

**SAMPLING AND ANALYSIS
PROTOCOL**

For Ontario Regulation 267/03 Made under the
Nutrient Management Act, 2002

July 20, 2007

Prepared by

**Ministry of Agriculture, Food and Rural Affairs
Ministry of the Environment**

Table of Contents

1.0	INTRODUCTION	5
1.1	Background to Act and Regulations	5
1.2	Health and Safety	5
1.3	Sampling Frequencies	5
1.3.1	Soils	5
1.3.2	Non-agricultural source materials	8
1.4	Averaging of Results	10
1.5	Sampling Locations	10
2.0	SAMPLING METHODS	11
2.1	Sample Handling	11
2.2	Fluid Materials in Tanks and Lagoons - Mixed Materials	11
2.2.1	Sampling Patterns for Use in Lagoons	12
2.3	Sampling Fluids in Tanks or Lagoons when Agitation is not Feasible	13
2.3.1	Supernatant Materials	13
2.3.1.1	Sampling Supernatant Materials in Enclosed Tanks	14
2.3.1.2	Sampling Supernatant Materials in Open Tanks	16
2.3.1.3	Sampling Supernatant Materials in Lagoons	16
2.3.2	Sludge Materials	17
2.3.2.1	Sampling Sludge Materials in Enclosed Tanks	18
2.3.2.2	Sampling Sludge Materials in Open Tanks	19
2.3.2.3	Sampling Sludge Materials in Lagoons	19
2.3.3	Sampling Materials in Straight Walled Tanks	20
2.4	Solid Materials in Piles or Large Containers	20
2.5	Solid and Mixed Materials from Continuous Processes and Unloaders	21
2.6	Field Quality Control (QC)	22
2.7	Cleaning and Prevention of Cross Contamination	23
2.7.1	Special Cleaning Procedures for Sampling for Trace Organic Analysis	23
3.0	LABORATORY ANALYSIS	25
3.1	Laboratory Quality Management	25
3.2	Laboratory Method	25
3.3	Method Detection Limit (MDL)	26
3.4	Reporting Detection Limit (RDL)	28
3.5	Precision	28
3.6	Accuracy and Recovery	29
3.7	Method Linearity	29
3.8	Recommended Laboratory QC/QA Procedures	30
3.9	Data Acceptance Criteria	31
3.10	Data Reporting	31
4.0	DATA QUALITY REQUIREMENTS	33

4.1	Guidance on Selecting Laboratories for Analysis	33
4.2	Analysis - Soil	34
4.2.1	Soil pH	34
4.2.2	Soil Buffer pH	35
4.2.3	Available Nutrients – Phosphorus	36
4.2.4	Available Nutrients – K, Mg and Ca	37
4.2.5	Available Nutrients – Zn, Zn Index	39
4.2.6	Available Nutrients – Mn, Mn Index	40
4.2.7	Available Nutrients – Nitrate N	41
4.2.8	Metals - Cd, Cr, Co, Cu, Pb, Mo, Ni, and Zn	42
4.2.9	Mercury	44
4.2.10	Arsenic and Selenium	46
4.2.11	Boron - Hot Water Extraction	48
4.3	Analysis – Land Applied Materials	49
4.3.1	Hydrogen Ion (pH)	49
4.3.2	Electrical Conductivity	50
4.3.3	Total Dry Matter	51
4.3.4	Total Volatile Solids (Organic Matter)	52
4.3.5	Total Kjeldahl Nitrogen	53
4.3.6	Ammonia and Ammonium - Nitrogen	54
4.3.7	Nitrate and Nitrite - Nitrogen	55
4.3.8	Organic Nitrogen	57
4.3.9	Metals - Cd, Cr, Co, Cu, Pb, Mo, Ni, and Zn	58
4.3.10	Mercury	60
4.3.11	Arsenic and Selenium	62
4.3.12	Total Phosphorus, Potassium, Sodium and Boron	64
4.3.13	<i>E. coli</i> (Only Sewage Biosolids)	65
5.0	ACRONYMS	66
6.0	GLOSSARY	67

LIST OF TABLES

Table 1-1	Standards for Regulated Metals for Sewage Biosolids	7
Table 1-2	Standards for Regulated Metals for Land Applied Materials Other than Sewage Biosolids	8
Table 1-3	Sampling frequencies for regulated metals ¹ , <i>E. coli</i> , total Kjeldahl nitrogen, ammonium nitrogen, nitrate nitrogen, total solids, volatile solids and total phosphorus	9
Table 2-1	Field Quality Control Procedures	23
Table 3-1	Method Performance Characteristics	26
Table 3-2	Student's t Values at the 99 Per Cent Confidence Level	28
Table 3-3	Laboratory QC Data	31

1.0 INTRODUCTION

Proper sampling and analytical techniques are critical to accurately determine the nutrient content and other properties of materials. This has always been important, but has now become a legal requirement under the *Nutrient Management Act, 2002* (“NMA”). The techniques described in this document are intended to meet the requirements of the Regulation under the Act. They can also provide guidance for other sampling and analysis requirements with similar goals.

