QUALITY ASSURANCE / QUALITY CONTROL POLICY

SOIL TESTING AND RESEARCH ANALYTICAL LABORATORY
UNIVERSITY OF MINNESOTA
Department of Soil Water and Climate

Rm 135 Crops Research Building
1902 Dudley Ave.
St. Paul, MN 55108

Major Sections

		Page No.
1.0	Introduction to Laboratory	3
2.0	Laboratory Organization and Responsibilities	6
3.0	Sample Custody	8
4.0	Calibration Procedures and Frequencies	10
5.0	Internal Quality Control Checks	13
6.0	Data Reduction, Validation, and Reporting	16
7.0	Performance and System Audits	20
8.0	Preventive Maintenance	20
9.0	Routine Procedures to Access Data Quality and Determination of Reporting Limits	21
10.0	Corrective Action	24
11.0	Quality Assurance Reports to Management	25
12.0	File Handling and Storage	25
13.0	Appendices	26

1.0 INTRODUCTION TO LABORATORY

A. Mission Statement of Laboratory

The mission of the Soil Testing and Research Analytical Laboratories is to provide accurate, verifiable, affordable, and timely analytical services. The laboratories are committed to quality assurance, and it is our goal to provide high quality project support and technical resources to meet the needs of our customers.

The Soil Testing Laboratory provides routine soil testing and recommendation services for the public including farmers, homeowners, florists, nursery owners, commercial vegetable and fruit growers, sod producers, golf courses, park and athletic field managers, cemeteries, composters, industrial lawn and landscape specialists, and agricultural lime producers. The Research Analytical Laboratory provides analytical services to researchers in universities, public agencies and selected commercial industries participating in University research.

B. Quality Assurance Policy of Laboratory

The Soil Testing and Research Analytical Laboratories (ST&RAL) will be responsible for the hiring and training of staff with the required qualifications and/or skills required to accomplish the mission of the laboratory. The academic qualifications of the section leaders will be a BS degree (or five years of comparable experience) in the chemical or physical sciences.

The best available sample preparation, handling, preservation and storage methods are used as recommended by the appropriate authority. US EPA procedures are used for water preservation, storage, and analysis. AOAC (Association of Official Analytical Chemists) or NCR-13 (North Central Region Soil Testing Committee) 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 ST&RAL is housed in the Crops Research Building and Crops Services Building on the St. Paul Campus of the University of Minnesota. The primary laboratory space is seven rooms on the upper floor of the Crops Research Building, each room being about 32 ft. by 20 ft. The various laboratory sections each have their own rooms. There are doors between the rooms that allow for ease of passage but also permit self enclosure to control cross contamination from dust or vapors. The room assignments in Crops Research are as follows:

Office and sample receiving: Rm 135
Soil preparation: Rm 139
Soil analysis: Rm 117 & 123
Water analysis: Rm 127
ICP-AES analysis: Rm 131
Plant analysis: Rm 138
Plant and Soil storage: Rm 19

Walk-in freezers and refrigerators are located in Rm 5 of the Crops Research building. Standard refrigerators are located in Rm 117, 131, 127, and 138.

The adjacent Crops Services Building has additional storage space, plant grinding equipment, and soil grinding equipment. The room assignments are as follows:

Plant grinding: Rm 30 Crops Services
Plant and Soil drying: Rm 10 Crops Services

Exhaust hoods are available in Rm 117,127,138 for digestion and hazardous fume work. The exhaust hood in Rm 117 has been specially modified for perchloric acid digestion work.

2. Equipment List (Major items)

Elemental Spectrometers:
- Perkin Elmer Optima 3000 ICP-AES (1)
- Perkin Elmer Optima 3000 DV ICP-AES (1)
- Perkin Elmer Aanalyst 100 (1)
- LDC Analytical Mercury Monitor (1)
- Continuous Flow Analyzers:
- Alpkem (Perstorp) Rapid Flow Analyzer 300 (4)
- Technicon Autoanalyzer II (2)

Analyzers:
- Dionex DX120 Ion Chromatograph (1)
- Dohrmann DC-80 Carbon Analyzer (1)
- Skalar Primacs Carbon Analyzer (1)
- LECO S144DR Sulfur Analyzer (1)
- LECO FP528 Nitrogen Analyzer (1)

