

QUALITY ASSURANCE / QUALITY CONTROL POLICY

BREG SOIL AND WATER QUALITY LABORATORY

UNIVERSITY OF DELAWARE

Department of Bioresources Engineering
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Major Sections

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1.0 INTRODUCTION TO LABORATORY

A. Mission Statement of Laboratory

The mission of the BREG Soil and Water Quality Laboratory (BREG SWQL) is to provide accurate, verifiable, affordable, and timely analytical services. The laboratory is committed to quality assurance, and it is our goal to provide high quality project support and technical resources to meet the needs of our department faculty as well as other University of Delaware researchers.

The BREG Laboratory provides routine water and soil analyses with special emphasis on nutrients and water quality parameters.

B. Quality Assurance Policy of Laboratory

Dr. Anastasia E. M. Chirnside will be responsible for the hiring and training of staff with the required qualifications and/or skills needed to accomplish the mission of the laboratory.

The best available sample preparation, handling, preservation and storage methods are used as recommended by the appropriate authority. Procedures from both Standard Methods for the Examination of Water and Wastewater and the US EPA are used for water preservation, storage, and analysis. AOAC (Association of Official Analytical Chemists) recommendations are used for agricultural and other types of materials. It is recommended that the client discuss sampling and preservation guidelines with the laboratory personnel since these steps will affect the quality of the data.

In addition to the above, Quality Assurance (QA) also includes control of the following: calibration and standardization, preventive and remedial maintenance, proper instrument selection and use, quality laboratory water, clean laboratory environment, replicate analysis, spiking of samples, holding facilities for samples, responsible evaluation of data, and recording and maintaining a Quality Control (QC) database. Examples of laboratory performance on QC samples are available on request. Results of QC samples are reported with the client's data upon request.

C. Size of Laboratory

1. Dimensions and Layout

The BREG SWQL is housed in WorriLOW Hall on the University of Delaware campus. The primary laboratory space is in Room 111 on the first floor of the WorriLOW Hall. Additional space is utilized in Room 112 of WorriLOW. A walk-in freezer and refrigerator are located in room 122 of WorriLOW Hall. Standard refrigerators are located in both rooms 111 and 112. A chest freezer is located in Room 112. Plant grinding equipment and soil grinding equipment are available in the adjacent Soil Testing laboratory. Sample driers and a large sample grinder are available in the Agronomy Building located on the research farm, which is adjacent to WorriLOW Hall. Exhaust hoods are available in both room 111 and 112 for digestion and hazardous fume work.

2.0 LABORATORY ORGANIZATION AND RESPONSIBILITIES

A. Organizational Chart

The BREG SWQL is part of the Bioresources Engineering Department in the College of Agriculture and Natural Resources of the University of Delaware. The laboratory is located on the Newark Campus in Worrilow Hall at 531 S. College Ave., Newark, DE 19716-2140. The laboratory provides analytical services primarily to University researchers.

Department Head: Dr. William F. Ritter

Laboratory Supervisor and Manager: Dr. Anastasia E. M. Chirnside

B. Description of Lines of Communication

The manager of the BREG SWQL, Anastasia Chirnside, reports to Bill Ritter, the Department Head of the Bioresources Engineering Department. Dr. Chirnside is responsible for accurate and timely analysis of the materials submitted to the lab. This includes all QA/QC procedures, equipment maintenance, hiring and supervision of necessary personnel, updating of equipment and procedures, organization of samples, and scheduling of tests. The laboratory manager is designated to be the QA/QC officer.

3.0 SAMPLE CUSTODY

A. Sample Receipt Policies

All samples are received in Room 111 of Worrilow Hall on the Newark Campus of the University of Delaware.

B. Sample Log-in

Once samples arrive at the laboratory, they are recorded into the laboratory sample logbook (Excel File). The logbook file contains the following information: date received, storage location, preservation required, number of samples in the set, analyses required, and date completed. Each project has a unique lab notebook. Each data set name and lab numbers are recorded in designated lab notebook. The lab number is used to identify the sample in all analyses. After analysis is complete, the samples are stored at 4° C until the project investigators accept results. Access to samples is limited to laboratory personnel.

For research samples, each sample set that is logged into the lab is then assigned to a project title and each sample is assigned a laboratory number. Each project is defined as to the type of analysis requested by the researcher.

C. Sample Storage and Preservation

If samples arrive in the laboratory unpreserved, it is the responsibility of the section leader to see that all preservation procedures necessary to the individual analysis requested are performed as soon as possible. Water samples are preserved by refrigeration, freezing, or by the addition of acid according to USEPA protocol. Soil and plant samples are dried, ground and sieved in accordance to NCR-13 and AOAC recommendations. In instances where a soil

sample is to be analyzed for percent moisture or ammonium, the sample will be refrigerated or frozen for storage.