1.1 Background to Act and Regulation

A key component of the Regulation is the requirement for a nutrient management plan (“NMP”). To complete a meaningful NMP, it may be necessary to know the concentrations of nutrients and contaminants in both the soil and the materials that may be applied to land.

The Regulation lays out what materials need to be sampled and analyzed, how frequently they need to be sampled, and which parameters need to be measured. These are minimum requirements. It may be desirable to sample more frequently, or to analyze for additional parameters, to optimize the management of land applied materials.

1.2 Health and Safety

There may be hazards associated with the physical act of sampling or with handling materials that could contain toxic material or *E. coli*. It is the responsibility of the sampler to have taken all necessary precautions and to act according to any applicable health and safety regulations.

1.3 Sampling Frequencies

1.3.1 Soils

Soils may be sampled for two different purposes: to assess the initial nutrient levels in the soil, which will guide the application of nutrient containing materials for agronomic and environmental purposes, and to determine the acceptability of the site for receiving the particular material.

Soils Receiving Nutrients

Persons applying nutrients to fields on farm units where a NMP is required, must collect a representative soil sample from each field as part of developing the initial NMP, and then at least once during each five-year period for subsequent plans. The results from analyzing these samples are entered into the NMP.

Where nutrient levels fluctuate widely within the five year interval it may be appropriate to sample a field more frequently than is required. This situation can occur on sandy soils where crops that are removing large amounts of nutrients are grown. Silage corn, forages and processing tomatoes all remove large quantities of potassium from soil; therefore, soil test levels for potassium can decline quickly to the point where yields are reduced.

Soils must be analyzed for soil pH and, if the soil has a pH below 6.0, for buffer pH. They must also be analyzed for available phosphorus (using the sodium bicarbonate extractant) and available potassium (using the ammonium acetate extractant). In addition, the sample may be analyzed for available magnesium, nitrate nitrogen, or the manganese and zinc availability indices.

It is necessary to know the available phosphorus concentration of a soil prior to applying nutrients so that application rates and setback distances can be properly determined. The soil must have been tested for sodium bicarbonate extractable phosphorus content within the five years immediately prior to applying the nutrients to land.

Soils Receiving Non-Agricultural Source Materials

Persons applying non-agricultural source materials must, in addition to the nutrient analyses, have representative samples analyzed for the total content of each of the eleven regulated metals (Tables 1-1 and 1-2). These samples must have been collected within five years prior to the application of non-agricultural source materials, as part of the preparation of the initial and subsequent NMPs.

In the Regulation, the maximum allowable metal concentrations in soils receiving sewage biosolids, are based on the "mean metal content of uncontaminated Ontario soils". In many soils, metal concentrations will be higher than the mean. For some soils, one or more metal concentrations may already exceed the maximum allowed in the Regulation. It is therefore necessary that soil testing be conducted prior to the first application of sewage biosolids or other wastes to determine the suitability of the soil. Samples collected as per Section 2.1 of this document shall be analyzed for the eleven metals listed in the Regulation. The sampling and testing for pH, sodium bicarbonate extractable phosphorus, and the eleven regulated metals must have been undertaken within the five years preceding application of a non-agricultural source material to land.

Summaries of acceptable analytical methods are presented in Section 4.

Table 1-1 Standards for Regulated Metals for Sewage Biosolids

Regulated Metals	Maximum metal concentration in material to be applied up to 22 tonnes per ha per 5 years	Maximum metal concentration in material to be applied up to 8 tonnes per ha per 5 years	Maximum permissible metal addition to soil receiving non-agricultural source materials	Maximum metal concentration in soils receiving non-agricultural source materials
	(mg / Kg of TS ¹ dw ²)	(mg / Kg of TS ¹ dw ²)	(Kg / Ha / 5 Years)	(mg / Kg of Soil, dw)
Arsenic	75	170	1.40	14
Cadmium	20	34	0.27	1.6
Cobalt	150	340	2.70	20
Chromium	1060	2800	23.30	120
Copper	760	1700	13.60	100
Mercury	5	11	0.09	0.5
Molybdenum	20	94	0.80	4
Nickel	180	420	3.56	32
Lead	500	1100	9.00	60
Selenium	14	34	0.27	1.6
Zinc	1850	4200	33.00	220
¹ TS means total solids. ² dw means dry weight.				

Table 1-2 Standards for Regulated Metals for Land Applied Materials Other than Sewage Biosolids

Regulated Metals	Maximum metal concentration in materials that contain total solids of less than 10,000 mg of material per litre	Maximum metal concentration in materials that contain total solids equal to or greater than 10,000 mg of material per litre	Maximum permissible metal addition to soil receiving non-agricultural source materials	Maximum metal concentration in soils receiving non-agricultural source materials
	(mg of material/ L)	(mg / Kg of TS ¹ dw ²)	(Kg / Ha / 5 Years)	(mg / Kg of Soil, dw)
Arsenic	1.70	170	1.40	14
Cadmium	0.34	34	0.27	1.6
Cobalt	3.40	340	2.70	20
Chromium	28	2800	23.30	120
Copper	17	1700	13.60	100
Mercury	0.11	11	0.09	0.5
Molybdenum	0.94	94	0.80	4
Nickel	4.20	420	3.56	32
Lead	11	1100	9.00	60
Selenium	0.34	34	0.27	1.6
Zinc	42	4200	33.00	220
¹ TS means total solids.				
² dw means dry weight.				

