APPENDIX C
INSTRUMENTATION AND ANALYTICAL METHODS

The analytical laboratory of S&EP Division is divided into 1) radiological, and 2) nonradiological sections to facilitate analysis of specific parameters in each category. The following analytes are analyzed in each category.

- Radiological: Gross alpha, gross beta, gamma, tritium, and strontium-90.
- Nonradiological: Purgeable aromatics, Purgeable halocarbons, PCBs, anions, and metals.

The methods and instrumentation for each category are briefly described below. Only validated and regulatory referenced methods were used during the analysis. All samples were collected and preserved by trained technicians according to appropriate referenced methods. Well-qualified, and trained analysts performed different analyses. The analytical laboratory is certified by NYS-DOH for the radiological and nonradiological parameters (except for PCBs) performed. The radiological laboratory participates in the following:

Gross Alpha and Gross Beta Analysis - Water Matrix

Water samples are collected in one-liter polyethylene containers, and preserved at the time of collection by acidification to pH 2 using nitric acid. If the samples are effluent or surface stream samples from locations DA, EA, HM or HQ, or Building 535B daily process samples, then 100 ml are extracted for analysis. Groundwater samples are typically analyzed using a 100-ml aliquot. The aliquot is evaporated to near-dryness in a glass beaker, which is rinsed to remove the solids and the combined solids and rinsate are transferred to a 5-cm diameter stainless-steel planchet, which is then evaporated to dryness. The planchettes are placed in a drying oven at 105°C for a minimum of 2 hours; removed to a desiccator and allowed to cool; weighed and counted in a gas-flow proportional counter for 200 minutes. Samples are normally processed in batch mode. The first sample of each batch is a background, which is subtracted from the raw data before computing net activity concentration. System performance is checked daily with NIST-traceable standards: Americium-241 for alpha, and Strontium-90 for beta. Laboratory duplicates and spiked duplicates are performed within batch of samples to determine precision and accuracy, respectively.

Gross Alpha and Gross Beta Analysis - Air Particulate Matrix

Air particulate samples are collected on 50-mm glass fiber filters at a nominal flow rate of 15 liters per minute. At the end of the collection, the filters are returned to the analytical laboratory for assay. Filters are counted twice in a gas flow proportional counter for 50 minutes. The first count occurs immediately upon receipt in the analytical laboratory, and is used to screen the samples for unusual levels of air particulate activity. The filters are then recounted approximately one week later. This delay permits the short-lived radon/thoron daughters to decay. The second analysis is used for environmental assessments. The first sample of each batch is a blank filter whose count rate is subtracted from the raw data before calculating net activity concentration. The system's performance is checked daily with NIST-traceable standards: Americium-241 for alpha, and Strontium-90 for beta.

Tritium Analysis - Water Matrix

Water samples are collected in polyethylene containers. No preservatives are added before collecting the sample. Effluent and surface stream samples from locations DA, EA, HM, or HQ, or Building 535B daily- process samples as well as groundwater samples were analyzed using a 7-ml aliquot. Potable-water samples were distilled following the method outlined in EPA 1980, 906.0

and a 7 ml aliquot analyzed. Liquid scintillation cocktail then is added to the aliquot so that the final volume in the liquid-scintillation-counting vial is 7 ml of sample plus 10 ml of cocktail. Samples then are counted in a low-background liquid-scintillation counter for 50 minutes. Samples are normally processed in batch mode. The first sample of each batch is a steam distilled water background value that is subtracted from the raw data before calculating the net activity concentration. The second sample in each batch is a NIST-traceable tritium standard, which is used to verify the system's performance and efficiency. Each sample is also monitored for quenching. Corrections for background, quenching, and efficiency for the sample matrix are factored into the final net concentrations for each sample. Laboratory duplicates and spiked duplicates are performed within batch of samples to determine precision and accuracy, respectively.

Tritium Analysis - Air Matrix

Concentration of tritium in ambient and facility air is measured by drawing the air through a desiccant at a rate of approximately 200 cc/min. At the end of each collection period, typically one week, the desiccant is brought to the analytical laboratory for processing. It is heated in a glass manifold system. Effluent samples have dedicated glassware, as do environmental samples. The off-gas, containing moisture from the sampled air, is collected by a water-cooled glass condenser. A 7-ml aliquot of this water is then assayed for tritium content. Liquid scintillation cocktail is then added to the aliquot so that the final volume in the counting vial is 17 ml. Samples are then counted in a low-background liquid scintillation counter for 50 minutes. Samples are normally processed in batch mode. The first sample of each batch is a steam distilled water background valve that is subtracted from the raw data before computing net activity concentration. The second sample in each batch is a NIST-traceable tritium standard, which is used to verify the system's performance and efficiency. Each sample is also monitored for quenching. Corrections for background, water recovery, air sample volume, quenching and efficiency for the sample matrix are factored into the final net concentrations for each sample. Laboratory duplicates and spiked duplicates are performed within batch of samples to determine precision and accuracy, respectively.