Balances:
- Mettler AE 163 Balance (1)
- Mettler PM 300 Balance (1)
- Mettler PR 5002 Balance (1)

Ovens, Digesters and Heating Baths:
- Labline Laboratory Oven (1)
- Precision Scientific Heating Bath (2)
- Large walk-in coolers and freezers, laboratory refrigerators (5)
- Block Digesters (3)
- Blue M Oven (1)
- CEM Corp. MDS 81D Microwave Digestion Oven (1)

Colorimeters and Spectrophotometers:
- Brinkman PC 900 Colorimeter (1)
- Brinkman PC 800 Colorimeter (1)
- Bausch & Lomb Spectronic 20 Spectrometer (1)

Miscellaneous:
- Centurion CEC Extractor (2)
- Accumet model 30 Conductivity Meter (1)
- Hach Digital Titrator (1)
- Beckman Zeromatic IV pH meter w/ Fisher Glass & Reference electrodes

D. Laboratory Certifications

This laboratory is certified annually by the Minnesota Department of Agriculture for soil fertility analysis. A copy of the certificate is attached in the appendix.

2.0 LABORATORY ORGANIZATION AND RESPONSIBILITIES

A. Organizational Chart

The Soil Testing and Research Analytical Laboratories is a division of the Department of Soil Water and Climate in the College of Agriculture, Food and Environmental Science of the University of Minnesota. The laboratories are located on the St. Paul Campus in the Crops Research Building at 1902 Dudley Ave. St. Paul, MN 55108.

The Laboratory is composed of two major branches. The Soil Testing Laboratory serves the general public as well as University researchers and Public agencies with soil and potting media fertility analysis and fertilizer recommendations. The Research Analytical Laboratory provides analytical services primarily to University researchers and Public agencies.

Department Head	Dr. Ed Nater, Professor
Faculty Advisor	Dr. Paul Bloom, Professor
Laboratory Manager	Roger Eliason, BS Chemistry, MS Ecology

Laboratory Section Leaders:

Water	Margaret Miller, BS Food & Nutrition
Soil	Som Lekakuhl, PhD Soil Science
ICP	Russ Anderson, AA Physics
Plant	Roger Eliason, BS Chemistry, MS Ecology
Special	Bill Dancer, MS Soil Science, PhD Soil Science/ Horticulture

B. Description of Lines of Communication

The manager of the Soil Testing and Research Analytical Laboratory, Roger Eliason, reports to Ed Nater, the Department Head of the Soil, Water, and Climate Department. The section leaders responsible for the soil, water, plant, ICP, and special materials sections report to the laboratory manager. Dr. Paul Bloom is the faculty advisor and chair of an advisory committee composed of College of Agriculture, Food and Environmental Sciences faculty. This committee oversees laboratory policy.

C. Units in Laboratory

Soils unit: Responsible for the testing of soil samples submitted by farmers, homeowners, florists, etc. to the Soil Testing Laboratory division and samples submitted by researchers to the Research Analytical Laboratory division. This includes analysis of peat, sludge and compost materials.

Water unit: Responsible for the testing of water samples submitted by researchers. Also responsible for testing sample extracts and miscellaneous liquids for certain parameters.

Plant unit: Responsible for the testing of plant materials including lichens, roots, seeds, grain, and wood samples submitted by florists and researchers.

ICP unit: Responsible for ICP Atomic Emission Spectroscopy analysis of liquids or extracts submitted directly by researchers or prepared in the soil, water, special, or plant section.

Special unit: Responsible for the testing of miscellaneous materials submitted by researchers. Includes a wide range of materials such as wood products, fish, blue-green algae fertilizer, diatomaceous earth, milk products, contact lenses and their solutions, chemicals, and fertilizers.

D. Brief Description of Key Positions

The section leaders of the five units mentioned above are responsible for accurate and timely analysis of the materials submitted to them. 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 the main office (Room 135) of the Crops Research Building on the St. Paul Campus of the University of Minnesota.