1.3.2 Non-Agricultural Source Materials

Non-agricultural source materials are required to be sampled and analyzed at least as frequently as specified in the following tables. The sampling requirements in Table 1-3 apply to all non-agricultural source materials. The requirements to sample for *E. coli* analysis apply only to Sewage Biosolids.

Table 1-3 Sampling frequencies for regulated metals¹, *E. coli*, total Kjeldahl nitrogen, ammonium nitrogen, nitrate nitrogen, total solids, volatile solids² and total phosphorus.

Size of Generators	Sampling Frequencies
Generators of sewage biosolids and with an approved design capacity not greater than 45,400 m ³ / day, or generators of other non-agricultural source materials that generate not more than 2,500 tonnes/year, dry weight basis.	Two samples within 30 days prior to actual land application and 2 additional samples within 90 days prior to land application with samples taken a minimum of 2 days apart.
Generators of sewage biosolids, with an approved design capacity greater than 45,400 m ³ /day, or generators of other non-agricultural source materials that generate more than 2,500 tonnes/year, dry weight basis.	2 samples per month, with samples taken a minimum of two days apart.
<p>¹See Table 1-1 for the list of regulated metals. ²For the purpose of the General Regulation, volatile solids shall be taken as equivalent to organic matter.</p> <p>For all situations, results must be available for at least one sample collected within 30 days prior to (and including) the day of land application and two additional samples collected within 90 days prior to land application.</p> <p>Reduction of Sampling Frequency</p> <ol style="list-style-type: none"> 1. For metals analysis, if the mean plus two standard deviations calculated using the last twelve samples or using the last year's worth of samples, whichever is the greater number of samples, is less than the allowable limits for all metals, then the sampling frequencies above may be reduced by half. 2. For <i>E. coli</i>, if the running four-sample geometric mean of the last twelve samples or of the last year's worth of samples, whichever is the greater number of samples, always meets the criteria of less than 2×10^6 CFU/g, then the sampling frequencies above may be reduced by half. 3. For nutrient analysis, if the coefficient of variation calculated using the last twelve samples or using the last year's worth of samples, whichever is the greater number of samples, is less than twenty per cent, then the sampling frequencies above may be reduced by half. <p>When any of the above three conditions are violated, sampling frequencies must return to the original frequencies.</p>	

In situations where materials are transferred from storage at the generating site to a temporary storage facility, for sampling purposes, the temporary storage

facility can be regarded as being part of the plant if and only if the material is in temporary storage for less than four weeks prior to land application.

If this requirement is met, then the most recent sample results from the generating facility may be used. If the material is in temporary storage for a longer period of time, if the material is mixed with any materials from other sources, or if the material is managed in such a way that the nutrient or contaminant concentrations could be expected to have changed, then samples must be collected for analysis from the material in the temporary storage in accordance with Table 1.3.

1.4 Averaging of Results

Where a material is required to be analyzed for regulated metals or *E. coli*, the concentration of metals or *E. coli* in the material is considered to be the average of the concentrations in the four most recent samples. This allows for any variation that may occur in sampling or analysis of the materials, while maintaining protection of the environment. Metal concentrations are calculated as a simple arithmetic mean, where the concentrations of each of the metals in the previous four samples are added together and the resulting total is divided by four. *E. coli* concentrations are calculated as the geometric mean where the concentrations of *E. coli* in each of the previous four samples are multiplied together and the fourth root of the resulting product is calculated.

Where the mean concentration of any parameter exceeds the allowable level, and the generator still intends to land apply the material, the generator has the option of re-sampling the material. This is done by continuing to take representative samples with an interval between samplings of at least two days. The analytical results are then used to calculate the mean value. Sampling can continue on this basis until the mean value of the four most recent samples is within allowable limits for all parameters. This method is for use where a large value is skewing the mean, and that value may be due to a spurious analytical result.

1.5 Sampling Locations

Samples for nutrient analysis must be taken at a location or locations from which the material is being transported to land application sites. This is to provide the farmer with the best possible estimates of concentrations of total N, available N, and total P.

Samples that are being collected for total solids, volatile solids and regulated metals analysis must be collected from both the storage location from which the material is being taken to land application sites and from the location (i.e. the generation facility) from which the material is being taken to the centralized storage facility if materials from different sources are being mixed.

Samples of material that are to be analyzed for *E. coli* must be collected at a generating facility or a storage location immediately after the treatment process as outlined below.

In situations where materials are transferred from storage at the generating site to a temporary storage facility, for sampling purposes, the temporary storage facility can be regarded as being part of the plant if and only if the material is in temporary storage for less than four weeks prior to land application. If this requirement is met, then the most recent sample results from the generating facility may be used. If the material is in temporary storage for a longer period of time, if the material is mixed with any materials from other sources, or if the material is managed in such a way that the nutrient or contaminant concentrations could be expected to have changed, then samples must be collected for analysis from the material in the temporary storage.