Strontium-90 Analysis

Strontium-90 analyses are currently performed on water, soil and aquatic biota samples. Ground water samples are processed in house using DOE Method RP500, which utilizes a crown ether to selectively separate strontium from the acidified sample matrix. The strontium is then eluted using dilute nitric acid. The resulting eluent is then evaporated on a 2.5 cm stainless steel planchet and the sample counted in a gas-flow proportional counter. Samples are prepared in batches, including a standard and a method blank in each batch. Chemical recovery is determined for each sample by the recovery of strontium carbonate. NIST-traceable strontium-90 standards are used to calibrate and verify the performance of the counting instrument. Samples are counted twice to verify strontium-90 and yttrium-90 in growth.

Potable water samples as well as samples of solids are shipped to a contractor laboratory, which is certified to perform the EPA 1980, 905.0 method for strontium-90 in drinking water. This method employ's time-consuming and costly wet-chemistry techniques to isolate strontium from the sample. Samples are counted twice to verify strontium-90 and yttrium-90 in growth. Samples are typically processed in a batch. Backgrounds and system performance are verified with each batch. Chemical recoveries are determined by a combination of gravimetric and strontium-85 standard addition techniques.

Gamma Spectroscopy Analysis

Surface, potable, and groundwater surveillance samples are typically of 12 liters and are placed in polyethylene bottles without preservatives. Samples are then passed through a mixed-bed ion-exchange column at a rate of 20 cc/min. The column is then removed, the resin placed in a Teflon-lined aluminum can and counted on a calibrated gamma spectroscopy detector for 50,000

seconds. Where effluent is sampled in a flow-proportional manner, a 10-ml aliquot is passed through the mixed bed column on an as needed basis. Typically, the sizes for such samples approach 50 to 100 liters. Air-particulate filters and air-charcoal canisters are counted directly on the calibrated gamma spectroscopy detector for 10,000 seconds. Soil, vegetation, and aquatic biota are all processed following collection. Typically, a 50, 100, or 300-g aliquot is taken, placed in a Teflon-lined aluminum can and directly counted. For gamma spectroscopy analyses, overnight backgrounds are counted once per week, with calibration check and background checked daily. Analytical results reflect net activity that has been corrected for background and efficiency for each counting geometry used.

Purgeable Aromatics and Purgeable Halocarbons

Water samples are collected in 40 ml glass vials with removable teflon-lined caps without any head space, and preserved with 1:1 HCl to pH <2.0. Samples are stored at 4° C and analyzed within 14 days.

Ten (10) purgeable compounds (benzene, toluene, ethyl benzene, total xylenes, chloroform, 1,1-dichloroethane, 1,1-dichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene) are analyzed under this category following EPA Method 624 protocols using GC/MS. These ten compounds were chosen as the target compounds since they are known or suspected to be present in the monitoring wells based on DOE's survey of the site in 1988 (USDOE, 1988) and a comprehensive analysis of 51 new monitoring wells installed in 1989 using EPA's Contract Laboratory Program (CLP) (EPA, 1987, 1988). There are currently two Hewlett-Packard GC/MS instruments. One instrument is exclusively used to analyze of purgeable compounds and the other for screening extractables and other extraneous compounds in non-routine samples. Since the groundwater under BNL is classified as a sole source aquifer under the Safe Drinking Water Act and Class GA groundwater by the NYSDEC, the detection limits reported for the compounds are close to drinking NYS DWS and AWQS. Even though the QC generated for the purgeable analysis meets the EPA drinking water method 524.2 requirements, to facilitate certification from NYSDOH for limited number of analytes required by BNL, EPA method 624 is used under non-potable water category.

