.

The usability of radiological data for the 2016 data was determined through a two-step process. The project manager initially reviewed all groundwater monitoring data. Data were considered acceptable for use if they were not significantly different than expected for a particular well, based on historical trends and were not qualified as unusable during the validation and/or verification procedures. Results for a particular well that were not expected, based on historical trends, were referred to the EPD radiochemist. The data then were assessed according to BNL's Procedures for Radiochemical Data Validation (BNL EM-SOP-209) and Radiochemical Data Usability (BNL EM-SOP-210). The data subsequently were assigned (if applicable) a revised qualifier and a data-usability code. A usability code of "N3" was assigned if the data were not usable based on the lack of expected daughter products. A usability code of "N2" was assigned if the data were not usable because the results and the propagated error are indistinguishable from background (i.e., the result minus the 2 sigma error is less than the detection limit). Data identified as being "not usable" were not considered in characterizing the presence or extent of contamination. Data usability report summaries are included as Appendix G.

1.4.5 Data Qualification

During the data validation, verification and/or usability processes, the data may be qualified to alert the user to limitations in the use of the data based on QA/QC violations. Table E-3 defines the qualifiers placed on the data by the analytical laboratory and Table E-4 defines the data validation, verification, and usability qualifiers. For organic and inorganic analytes, three primary qualifiers may be applied to laboratory data: "U," "J," and "R." In addition, there may be no qualifier if QA/QC issues are not identified. For radiological data, in addition to the "U," "J," and "R" qualifiers, qualifiers such as "DL," "N2,", and "N3" were also applied to the results.

A "U" qualifier, which is a laboratory qualifier, indicates that the analyte was a target of the method but was not detected. The "U" qualifier also may be used in conjunction with the "J" qualifier, which indicates that the reported concentration is an estimated value because the

reported value is lower than the required reporting limit, or because one or more analytical deficiencies were noted during the data validation review. Thus the designation "UJ" indicates that the analyte was not detected and the reported quantitation or detection limit is an estimate due to QA/QC deficiencies. The "R" qualifier indicates that the datum is rejected. An "R" qualifier can be reported for analytes that either were, or were not, detected. In other words, an "R" qualifier may be assessed upon a reported concentration or a result reported with a "U" qualifier.

Data reported as either unqualified, or with "U" or "J" qualifiers are typically usable, in assessments of the extent of contamination or effectiveness of remedial actions. Data qualified by "R" are considered unusable.

Table E-1. Concentrations of Constituents Detected in Field Blank Samples Associated with the CERCLA and Facility Monitoring Groundwater Sampling Programs

Constituent	Number of Analyses	Number of Detects	Minimum	Maximum	Typical Reporting Limit	Units
Organic Compounds						
Acetone	2	1	1	1	10	µg/L
Butyl benzyl phthalate	2	1	0.41	0.41	9.7	µg/L
Bis(2-ethylhexyl)phthalate	2	1	0.56	0.56	9.7	µg/L
Di-n-butyl phthalate	2	1	0.73	0.73	9.7	µg/L
Chloroform	37	5	0.1	0.22	0.5	µg/L
Methylene chloride	37	2	0.17	0.33	0.5	µg/L
Metals						
Zinc	3	1	3.64	3.64	3.3	µg/L
Calcium	3	1	61	61	50	µg/L
Potassium	3	1	78.6	78.6	50	µg/L
General Chemistry Parameters						
Alkalinity	3	1	0.335	0.335	1.45	mg/L
Ammonia (as N)	3	3	0.0389	0.0992	0.017	mg/L
Nitrogen	3	1	0.0663	0.0663	0.033	mg/L
Total Kjedahl Nitrogen	3	1	0.0663	0.0663	0.033	mg/L
Chloride	2	2	0.0909	0.109	0.067	mg/L
TDS	3	2	0.0167	64.3	3.4	mg/L

µg/L Micrograms per liter.
mg/L Milligrams per liter.

Table E-2 Concentrations of Constituents Detected in Trip Blank Samples Associated with the CERCLA and Facility Monitoring Groundwater Sampling Programs

Constituent	Number of Analyses	Number of Detects	Minimum	Maximum	Typical Reporting Limit	Units
Chloroform	107	23	0.1	0.25	0.5	µg/L
Methylene chloride	107	1	0.15	0.15	0.5	µg/L
Methyl chloride	107	1	0.12	0.12	0.5	µg/L

µg/L Micrograms per liter.