2.0 SAMPLING METHODS

2.1 Sample Handling

A variety of containers are available for shipping subsamples to a laboratory for analysis. The receiving laboratory may have a preference for the type of container. Plastic bags or plastic lined paper are generally favoured because they keep each sample separated from the other, and prevent moisture from soaking any information sheets included with the samples. Samples to be analyzed for trace contaminants will require special handling and containers that are specific to each contaminant. The laboratory will provide information on the handling requirements for trace contaminants.

No special handling is required for samples to be analyzed for pH, metals, or most nutrients. It is desirable to air dry the samples if they are to be held for a long period of time. The samples should be held in a cool, dry location. The exception to this is samples to be analyzed for nitrate nitrogen, which must be cooled to below 10°C (preferably to below 4°C), and kept cool until analysis. If the samples for nitrate nitrogen are stored at room temperature, nitrification can occur within the sample and distort the analytical results.

2.2 Fluid Materials in Tanks and Lagoons - Mixed Materials

Fluid and semi-solid materials pose special challenges in collecting representative samples. Most of the fluid materials considered for application to land are suspensions rather than true liquids, and tend to settle into layers of varying density and nutrient content. Where these are to be applied to land in separate applications, (for example, the supernatant and the sludge from a lagoon), each layer must be sampled separately. In most situations, however, the material will be agitated prior to application to produce a relatively uniform

mixture. It is easiest to obtain a representative sample of the material in the tank or lagoon after it has been thoroughly agitated. These materials need to be sampled so that the sample represents the entire volume of material. Where agitation prior to sampling is not feasible, the procedures in Section 2.3 must be used.

Grab samples can be collected either directly from the storage following agitation, or as the material is being loaded onto the hauling or application equipment. A grab sample is single sample taken directly from the material being sampled, sub sample or a portion of a composite sample. A minimum of five grab samples must be collected from each storage. Lagoons or tanks containing more than 1,000 m³ should have additional grab samples taken at a rate of at least one additional grab per 200 m³ of material above 1,000 m³. Samples must be collected using a clean, non-metallic container (a 20 litre plastic pail works well). Place these grab samples in a larger non-metallic container, and keep the container covered except when the next grab sample is being added. Mix the resulting composite sample thoroughly to ensure homogeneity. Collect composite samples from it as required. Sample bottles must not be filled more than 1/2 to 2/3 full, so that there is enough headspace in the bottle to allow for the build-up of pressure and prevent bursting. Normally one 500 mL sample bottle will suffice for nitrogen, phosphorus and total solids analyses, and an additional 500 mL sample bottle, which can be taken from the composite mixture already collected, is required for metals analyses when these are required.

At large facilities, on-site nitrogen analyses may be useful to provide accurate information to individual farmers. Portable testing equipment can have advantages. If such equipment is used, source material from each storage location should be sampled at the time the material is being removed for spreading. Samples may be taken either from the spreader or from the tanker that conveys the material to the spreader.

2.2.1 Sampling Patterns for Use in Lagoons

Transect Method

When using the transect method, two transects should be carried out: one (1) transect across the length of the lagoon; and (1) transect perpendicular to the other across the width. The point where both transects intersect should be near the centre of the lagoon. Sampling along each transect should be carried out at a minimum of five (5) pre-determined sampling locations (e.g. take samples every 15 m along the transect).

Grid Method

When using a grid approach, the lagoon should be divided into blocks and sampling should be carried out at a minimum of five (5) pre-determined locations

equally spaced within the blocks. Additional sampling at a greater number of equally spaced locations within a greater number of blocks will improve the accuracy of the results.

2.3 Sampling Fluids in Tanks or Lagoons when Agitation is not Feasible

There are two situations where tanks or lagoons may be sampled without agitation: first, where the materials will be agitated prior to application, or second, where the stratified materials will be applied without mixing (i.e. supernatant and sludge). Sampling requirements in each case will be similar. However, in the special case of materials in tanks with vertical sides, which will be agitated prior to land application, a simplified sampling method can be used (see Section 2.3.3).

Samples for analysis must be representative of the contents of tanks or lagoons.

Special care is required to obtain representative samples from materials that have stratified. Each layer to be land applied separately should be sampled separately, and it may be appropriate to subdivide these layers. Because of the inherent variability in taking this type of sample, a minimum number of 10 grab samples should be taken for each composite, and at least 2 composite samples should be taken and analyzed separately for each identified layer. Lagoons or tanks containing more than 1,000 m³ of material should have additional grab samples taken at the rate of at least one additional grab per 100 m³ of material above 1,000 m³.

Lagoons with sloping sides present an even greater challenge, because the stratification will not be consistent across the entire area of the lagoon. A sample transect will need to be established to accurately represent the entire volume of material in the lagoon, with proportionately more samples from the deeper parts of the lagoon than from the shallow parts. All precautions must be taken to protect workers from injury when this type of sampling is carried out.