B. Sample Log-in

The office secretary logs in the samples, along with the completed analysis request sheet (provided by the laboratory) and all other accompanying paperwork.

For research samples, each batch is assigned a job number specific to the type of analysis requested (Soil, Water, ICP, Plant, Compost or Special) and the appropriate section leader is notified of the samples presence for transfer of custody.

For florist and soil testing samples, each sample is assigned a unique laboratory number. In the soil testing laboratory, this number is stamped next to the sample description on the sample information sheet submitted by the customer. For florist samples, a sample number is assigned at the time the sample information is recorded in the florist log book.

C. Example Laboratory Chain of Custody

The samples are delivered by the client or a delivery service (usually US Mail or UPS) to the office of the Soil Testing and Research Analytical Laboratory. The office secretary assigns a laboratory Job number to the samples and asks the client to fill in an analysis request sheet. This sheet requests the following information: Name, address, and phone number of client, current date, job number, the number of samples and their identification sequence, sample storage requirements, whether client needs the samples returned, and the analytical tests requested. A two part tag, color coded for each laboratory section, is separated into two, with one part given to the client and the second part retained with the samples. This tag has the name and address of the laboratory, the laboratory section type (water, soil, plant, ICP,

or special), the job number and year printed on each part. For the client, this tag becomes a receipt of sample drop off, and for the laboratory the tag labels and identifies the sample group. The office will then notify the proper section leader and transfer custody of the request sheet and samples to the section leader. A photocopy of the analysis request sheet is filed in the office for reference. The section leader then logs the job into the Job-Log book and becomes responsible for all subsequent procedures including storage, analysis, and disposal of the samples.

D. 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. Most often this means that soils are air dried at 36^{o} C and plant and compost materials at 65^{o} C. In instances where a soil sample is to be analyzed for percent moisture or ammonium, the sample will be refrigerated or frozen for storage. Any necessary deviation from the recommended policies will be discussed with the client.

Sample storage is provided by the laboratory. For water samples and others as needed, storage facilities include large walk-in freezers and refrigerators that can accommodate large numbers of samples. Soil and plant samples are stored at room temperature in designated indoor areas except for situations outlined above.

E. Tracking of Samples

The current status of samples submitted for analysis can be determined by contacting the appropriate section leader. Each section leader has the responsibility of maintaining a Job log of all jobs received. The Job-Log contains the following information: the job number, client name, date received, tests requested, and date completed. The status of a particular job can be determined by examination of the Job-Log book.

F. Evidence Files

All log in sheets, notes, raw data, QA/QC results, calculations used for data reduction, and copies of reports produced by the laboratory are collected and

stapled together to form a file. Loose bound books of the job files are kept in the office for one year and then retained in long term storage for at least seven years.

G. 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. Actual length of storage depends on the availability of storage space.

If the samples are considered hazardous waste, then disposal procedures follow the guidelines set up by the University of Minnesota Chemical Waste Program, Department of Environmental 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 unknowns. 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.

1. Minimum Number of Points for a Curve

The minimum number of points for a curve is dictated by the type of analysis being performed. Those parameters can be found in the individual analysis SOP. For example, USEPA protocol requires a blank and at least three standards encompassing the full concentration range of the samples for most routine analysis. ICP-AES calibration curves are generally two points, due to the wide linear range of the method. Reportable analytical results are those below the highest standard. Values greater than the highest standard will not be reported unless a demonstration of greater linear range has

been established or the sample has been diluted to fall within the linear range and reanalyzed. For other measurements such as pH, conductivity and turbidity, instruments are calibrated according to manufacturer's instructions. One or two verification standards are generally involved in these situations.

2. Type(s) of Curve(s)

The types of curves used for calibration are dictated by the instrument used for each analysis. This information is listed in the SOP for each method. The curve is forced through zero when applicable for low level work. If it is not possible to force the curve through zero, then a separate linear curve is established for samples that are below the lowest working standard and near the MDL.. This curve is based on a zero standard and the lowest standard that is available.

B. Criteria for Acceptance of Calibration

The acceptance or rejection of the calibration is the responsibility of the laboratory section leader. In general, the calibration will be accepted only if the r (correlation coefficient) is > 0.999. A second degree quadratic equation may be used for calibrations of four or more points to achieve this degree of fit.