The method involves purging a 25-ml-aliquot of the sample with ultra pure helium in a specially designed sparger using the Purge and Trap technique. Each sample is spiked with a known concentration of internal standards and surrogates before purging to facilitate identifying, quantifying, and determining the extraction efficiency of analytes from the matrix. The purged analytes are trapped on to a specially designed trap and thermally desorbed on to the DB-624 megabore capillary-chromatographic column by back flushing the trap with helium. Individual compounds are separated with a temperature program of the GC and enter the mass spectrometer where they undergo fragmentation to give characteristic mass spectra. The unknown compounds are identified by comparing their mass spectra and retention times with reference compounds, and quantitated by internal standard method. The quantitation data is supported by extensive QA/QC, such as tuning the mass spectrometer to meet bromofluoro-benzene criteria, initial and continuing calibrations verifying daily response factors, method blanks, surrogate recoveries, duplicate analysis, matrix spike and matrix spike duplicate analysis, and reference standard analysis to verify the daily working standard.

PCB Analysis

Samples are collected in 50-100 ml glass containers with teflon-lined lid and stored at 4° C and analyzed within 30 days.

Transformer oil, mineral oil, hydraulic fluid, waste oil, and spill wipe-samples are analyzed for PCBs using gas chromatography-electron capture detector (GC-ECD) method. This method is similar to EPA SW-846 method 8080 and is targeted to identify and quantitate seven different mixtures of PCB congeners in the samples.

The method consists of diluting a known weight of the sample with isooctane and removing the interfering compounds with one or more aliquots of concentrated sulfuric acid till the acid layer is almost colorless. The entire oil matrix, along with other interfering polar compounds, are selectively removed from the sample, leaving the PCBs in isooctane solvent.

There are two GC-ECD instruments for analyzing PCBs. Each GC-ECD instrument is calibrated with different concentrations of each PCB mixture to establish linearity. The PCBs found in the samples are identified and quantitated by comparing the retention times and chromatographic patterns with the standards. Methods blanks, duplicates, spikes, and reference standards are run as part of QA/QC.

Anions

Chloride, nitrate-N, and sulfate are analyzed using Dionex Ion-chromatography (IC) with ion suppression and conductivity detection technique.

Samples from monitoring wells are collected in 100-ml polyethylene bottles, cooled to 4° C, and analyzed within 28 days. For nitrate analysis in drinking water analysis, samples are supposed to be analyzed within 48 hrs. However, even though holding times were exceeded for nitrate analysis of some non-potable monitoring well samples, the depletion of nitrate is expected to be negligible.

The anions are passed through an anion-exchange polymer column and eluted with carbonate/bicarbonate solution. Then the eluent passes through an ion-suppressing column where the background contribution from the eluent is suppressed, leaving the target anions to be detected by conductivity meter.

Initially, the IC system is calibrated with standards to define its working range. The target anions in the samples are identified and quantitated by comparing the retention times and areas with the standards. Method blanks, duplicates, replicates, spikes, and reference standards are routinely analyzed as part of QA/QC.

Metals

Samples are collected in 500-ml glass bottles and stabilized with ultra-pure nitric acid to a pH of <2. The samples are analyzed within 6 months, except for mercury, which is analyzed within 26 days.

Cadmium, chromium, lead (furnace), copper, iron, manganese, silver, sodium, zinc (flame), and mercury (manual cold vapor) are analyzed with Perkin-Elmer atomic absorption spectrometer. Using the flame technique, the sample containing the target element is nebulized and atomized in an oxy-acetylene flame. At the same time, a beam of light from a element-specific hollow cathode lamp corresponding to the absorption frequency of target element is passed through the flame. The atomized element absorbs the energy specific to that element from the cathode lamp and the intensity of absorption is proportional to the concentration of the element in the sample. Calibration curves establish the linearity of the system and samples are quantitated by comparing with standards.

Using the furnace technique, chemical interference is eliminated in two stages: first, by heating the sample at 105 - 110° C to remove moisture, and second, at 600 - 900° C to burn out any organic matrix. Final atomization is achieved by heating the furnace to 2400 - 2700° C. The rest of the technique is similar to the flame method, above. Using this furnace technique, sub-ppb detection limits are possible for water samples.

Using a cold-vapor technique for mercury, a 100-ml aliquot of the sample is digested with potassium permanganate/persulfate oxidizing solution at 95° C for 2 hours to oxidize any organically bound and/or monovalent mercury to mercury (II) ion state. Excess oxidizing agent is destroyed with hydroxylamine hydrochloride. The mercuric ion later is reduced to elemental mercury with

excess stannous chloride, which is purged with helium into the absorption cell. The absorption is directly proportional to the concentration of mercury in the sample.

All these atomic absorption techniques involve initial calibrations to define the calibration range, continuing calibrations, method blanks, duplicates, replicates, matrix spikes, and reference standard analysis as a part of QA/QC.