2.3.1 Supernatant Materials

When a fluid material containing suspended solids is stored in a tank or lagoon, the heavier suspended solids will settle to the bottom leaving a low-solids fluid that is commonly referred to as supernatant. For sampling purposes, supernatant is the fluid material between the settled solids sludge at the bottom and the scum on the surface. When only the supernatant is to be removed (i.e. irrigated on to land), the depth and thickness of the supernatant above the lower sludge interface, and the number of layers within the supernatant, must be determined in order to sample the supernatant.

2.3.1.1 Sampling Supernatant Materials in Enclosed Tanks

Sampling a supernatant material in an enclosed tank should be carried out from at least one sampling port (or hatch) at the top of the tank. If a second sampling port is available, repeat the sampling procedure. Sampling an enclosed fluid material from a sampling port at the top of the tank may be hazardous depending on the material stored in the tank and the potential for toxic or explosive vapours in the headspace of the tank. Before proceeding to sample an enclosed tank, sampling personnel should follow all appropriate health and safety procedures, including, but not limited to, the following:

- review all information concerning the tank, such as the type and capacity of tank, condition of tank, and known/suspected contents;
- inspect the ladder, stairs, catwalk or other structure to be used to access the sampling port to ensure that they will support the person(s) doing the sampling;
- inspect all sampling equipment (i.e. do you have all of the necessary sampling equipment?; has it been properly cleaned?)
- review all safety procedures and emergency contingency plans with regard to potential toxic or explosive vapours in the tank headspace;
- if the tank is metal, ensure that the tank is properly grounded; and
- remove all sources of ignition from the immediate area.

Where toxic or explosive vapours are likely to be present in the tank headspace, air quality measurements should be taken and sampling should only proceed if the readings meet acceptable air quality standards. In addition, before sampling commences, the tank headspace should be cleared of any toxic or explosive vapours using a high volume explosion proof blower.

Sampling Procedure

First determine the depth of the supernatant at the sampling location, from the upper scum interface to the lower sludge interface, using a weighted tape measure, probe line or other suitable measuring device. Then collect one (1) sample of supernatant from 30 cm below the upper interface with the scum layer, one (1) sample from mid-depth, and one (1) sample from 30 cm above the bottom interface with the sludge layer. These samples can be collected using various sampling equipment such as a subsurface grab sampler or bacon bomb sampler. For supernatants that are less than 1.5 m in depth, use a glass thief or Composite Liquid Waste Sampler (COLIWASA) to collect the sample.

Three (3) to five (5) samples taken at a sampling location usually will suffice for supernatants in a tank or lagoon where the original fluid material has been subjected to a prolonged settling period. Additional mid-point samples may be

necessary for materials recently placed in a tank or lagoon, or which contain solids that have a tendency to remain in suspension for long periods.

Mark the sample identification number, location and depth on the outside of each sample container. The sample container should be non-reactive with the sample material (see Table 2.1).

The three samples should then be compared for visual phase or layer differences. If there is a readily observable difference in colour or viscosity between the upper and mid-point samples, or between the mid-point and lower samples, an additional sample should be taken at the mid-point (half-way) depth between the two samples. By halving the distance between two discrete sampling points, the person doing the sampling can then determine the depth of each phase change and, more importantly, the thickness of each distinct layer.

A minimum of one sample from each phase or layer within the supernatant material must be collected and placed in a glass or plastic sample bottle or container. Sample bottles must not be filled more than 1/2 to 2/3 full, so that there is enough headspace in the bottle to allow for the build-up of pressure and prevent bursting. Normally one 500 mL sample bottle will suffice for nitrogen, phosphorus and total solids analyses, and an additional 500 mL sample bottle, which can be taken from the mixture already collected, is required for metals analyses when these are required.

Transport all collected samples to the laboratory for analysis as soon as possible after sampling to minimize potential sample transformations within the container.

Determining the Weighted Mean Concentrations of Test Parameters

The purpose of multi-layer sampling of a supernatant is to determine the concentrations of test parameters in the various layers on a volumetric basis. This information can then be used to determine the weighted mean concentrations of test parameters in the total volume of supernatant.

When the sampling is completed at all sampling locations, determine the measurements of the containing structure (i.e. inside diameter of the tank), and then use the layer depth and thickness information previously determined to calculate the volume of each layer of supernatant. Using the volume determined for each layer and the analytical results for the test parameters for each layer, calculate the weighted mean concentrations of the test parameters in the total volume of supernatant. Where replicate samples are taken from two or more sampling locations, first determine the mean depth and thickness of each layer, and mean concentrations of the test parameters in each layer, before calculating the weighted mean concentrations.

2.3.1.2 Sampling Supernatant Materials in Open Tanks

The procedure for sampling a supernatant material in an open (non-enclosed) tank is the same as that outlined in the 'Sampling Procedure' description in Section 2.3.1.1, except for the number of sampling locations. A minimum of two different locations must be sampled in order to characterize the supernatant material. Where there is a walkway over the tank, the locations may consist of randomly selected sites below the walkway. If there is no walkway, the sites should be randomly selected around the perimeter of the tank. Sampling locations should not be located close to inflow pipes or other inlets.

While the potential for toxic or explosive vapours is not as great as for enclosed tanks, they may still occur above an open tank. Sampling personnel should therefore follow the same safety procedures and take the same safety precautions as outlined in Section 2.3.1.1. At no time should sampling be carried out from above an open tank containing hazardous material. Where a material to be sampled is considered hazardous, sampling should only be undertaken from outside the perimeter of the tank using appropriate protective equipment.