In ICP-AES analysis, linear two standard calibrations are the norm. To verify calibration, the elemental calibration check standard must be within 5% of the expected value for each element. If it is outside this range, then the calibration curve will be normalized before proceeding with analysis.

For pH and conductivity, the calibration standards are read as unknowns and must read within 5% of the accepted value.

C. Updating and Verification of Calibrations

New calibration curves are established or normalized daily before each analytical run. A continuing calibration verification standard and associated blank is run after every 10 to 20 unknown sample analyses. If the calibration verification standard deviates more than 5% from the expected value but less than 10%, then the calibration curve is updated by recalibration or renormalization and analysis proceeds. If the calibration check standard is outside of 10% from the expected value, the calibration curve will be updated and the samples rerun from the point of the last acceptable verification standard.

D. Labeling of Records of Calibration for Instruments

All records of the calibration of instruments are kept in the laboratory by the section leader. Each record is labeled by indicating date, analyte type, job number, and analyst initials.

E. Standards

1. Expiration Dates

Expiration dates for all commercially purchased check samples are supplied by the manufacturer. Outdated standards are discarded. Expiration dates for all internal check samples are determined by the section leader. These dates will vary with the individual analysis being requested. Some standards have shown historically to be very stable, while others need to be prepared fresh for each day's run. An attempt is made to prepare standards in small volumes to promote turnover times of 6 months or less.

2. Testing for Purity and Validation

Stock standards for ICP-AES grade solutions range in purity from 99.99% to 99.9999%, depending on the element. These standards are the highest purity available.

When the working standards currently in use are nearing their expiration dates, new standards are prepared and their values are compared to the standards currently in use. The new standards must be verified to be within 5% of the current ones to be acceptable. If there is a discrepancy, then a third standard is prepared for verification.

3. Records of Receipt and Tracking

Records of dates ordered and dates received of all commercially prepared check samples are kept on file in the laboratory office. Additionally, if a check sample needs to be diluted prior to use, the preparation dates are kept on file by the section leaders.

4. 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.

F. Analyses Needing No Calibration

The majority of the analyses performed in the ST&RAL require calibration. For those that do not, such as alkalinity, solids, and specific conductance, a commercially prepared or in house check sample accompanies the analysis of the unknowns.

G. Standard Additions

Standard additions method of analysis is performed at the request of the client or when dictated by the sample type or method. This technique is generally used for difficult matrices, where matrix matching is not practical. Clients are notified if this method is used and the data is flagged.

5.0 INTERNAL QUALITY CONTROL CHECKS

A. Matrix Spikes

Matrix spikes are used to evaluate the effect of the matrix on the compatibility and accuracy of the method used for analysis of the analyte. For a client requiring “certified protocols” in the SOP, ten percent of the samples will be spiked. For researchers or clients not requiring certified protocols, samples are spiked on new projects or when the sample matrix is known to have changed by information from the client. For most types of analyses, recoveries between 90 and 110% are acceptable and indicate no matrix problems. In some situations and for certain analytes, i.e. for Hg, As, and Se water analysis in the ug/L range, recoveries of 80 to 120% are acceptable. Unless specifically requested by a client, the spiking data is for internal QA/QC use only and is not recorded on the data report. A continuing log and record of spike recovery for water analyses is maintained by the laboratory section leader. For other analysis, the spike recovery information is included in the job file.

B. Spiked Blanks

Spiked blanks are useful to evaluate the potential spectral interference effects in ICP-AES analysis. Spiked blanks are run in unfamiliar situations where spectral interferences may present a problem. For example, if a soil has high levels of Pb due to the presence of paint chips, a blank spiked with similar levels of Pb can determine the spectral interference from the high concentration of Pb on the analysis of other elements.

For other methods, the use of spiked blanks is performed at the request of the customer.

C. Surrogates and Internal Standards

The analysis of surrogates, normally used in organic analysis, does not apply to the inorganic analysis performed in this laboratory.