D. Evidence Files

Each specific project is assigned a lab notebook in which all log in sheets, notes, raw data, QA/QC results, calculations used for data reduction, and copies of reports produced by the laboratory are recorded. Note books are kept in the lab for at least 7 years.

E. Sample Disposal

Unless the client requests a return of their samples, the laboratory is responsible for the disposal of all samples. Samples are stored for at least three months after the completion of analysis. After this time, the samples will be subject to disposal after approval by researcher.

If the samples are considered hazardous waste, then disposal procedures follow the guidelines set up by the University of Delaware Chemical Waste Program, Department of Occupational Health and Safety. Otherwise the samples are sewered (water), composted (soil), or placed with other refuse (plant and other).

If the client wishes to have either the samples or the sample containers returned, those arrangements must be made with the laboratory, preferably at the time of the sample drop-off.

4.0 CALIBRATION PROCEDURES AND FREQUENCIES

A. Frequency of Calibration of All Instruments

The calibration of all instruments will be verified at least once each day at the beginning of analysis of unknown check samples. The calibration generally includes at least one blank and several standards bracketing the range of the samples. Some instruments, like pH meters, do not require blanks, but use several standards instead.

B. Labeling of Records of Calibration for Instruments

All records of the calibration of instruments are kept in the laboratory analysis log book by the section leader. Each record is labeled by indicating date, analyses type, and analyst initials.

C. Reagents and Standards

1. Records of Receipt and Tracking

Records of dates ordered and dates received of all commercially prepared check samples are recorded in the QA/QC lab notebook. Additionally, if a check sample needs to be diluted prior to use, the preparation dates are kept on file by the section leaders. Preparation of all lab standards is recorded in the QA/QC notebook. Information recorded includes: lot number of reagents, date made, analyst performing task, and exact recipe of how solutions were made.

2. Control Charts and Curves

Records of all raw data for control charts and standard curves are recorded in the QA/QC notebook.

3. Disposal of Unused Standards

The disposal of unused standards follows the guidelines established by the University of Minnesota Chemical Waste Program, Department of Environmental Health and Safety.

5.0 INTERNAL QUALITY CONTROL CHECKS

A. Internal Quality Control Checks:

In the laboratory, for each batch of 10 water samples, a set of duplicate samples and a spiked sample will be analyzed along with two standards; one in the high concentration range and one in the low concentration range. The standard and spiked samples will be compared against previously developed percent recovery data using the Shewhart control chart. The duplicate analysis will be compared to previous precision quality control data using an R chart (EPA, 1979).

B. Performance and Systems Audits:

Quality control samples will be analyzed at the beginning of the project and every 6 months to evaluate measurement performance systems. Once the project is initiated and on an annual basis; all laboratory procedures will be checked and evaluated. Checklists suggested in Procedures for Evaluation of Environmental Monitoring Laboratories will be used (EPA, 1978).

C. Preventive Maintenance:

All analytical balances are serviced on an annual basis. In addition, the accuracy is evaluated weekly by checking each balance with the appropriate NIST weights.

D. Specific Routine Procedures Used to Assess Data Precision, Accuracy, Representativeness and Completeness.

Data accuracy will be checked for each set of samples by comparing the spiked and standard recoveries against a Shewhart control chart. Precision will be checked on duplicate samples for each set of analysis using an R chart. The equations and procedures for checking precision and accuracy are presented in the EPA Manual on Handbook for Analytical Quality Control in Water and Wastewater Laboratories (EPA, 1979). Representativeness of the analysis will be checked by comparing individual data sets with mean concentrations and standard deviations established from previous analysis. Completeness of the data set will be checked by determining what percent of data is rejected from data sets based on all data collected.

E. Laboratory Water Purity

The water used for all analytical purposes in the laboratory is triple deionized to a minimum resistivity of 17.5 megohm. Worrielow Hall, where the laboratory is located, has a building reverse osmosis system that produces 2 megohm DI water. This is piped to the various laboratory rooms for general use. In the BREG SWQL, the water is piped to a Barnstead E-Pure system which uses macroporous resins as an initial step to remove colloids, activated carbon as a second step to remove organics and chlorine, two ultrapure mixed bed cartridges to remove all ionic contaminants, and finally a 0.2 micron cross flow filter in a remote dispenser.

This process produces water which is continually digitally monitored to be at least 17.5 megohms, and meets the requirements of Type I water as determined by the ASTM (American Society for Testing and Materials).

F. Reagent Storage and Purity

Chemicals and reagents used in the laboratory are Certified ACS grade as required in the SOPs. For trace metal digestions and ICP-AES analysis, the acids are TraceMetal grade which are manufactured to achieve low metal contamination measurable in the mg/L to u/L range.