The procedure for determining the weighted mean concentrations of test parameters in the total volume of supernatant is the same procedure as outlined in the 'Determining the Weighted Mean Concentrations of Test Parameters' description in Section 2.3.1.1.

2.3.1.3 Sampling Supernatant Materials in Lagoons

Sampling supernatant materials in lagoons poses a challenge because the sides are sloping rather than vertical, as is the case for tanks. The length and width of the lagoon and the steepness and length of the side slopes, must be known when determining the volume of each layer of supernatant.

When supernatant is only pumped from the upper portion of a lagoon (e.g. the top 60 cm), it is only necessary to take samples from that portion. Samples taken from this upper layer should represent the contents of the layer for several weeks. However, the surface contents of a lagoon will change from month to month due to precipitation, evaporation, and temperature fluctuations. Therefore, time of sampling should be as near as possible to when the supernatant is to be pumped out or removed. Two simple methods for sampling follow:

Bucket-Toss Method

Attach a rope to a small plastic bucket and then throw the bucket out into the lagoon and let it sink. Then carefully pull the bucket back to shore making sure that it does not contain surface scum or solids. Swirl the bucket and then pour about 1 litre of the contents into a second clean plastic bucket. Repeat this four (4) more times from different locations around the perimeter of the lagoon. Then swirl the bucket with the composite sample and pour a subsample into a clean,

plastic or glass container such as a 500 ml wide mouth amber glass jar with a Teflon-lined screw cap. The number and amount of samples required for various analyses are outlined in the 'Sampling Procedure' description in Section 2.3.1.1. More than one subsample may be required.

Dipper Method

Tape a clean plastic bottle securely to a pole that is long enough to reach over any scum collected at the edge of the lagoon. Dip out at least five (5) individual samples at different depths and locations and pour them into a clean plastic bucket. Swirl the bucket and then pour a subsample into a clean plastic or glass container. The number and amount of samples required for various analyses are outlined in the 'Sampling Procedure' description in Section 2.3.1.1. More than one subsample may be required.

Sampling deep supernatant materials (e.g. 3 to 4 m deep) in lagoons, particularly in large lagoons, should be carried out from the surface by boat using either a transect or grid sampling approach (see Section 2.2.1). Large lagoons containing liquid manure or sewage biosolids should be sampled using one of these methods. Lagoons that contain potentially hazardous materials, however, should never be sampled from a boat. Instead, they should be sampled from the perimeter banks or piers using appropriate protective equipment.

When sampling from a boat at a sampling location, follow the sampling procedures outlined in the 'Sampling Procedure' description in Section 2.3.1.1.

When the sampling is completed at all sampling locations, determine the surface area of the lagoon (i.e. length and width) and the steepness of the side slopes underneath the stored material by referring to the engineering design or by consulting with the owner. This information, along with the mean depth and thickness of each layer (determined by averaging the depths and thicknesses obtained at all sampling locations), should then be used to calculate the volume of each layer of supernatant. Then combine the volume determined for each layer with the analytical results for the test parameters for each layer, and calculate the weighted mean concentrations of the test parameters in the total volume of supernatant.

2.3.2 Sludge Materials

When a fluid material containing suspended solids is stored in a tank or lagoon, the heavier suspended solids settle to the bottom resulting in a high-solids material called sludge. For sampling purposes, sludge is the solid that has settled at the bottom of a tank or lagoon that has separated from a liquid either during processing or as a result of prolonged storage in a tank or lagoon.

2.3.2.1 Sampling Sludge Materials in Enclosed Tanks

Sampling a sludge material at the bottom of an enclosed tank should be carried out from at least one sampling port (or hatch) at the top of the tank. If a second sampling port is available, repeat the sampling procedure. Sampling any fluid or high-solids materials in an enclosed tank from a hatch at the top of the tank may be hazardous depending on the material stored in the tank and the potential for toxic or explosive vapours in the headspace of the tank. Therefore, before proceeding to sample a sludge in an enclosed tank, sampling personnel should undertake the same assessments and take the same precautions as outlined in Section 2.3.1.1.

Sampling Procedure

The concentrations of settled solids in sludge at the bottom of a tank or lagoon will vary both horizontally and vertically. And, while the sludge at the bottom of a tank or lagoon will separate into layers, it is often difficult to make visual distinctions between layers. Therefore, grab sampling of the sludge at different depths should be undertaken.

Sludge samples should be taken using a bacon bomb sampler, sludge judge or other suitable sampling device.

First determine the depth of the sludge at the sampling location. This can be accomplished using a weighted tape measure, probe line or other suitable measuring device. Then collect one (1) sample of sludge at 50 cm depth intervals (e.g. at 50 cm, 100 cm, 150 cm, etc.). Pour each sample into a clean plastic bucket or other suitable container. Then mix the composite sample in the container and pour a subsample into smaller container for transport to the laboratory. Mix the resulting composite sample thoroughly to ensure homogeneity. Collect composite samples from it as required. Sample bottles must not be filled more than 1/2 to 2/3 full, so that there is enough headspace in the bottle to allow for the build-up of pressure and prevent bursting. Normally one 500 mL sample bottle will suffice for nitrogen, phosphorus and total solids analyses, and an additional 500 mL sample bottle, which can be taken from the composite mixture already collected, is required for metals analyses when these are required.