The use of internal standards for ICP-AES analysis can be helpful to correct for drift or matrix variations that may occur during the analytical run. In this method, a known level of an internal standard, such as Yttrium (Y), is added to each unknown. The concentration of Y from each sample is monitored and the concentration for other elements is normalized to the recovery in that sample. This technique is available on the Perkin Elmer Optima 3000 DV.

D. Blanks (Field, Trip, Reagent, Instrument...)

Upon request, the laboratory will provide supplies for a client to prepare and submit field or trip blanks for water samples. These blanks will be treated in the laboratory in the same manner as an unknown sample. Reagent and instrument blanks are prepared as dictated by the SOP for the test being performed. When samples must be digested or extracted before analysis, it is preferred that a minimum of three method blanks are prepared for each batch of sample unknowns.

E. Calibration Standards

Calibration standards are prepared as dictated by the SOP for each analysis. Some standards need to be prepared daily or weekly, others will be stable for a longer period of time. When using water analysis standards that are stable for an extended period of time, at least one or two standards in the standard set are prepared daily and compared to the older counterparts. Standards are assigned expiration dates when prepared, and fresh standards are prepared and verified before the current ones expire. For general

automated colorimetric water analysis, standards are used for 6 months or less.

F. Proficiency Testing of Analysts

The proficiency of the analysts is determined by the observation of their QA/QC performance. This includes factors such as: the relative percent difference (RPD) on duplicates of unknowns, external and internal check sample results, spike recoveries, their technique for standard and reagent preparation and ability to follow standard laboratory procedures.

G. Proficiency Testing of the Specific Analysis

The proficiency of specific analyses is determined by participating in external sample exchange studies. See section 6.0 part J for a complete list of the sample exchanges in which the laboratory participates.

H. Sample Preservation and Holding Times

Guidelines established by the EPA for water samples are carefully followed for both water sample preservation and holding times. In unusual circumstances when there is some deviation, the deviation is discussed with the client and the data is flagged.

I. Laboratory Water Purity

The water used for all analytical purposes in the laboratory is triple deionized to a minimum resistivity of 17.5 megohm. The Crops Research building, where the laboratory is located, has a building deionizing system utilizing replaceable cartridges that produces 2 megohm DI water. This is piped to the various laboratory rooms for general use. In the ICP room, the building DI is piped to a second replaceable cartridge system which produces 1 megohm water. This water is piped to a Barnstead E-Pure system which uses macroreticular 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).

J. 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.

K. Bottle Cleaning

All glass and plasticware 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.

In cases where ppb (u/L) level analysis is required, virgin containers can be acquired from the laboratory which have been soaked in 50% Nitric Acid overnight, then 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 section leader 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 Spikes and Duplicates in Accessing Data

The relative percent difference between duplicates varies with the type of analysis, the target analyte, and with the amount of target analyte present. In most procedures, a 5 to 10% relative percent difference (RPD) is acceptable. However much larger differences for analyte levels near the detection level are not cause for concern, and are not flagged unless they are accompanied by low matrix spike recoveries. Under such circumstances a more precise estimate of very low analyte levels may be obtained by the standard addition method. This would be done only at the request of the client and the data would be flagged.

The acceptance criteria for matrix spike recovery will also vary with the type of analysis and with the magnitude of the analyte present. Analyte spike recovery is meaningful when spiking is equivalent to 75 to 125% of the analyte magnitude. Spike recoveries become highly variable when analyte values are high, and are not considered informative when analyte concentrations exceed the spiking level by a factor of four or more.

D. Use of Reference Standards in Accessing Data

Standard reference materials (SRAMs) containing certified concentrations of elements and supplied by the US National Institute of Standards and Testing

are routinely used to check the accuracy of soil, plant, and sediments analyzed in the laboratory. SRM 2711, a Montana soil and SRM 2704, a contaminate river sediment from Buffalo River in New York, are used to check accuracy for total metal analysis in soil and sediment samples. A large variety of SRMs are used for reference checks in plant analysis, including but not limited to SRM 1515 (apple leaves), SRM 1570 (spinach), SRM 1672 (citrus leaves), SRM 1573 (tomato leaves), and SRM 8412 (corn stalk). A certified reference material, BCR 146 (industrial sewage sludge) supplied by the Community Bureau of Reference from the Commission of the European Communities, and an EPA quality control reference, Municipal Digested Sludge (WP976), are used for quality control when analyzing composts, sewage sludge or similar waste material(s). For water analysis, SRM 1643c, Trace Elements in Water, is used for water metal determination.