All prepared reagents used in the laboratory are stored according to the specifications prescribed in the SOP, i.e. brown bottles, glass only, under refrigeration etc. Only the amount of reagent necessary for each day's run is removed from the stock bottle. This helps eliminate the possibility of contamination of the stock reagent and also allows for continuous refrigeration of those reagents for which that is a concern. The purity of the reagents is ensured by the laboratory's procedures for glassware cleaning, water purity, and technical procedures in the preparation. All these are designed to protect against contamination. The purity is protected by the policy of only pouring out enough reagent for each day's run, never withdrawing reagent from the original container with any type of apparatus, never pouring excess reagent back into the container, and following as closely as possible all conditions for storage.

G. Bottle Cleaning

All glass and plastic ware are to be washed with nonphosphate detergents and thoroughly rinsed (see glassware cleaning appendix). Some tests call for an appropriate acid rinse as outlined in the SOP for that test. For most procedures, it is recommended to use newly purchased containers. This eliminates any concern of contamination from a previous sample. All glassware is then rinsed with chromerge (acid rinse). The plastic ware and plastic bottles are treated by a double acid rinse of 5% Nitric acid followed by 5% Hydrochloric acid. After the acid rinse step, they are thoroughly rinsed with deionized water (at least three final rinses with 18 megohm deionized water), and air dried upside down.

6.0 DATA REDUCTION, VALIDATION, AND REPORTING

A. Procedures of Rerunning Data

Samples are rerun when they are associated with a QC check sample that does not fall within the 95% confidence interval of the expected value. All of the samples following the last valid QC check are rerun. If the QC check sample is still outside the 95% confidence interval or if the associated check sample does not fall within 3 standard deviations of the historical or established mean, the procedure is considered out of control. These events initiate trouble shooting and corrective action procedures. The QC check sample is rerun and validated before reruns of the unknowns resume.

B. Procedures for Flagging Data

Data is flagged when there is a deviation from the established SOP or QA/QC criteria. This action is communicated to the lab manager by the analyst performing the analysis. The deviation that caused the flagging and any resultant corrective actions are discussed with the laboratory manager. Samples are generally rerun following the corrective action, but in cases where no corrective action can resolve the problem (i.e. a holding time was missed, the sample

is depleted and cannot be rerun, or the standard addition procedure was used for calibration etc.), then the data on the final customer report is flagged and an explanation is given on the report which notifies the customer of the deviation.

C. Use of Performance Evaluation Standards

Performance evaluation standards are used to evaluate the method, the SOP, and the performance of the analyst. If the performance evaluation of the laboratory is not acceptable to the reviewing agency, then trouble shooting and corrective action is initiated. The validation resulting from the successful analysis of performance evaluation standards lends confidence to the methods, procedures, and analysis of the laboratory. The performance evaluation groups in which this laboratory participates are listed in part J below.

D. Practical Quantitative Limits

Practical method detection limits (see section 9.0 part E) are established for each analysis in the laboratory. Result values that fall below the MDL will be reported as less than the MDL value.

7.0 ROUTINE PROCEDURES TO ACCESS DATA QUALITY AND DETERMINE REPORTING LIMITS

A. Precision

Precision is the agreement among a set of replicate measurements without the assumption of knowledge of their true values. There are two primary means of evaluating precision in this laboratory. The best mechanism to evaluate precision is the examination of relative percent difference of duplicate samples in the analytical run. This is expressed in the formula:

$$RPD = 100[(X1-X2)/\{(X1+X2)/2\}]$$

Where RPD = Relative Percent Difference

X1 = First observation of unknown X

X2 = Second observation of unknown X

Sample unknowns are duplicated at the rate of one per every 10-20 unknowns, depending on the SOP. Relative percent differences of 10% are expected at levels of ten times the MDL and above. When unacceptable RPD values are encountered, the associated data (a batch of 10 to 20 samples) is rerun after a QA review. As the analyte level approaches the MDL, 10% RPD is too strict and higher RPDs are acceptable. At these low levels, the RPD is evaluated with reference to the PQL and other QC data in the run.

Another mechanism to evaluate precision involves a comparison of a check sample run daily with each batch of samples. If the check sample is run several times during the analytical run, then an estimate of replicability of the run can be obtained. The standard deviation of these results is an estimate of daily precision. The repeatability of the SOP over time can be evaluated by the comparison of the results of this check sample on a day to day basis. The pooled standard deviation of the check sample over many days and analyses gives an evaluation of the precision of the method over time.