Transport all collected subsamples to the laboratory for analysis as soon as possible after sampling to minimize potential transformations within the container.

Determining the Mean Concentrations of Test Parameters

When sampling is completed at all sampling locations, determine the measurements of the containment structure (e.g. inside diameter of the tank).

Then determine the mean depth and thickness of the sludge using the values recorded at all sampling locations. The volume of sludge can then be determined using this information. Next determine the mean concentrations of test parameters in the sludge by averaging the analytical results obtained for all subsamples.

2.3.2.2 Sampling Sludge Materials in Open Tanks

The procedure for sampling a sludge material in an open (non-enclosed) tank is the same as that outlined in the 'Sampling Procedure' description in Section 2.3.2.1, except for the number of sampling locations. A minimum of two different locations must be sampled in order to characterize the sludge material. Where there is a walkway over the tank, the locations may consist of randomly selected sites below the walkway. If there is no walkway, the sites should be randomly selected around the perimeter of the tank. Sampling locations should not be located close to inflow pipes or other inlets.

While the potential for toxic or explosive vapours is not as great as for enclosed tanks, they may still occur above an open tank. Sampling personnel should therefore follow the same safety procedures and take the same safety precautions as outlined in Section 2.3.1.1. At no time should sampling be carried out from above an open tank containing hazardous material. Where a material to be sampled is considered hazardous, sampling should only be undertaken from outside the perimeter of the tank using appropriate protective equipment.

The procedure for determining the mean concentrations of test parameters in the sludge as a whole is the same procedure as outlined in the 'Determining the Mean Concentrations of Test Parameters' description in Section 2.3.2.1.

2.3.2.3 Sampling Sludge Materials in Lagoons

Sampling sludge materials in lagoons poses a challenge because the sides are sloping rather than vertical, as is the case for tanks. The steepness and length of the side slopes, and overall depth of the lagoon, must be known when determining the depth and volume of sludge in a lagoon.

Sampling sludge materials, particularly in large lagoons, should be conducted by boat using either a transect or grid sampling approach (see Section 2.2.1). Lagoons that contain potentially hazardous materials, however, should never be sampled from a boat. Instead, they should be sampled from the perimeter banks or piers using appropriate protective equipment.

When sampling from a boat at a sampling location, follow the sampling procedures outlined in the 'Sampling Procedure' description in Section 2.3.2.1.

When the sampling is completed at all sampling locations, determine the surface area of the lagoon and the steepness and length of the side slopes underneath the stored material by referring to the engineering design or by consulting with the operator. This information, along with the mean depth and thickness of sludge (determined by averaging the depths and thicknesses of sludge obtained at all sampling locations), should then be used to calculate the total volume of sludge in the lagoon.

Then determine the mean concentrations of test parameters in the total volume of sludge by averaging the analytical results obtained at all sampling locations.

2.3.3 Sampling Materials In Straight Walled Tanks

In the special case where the material is not mixed prior to sampling, but will be mixed prior to land application, and is in a tank with vertical sides, a simplified sampling procedure may be used. The layers do not need to be sampled or analyzed separately, but samples can be taken to include the entire depth of the tank. This can be accomplished with a pipe or tube that is inserted vertically to the entire depth of the tank, and then sealed at the bottom end to collect a complete sample.

2.4 Solid Materials in Piles or Large Containers

Sampling from large piles of materials, such as solid manure or paper fibre biosolids, can pose problems with respect to obtaining samples that are representative of the piles. It is difficult to collect any samples other than surface samples. Since some materials have a tendency for fine and coarse fractions to separate when piled, surface samples are not likely to be representative. Because many piled materials have a large amount of inherent variability collecting a representative sample will be difficult at any time.

The preferred method of sampling piles is for samples to be obtained from different depths and mixed together such that the resulting composite sample is representative of the pile. This is most easily accomplished when the storage is being emptied, as grab samples can be collected as the material is being loaded. If the piles must be sampled in situ, then some form of equipment to extract cores from the entire depth of the pile will be necessary.

Solid materials can be highly variable in their chemical or bacterial concentrations, and it is therefore necessary that for such materials at least 10 grab samples for piles of 100 m³ or less be collected and mixed to form the sample. For larger piles, proportionately more grab samples should be taken. Place the grab samples in a clean container (see Table 2.1) that can be covered or sealed between sample additions to prevent moisture loss. Once all the grab samples have been collected, empty them onto a large surface (of appropriate

composition) for mixing. The most efficient way of obtaining a representative sample is to mix and chop the material with a clean shovel, then divide the pile into quarters. Discard two opposite quarters, combine the remaining two, and repeat the process until a composite sample of the desired size is obtained. The composite sample should total approximately 1 kg. The same result can be obtained by taking small subsamples from all sections of the sample until a sample of approximately 1 kg has been obtained. Alternate methods approved by a recognized standards organization may also be followed. Place the composite sample in a container or bag (see Table 2.1), then place in an appropriate container for shipping to the laboratory for analysis.