For routine analysis, water quality control checks are prepared from commercial certified standards [Spex Multielement Plasma Standard from SPEX Industries, Inc. and PE Pure from Perkin Elmer Corp.] which are diluted to obtain the appropriate acid content or matrix used for fixing or preserving the target analytes.

A wide variety of in-house checks have been developed and are maintained at the laboratory, including diverse materials such as rocks, soils, minerals, wood, lichen, and honey bees. Details about these in-house check samples will be provided to the client upon request. In some instances clients have supplied their own quality control samples.

Reference standards are a key factor in accessing data. Each analysis performed by the laboratory has an external or in-house reference standard included in the analytical run. External standards have accompanying quality control data such as expected values and standard deviations to aid in the assessment. Internal standards have running means and standard deviations that are used to access the analytical run. Whenever a value falls outside of the 95% confidence level as given in the reference statistics, the analysis would be flagged or rerun after appropriate corrective action.

E. Data Reporting Format

The data reporting format includes the client's name, the name of the study, the laboratory reference number, the type of sample material, the date the samples were received, the date that the analysis was reported, the identification of the individual unknowns, the results of the analysis performed in the laboratory, and the initials of the person performing each analysis. For water analysis, the laboratory also reports the results from the externally

prepared check sample(s), and the statistical information supplied to the laboratory by the manufacturer of the QC check sample(s). Any data that must be flagged (see section 6.0 part B) will be placed in parenthesis or asterisked with a footnote explicitly explaining the reason for the flagging. If requested, the data can be placed in electronic format (computer disk). A hard copy of results accompanies the electronic format sent to the client.

F. 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.

G. Blanks

Various types of blanks are utilized by the laboratory in accessing data. In analyses where samples are extracted or digested, blanks are used to evaluate background analyte levels in the procedure. When blank values exceed the MDL, reanalysis and blank spiking are considered. However, re-analysis is unnecessary when unknown values exceed the blank by several orders of magnitude. Method blanks are not subtracted from the unknown results but rather are reported to the customer for their evaluation. Data associated with unusually high blank values is flagged for review by the laboratory section leader. If the reason for unusually high blanks can not be resolved, these values remain flagged in reports to the client and laboratory manager. In most instances these matters are resolved with appropriate corrective action.

In ICP-AES analysis it is sometimes desirable to run blank samples between each unknown to monitor low level drift during analysis. This will be done only by request from the client and at additional charge.

H. Holding Times

Holding times for water samples as recommended by the EPA are strictly monitored (see appendix for list). Whenever holding times cannot be met, the

data is flagged and concerns and possible solutions will be discussed with the client.

I. Practical Quantitative Limits

Practical quantitative limits (see section 9.0 part E) are established for each analysis in the laboratory. Result values that fall below the PQL will be reported as less than the PQL value with a "<" sign and numeric value.

J. External QA/QC Groups

The ST&RAL currently participates in several exchange programs for QA/QC purposes.

For Soil samples:

MN Department of Agriculture Soil Testing Laboratory Certification Program (MN Department of Agriculture, 90 West Plato Boulevard, St. Paul, MN 55107-2094)

North American Proficiency Testing Program (Soil Science Society of America, 677 South Segoe Road, Madison WI 53711)

For Plant Samples:

North American Proficiency Testing Program (Soil Science Society of America, 677 South Segoe Road, Madison WI 53711)

7.0 PERFORMANCE AND SYSTEM AUDITS

A performance audit of the laboratory system is done at least annually by the laboratory manager often in conjunction with a review of the exchange sample results. Included in the audit are sample login procedures, sample storage, sample preparation and analysis, instrument records, and QC sample performance. Results of the audit will be discussed with the appropriate section leader along with any recommendations.