B. Accuracy

Accuracy is the measure of bias of an analytical procedure which reflects the closeness of a measured value to a true value. In this laboratory, accuracy is daily measured on water, soil, compost and plant samples for those tests where certified values are available. Standard reference materials (SRM) of soil, sediments, and plants containing certified levels of analytes are purchased from US NIST for use as control checks on accuracy. Certified water control samples are prepared by dilution of water standards obtained from SPEX Industries, Inc., Edison, NJ and Perkin Elmer Corp., Norwalk CT.

For water analysis, at least one check control sample containing the appropriate certified analytes is run in conjunction of each batch sample unknowns. For other analyses, a certified or in-house control check sample is included in each run. For large sample batches, one check sample is run for each group of 20 unknowns. A batch of samples is rerun when the observed value for the associated check falls outside of the expected two standard deviation confidence interval. The analysis is considered out of control if the observed check values are not within three standard deviations of the known mean. In this case trouble shooting and corrective action is initiated.

In addition, no more than seven consecutive control check values should fall on one side of the historical mean, even if they are within the acceptable confidence limits. Such an event would be evidence that there is drift or bias in the procedure, and initiates a QC evaluation.

C. Representativeness

Representativeness is the assurance that the sample or subsample used in the laboratory is indeed representative of the field entity that is being measured. There are two major stages involved in representativeness. One is the collection of the sample from the entity being measured, and the other is sample preparation and homogenization before the sample is subsampled by the laboratory.

Sample collection is not a service offered by the laboratory except in very special circumstances. However, to help ensure that the sample is collected in a manner that insures it is representative of the field entity, the laboratory will offer to a client upon request any information we might have on sampling techniques and preservation. The conditions applied to the actual sampling procedure, the decision as to how to preserve the samples, the interim storage, and the means of delivering the samples to the laboratory are the responsibility of the client.

Sample preparation and subsampling services are provided by the laboratory. Each sample submitted must be prepared and homogenized to ensure that any subsequent subsample taken by the laboratory is representative of the sample originally submitted by the client. This can include tasks such as drying, grinding, sieving and mixing of the sample, depending on its composition. Plant samples are ground to pass a 20 mesh sieve and soil samples are crushed and sieved to pass a 10 mesh sieve. All samples are shaken or stirred before subsampling. For water samples with significant sediment, the client is consulted for instruction. Water samples are not filtered unless specified by the client. Water samples are thoroughly mixed before a subsample is withdrawn.

D. Completeness

It is the responsibility of each laboratory manager to review the analytical report for each job to insure that (1) all the samples required for quality assurance and quality control have been processed and (2) that the analytical report to be retained on file contains a complete record for each analysis and the associated QC samples and (3) that all procedures specified by established QA/QC protocols have been implemented.

E. Reporting Limits

1. IDLs

The instrument detection limit is the smallest signal above the background noise that the instrument can reliably detect. For most methods this would be a concentration of analyte that produces a signal greater than five times the signal/noise ratio for that instrument.

2. MDLs

The method detection limit is the analyte concentration derived from the method that yields a signal which is large enough to be considered significantly different from the blank with a statistical 99% probability. The method detection limit is determined by analyzing reagent water fortified at a concentration considered to be two to three times the estimated detection limit. At least seven replicates of this fortified blank are analyzed by the same procedure followed in the determination of unknown samples. The MDL is then calculated using the equation $MSDL = (t) \times (S)$, where $t = 3.14$ (for seven replicates) and S = the standard deviation of the replicate analysis. Upon request of the client, this value can be used as a reporting limit.

3. MDLs

The method detection limit is the lowest value that can be arrived at reliably during normal routine laboratory analysis. For most analyses, this is specified as three times the MSDL. This value is routinely used as the reporting limit for unknowns reported to the client.

8.0 CORRECTIVE ACTION

When quality control observations fall outside established acceptance criteria in terms of precision and accuracy, and continue to fail with reanalysis within SOP, the procedures are reviewed by the Laboratory Manager. More specifically, the following actions might be taken: (1) standards and samples are rerun to check if the instrument is running properly and operating conditions are stable, (2) new standards are prepared from a second stock solution and run to check the original standards, (3) the equipment is recalibrated and (4) new reagents are prepared. The exact corrective action conducted by the laboratory section leader will vary depending upon their observation and experience, e.g. whether the issue is one of precision or accuracy. The action taken is recorded in the log book accompanying each instrument.

9.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

Detailed quality assurance reports are available upon request. The report could include factors such as (1) changes or modifications to the QA/QC Plan, (2) changes to the SOP in methods performed for the client, (3) significant QA/QC problems and the recommended solutions, (4) corrective actions taken and the results, (5) limits that shall be imposed on the data, (6) holding times that have been missed, (7) recent management or personnel changes that may have affected the work, and (8) other issues that may have affected the analysis. Clients in ongoing projects are notified if major changes, such as new methods, different instrumentation, personnel changes etc. take place.