8.0 PREVENTIVE MAINTENANCE

Preventive maintenance in the laboratory is the responsibility of the section leaders. Each SOP contains recommendations to be followed on a daily usage basis. Individual instruments have an accompanying log book where the maintenance performed is documented. In the event that staff can not repair the equipment on the premises, an electronic repair service is available on the St. Paul campus at Electronic Instrument Services, 25 Biological Sciences Center.

9.0 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:

$$RPD = 100[(X_1-X_2)/\{(X_1+X_2)/2\}]$$

Where RPD = Relative Percent Difference

X_1 = First observation of unknown X

X_2 = 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 and from the Canadian Centre for Mineral and Energy Technology for use as control checks on accuracy. An industrial compost containing certified levels of trace metals and analytes is obtained from the European Community Bureau of Reference and a municipal sludge certified by the US EPA are used for daily control of accuracy for compost analysis. 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 section leader 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. For ICP-AES analysis, the IDL is defined as two times the standard deviation calculated by observation on eleven replicate reagent blank samples. For reporting purposes, the laboratory prefers to not use this value for the lower reporting limit.

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 for the ICP-AES 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 MDL = (t) x (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. PQLs

The practical quantitation limit is the lowest value that can be arrived at reliably during normal routine laboratory analysis. For most analyses, including ICP-AES, this is specified as five times the IDL. This value is routinely used as the reporting limit for unknowns reported to the client.

10.0 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 and Section Leader. Since laboratory section leaders are in direct control of and are well experienced in laboratory procedures, they perform most corrective action with established protocol. 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. If the problem cannot be corrected by the section leader, the laboratory manager is consulted on how to proceed. The action taken is recorded in the log book accompanying each instrument.

11.0 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.

12.0 FILE HANDLING AND STORAGE

Analytical data files including data, calculations, and QA/QC results are stored in the Crops Research or Crops Services Building for a minimum of seven years. The analytical request form filled out by the client, a copy of the final report sent to the client, and all pertinent raw data is filed by date received and job number given to each sample batch submitted by the client upon arrival. The initial storage is located in the laboratory office where files are placed in binders by fiscal year and held for two years. Subsequently, the files are stored in boxes in the Crops Services Building for seven years or as long as space allows.

13.0 APPENDICES

Appendix A. ANALYTICAL SOPs

Copies of any or all procedures currently being performed in the ST&RAL are updated on a timely basis and made available to any client upon request.

Appendix B. RESUME SKETCHES

Roger Eliason: Laboratory Manager, MS Chemistry, 26 years experience in ST&RAL

Russell Anderson: ICP Section Leader, 27 years experience in ST&RAL

William Dancer: Special Materials Section Leader, MS Soil Science; PhD Soil Science/Horticulture, 16 years experience in ST&RAL

Som Lekhakul: Research Soil and Soil Testing Section Leader, PhD - Soils, 18 years experience in ST&RAL

Margaret Miller: Plant Section Leader, BS Horticulture, 12 years experience in ST&RAL

Appendix C. CLEANING PROCEDURE FOR GLASSWARE AND PLASTICWARE

I. Remove contents from labware containers (soil, plant tissue, acid, extracting solution, etc.) and dispose according to environmental guidelines. Rinse container once with tap water.

NOTE: Never leave an unmarked container of solution or solid material standing around. It could be dangerous!

Throw out chipped or cracked labware.

II. Soak and wash labware in warm soapy water.

A. A 1% solution or stronger of liqui-nox phosphate-FREE detergent should be used.

B. Use a soft-bristled brush for cleaning labware.

Check brush for exposed sharp edges or metal points which can scratch labware. Throw out old brushes.

C. Volumetric flasks and other labware in which the brush cannot clean all interior surfaces should be filled 1/2-full with soapy water and swirled.

D. Pipettes and burettes should soak in soapy water with the tip up. Pipettes are cleaned with an auto-washer and acid rinsed.

III. Rinse soap film from labware with tap water.

A. For labware that does not require acid rinse (check test procedure), rinse 3 times with deionized water (DI H_2O). Labware used for trace metal analysis is rinsed at least three times with Type I water.

B. For labware that requires an acid rinse (check test procedure):

1. 10% HCl bath, (800 mLs of concentrated hydrochloric acid in one dishpan of DI H_2O, about 8 liters). Soak labware overnight and rinse 3 times with DI H_2O.

2. 10% HNO_3, (800 mLs of concentrated nitric acid in one dishpan of DI H_2O, about 8 liters). Soak labware overnight and rinse 3 times with DI H_2O.

C. Labware used for total phosphorus requires a 50% HCl acid soak overnight, followed by a DI rinse.

D. Labware used for total metals, AA Hydride and AA furnace work requires a 25% HNO_3 rinse. (Use instra-analyzed or double-distilled nitric acid.)

E. Acid rinse notes:

1. The acid used in the 10% HCl and 10% HNO_3 bath can be any reagent grade.

2. When preparing an acid bath, add concentrated acid to deionized water and mix. (Never add water to acid.)

3. Dishpans used for soapy water, HNO_3, and HCl acid baths should be labeled and not used for other rinses. (i.e. a dishpan labeled HNO_3 should not be filled with 10% HCl or soapy water.)

4. All acid baths should be prepared and stored in a fume hood. Prepare fresh baths after 1 week of use.

CAUTION: ALWAYS WEAR GLASSES AND GLOVES WHEN HANDLING ACID SOLUTION.

IV. Allow labware to dry overnight inverted on drying racks or trays.

NOTE! Water will spread out and flow evenly on clean labware. Water will form droplets caused by oil and dirt on dirty labware.

V. Store in a dust- and contaminate-FREE area (cabinets, sealed bags, etc.) in the designated location.

A. Keep glassware designated for low level ICP and AA metal work stored separately in a well protected environment to avoid contamination.

B. Whenever possible, do not use glassware dedicated to a particular test for another test. If it is unavoidable, then make sure that the glassware is thoroughly cleaned, including acid rinsing when necessary, before replacing. A glassware blank is highly advisable if this is necessary.

C. Acid rinse any glass ware that has been used for high levels of a chemical. This will prevent the accidental contamination of the next reagent or standard by a carry-over from the previous solution.

VI. Other cleaning solutions

A. Dichromate - sulfuric acid solution

1. Dissolve 92 g $Na_2Cr_2O_7 2H_2O$ (sodium dichromate); potassium dichromate can be used, but is less soluble) in 485 mL H_2O cautiously

add while stirring 800 mL concentrated H_2SO_4. The final solution is red in color.

2. This solution can be re-used until it begins to turn green. At that point it should be discarded properly as a hazardous waste.

3. After this solution is used to clean labware, rinse the labware with 10 washings to remove cleaning solution.

4. Handle this solution carefully. IT IS DANGEROUS!

B. Aqua Regia Solution

1. 3 parts concentrated HCl, 1 part concentrated HNO_3
CAUTION: VERY CORROSIVE!

C. Alcoholic potassium hydroxide or sodium hydroxide

1. Add 1 liter ethanol (95%) to 120 mLs H_2O containing 120 g NaOH or 105 g KOH.

2. Good for removing carbonaceous material. Avoid prolonged contact with ground glass joints.

D. Trisodium phosphate

1. Add 57 g Na_3PO_4 and 28.5 g sodium oleate to 470 mLs H_2O.
2. Good for removing carbon residue.

E. NaOH - EDTA

1. Prepare a solution consisting of 2% NaOH and 1% EDTA.

2. For metal decontamination, soak labware for about 2 hours.

F. No-chromix brand cleaning solution

1. This is available commercially. It has the advantage of containing no metallic ions.

2. Dissolve powder in concentrated sulfuric acid. The final solution is clear.

3. The solution can be re-used. It will turn orange when the oxidizer is used up.

4. HANDLE WITH CARE ... its clear nature is deceptive.

G. Acetone

1. Should be used to remove oil and grease from glassware.

2. It is extremely flammable, DO NOT USE near flames or in poorly ventilated situations.

3. It is miscible with water. Wash with soapy water and rinse well after use.

Appendix D. Summary of Water Sampling and Handling Requirements

See attached

Appendix E. Hazardous Waste Form (Example)

See attached

Appendix F. Analytical Data Report (Example)

See attached

Appendix G. Minnesota Department of Agriculture Soil Testing Laboratory Certificate

See attached