2.5 Solid and Mixed Materials from Continuous Processes and Unloaders

In some situations it may be necessary or desirable to sample a material that is resulting from a continuous process or from an unloader. It is likely that proper sampling from the waste stream will produce more accurate and representative samples at less cost than sampling of the final large pile or hopper. The main principle in sampling waste streams is that the sample must be representative of the entire waste stream.

Discharges from a belt should be sampled with a scoop or shovel which has been chosen or fabricated to match the width and general contour of the belt as closely as possible. Grab samples can be taken at any convenient point along the belt as long as the entire width of the belt is being sampled. Any fines or liquid present on the belt must be included in the sample.

For any sampling strategy for waste streams, the sampling frequency and the number of grab samples combined into composite samples depend on the variability of the waste over time. Possibilities for taking representative samples include taking samples every hour over eight to twenty four hours (depending on the process schedule) and combined to form daily composites, as well as taking daily samples for a week and combining them into a weekly composite. Since the sampling period and number of samples will vary for each process, it is important that sampling personnel be familiar with the variability of the waste stream both over time and at different locations in the process. The sampling program must result in characterization of this variability as well as in the ability to properly classify the waste.

Often, solid discharges fall into a hopper or storage area directly from a process. In these situations, long-term composites may be obtained by sampling the material after it has accumulated. Random grab samples can be taken from the hopper or storage area provided that the sampling strategy provides samples that are representative of the material. It may be necessary to mix materials prior to sampling if separation of materials has occurred in the container.

2.6 Field Quality Control (QC)

Table 2-1 provides a summary of the field quality control procedures that must be used for sampling for nutrient management activities. Laboratories accredited through the Canadian Association for Environmental Analytical Laboratories (“CAEAL”) may have additional requirements for samples beyond what is required in the Sampling and Analysis Protocol. Those must be followed as well.

Table 2-1 Field Quality Control Procedures

	Nutrients	Metals	Organics	<i>E. coli</i>
Type of Sample	Composite	Composite	Composite	Composite
Container	Plastic, glass	Plastic, glass with plastic or Teflon lined lids	Solvent rinsed, amber glass with foil or Teflon lined lids	Sterilized plastic bags/appropriate container
Field QC samples	Recommend that QC program uses duplicates.	Recommend that QC program uses duplicates.	Recommend that QC program uses duplicates.	Recommend that QC program uses duplicates.
Storage	For nitrogen, in field keep cool and out of sun and refrigerate <10°C for storage		In field keep cool and out of sun and refrigerate <10°C for storage	In field, keep cool and out of sun and refrigerate at 0- 10°C for storage.
Additional Requirements			No contact of sample with plastics during sampling or storage	N/A

2.7 Cleaning and Prevention of Cross contamination

For all forms of sampling, equipment and containers must be cleaned and rinsed between collection of separate samples for analysis (that is, between sites, locations or sampling times), such that cross contamination of samples is minimized. Thorough washing of equipment with soap or detergent followed by a thorough rinse with clean water (preferably distilled or de-ionized) should be adequate for the standard parameters to be analyzed.

2.7.1 Special Cleaning Procedures for Sampling for Trace Organic Analysis

Analysis for trace organic compounds is not normally required; however there may be situations where materials proposed for land application are suspected of containing specific trace organic compounds due to the particular process used to produce them. Special considerations regarding prevention of cross contamination apply should there be a need to sample for trace organic constituents. The basic methodology for sampling for trace organics is the same as that for inorganics described in the preceding sections. However, samplers must adhere to the following additional procedures:

a) Control of Cross-contamination

Soil sampling for trace organic contaminants requires special techniques in order to avoid contamination both from other samples and from sampling equipment and containers. Where potentially dangerous levels of contaminants are suspected, the sampler should wear protective gloves made of solvent-resistant material (e.g., latex). Neither gloves nor bare hands should contact the sample directly.

b) Equipment Cleaning Procedures

The sampler must carefully clean all sampling equipment which contacts material directly (i.e. samplers, corers, knives) between sites. The recommended cleaning procedure is as follows:

1. Remove adhering particles of the material by scrubbing with dilute laboratory soap solution.
2. Rinse thoroughly with distilled water.
3. Rinse with acetone. *
4. Rinse with hexane. *

*Use methanol as the rinsing solvent where acetone or hexane are potential contaminants of concern.

5. Allow equipment to air-dry before sampling. Do not use a paper towel or cloth.

The sampler should place all grab samples in a stainless steel bowl and mix the soil prior to placing it in the sample jars. The bowl and mixing spoon/rod are cleaned as per the usual wash/rinse procedure described above. For analysis for volatile organic compounds ("VOCs"), grab samples must not be mixed, as these processes cause losses of the compounds of interest. Rather, the samples should be placed immediately into the appropriate containers.

c) Sample Containers and Sample Preservation

Solvent (hexane and /or acetone) rinsed, wide-mouthed amber-coloured glass jars with foil or Teflon lined lids are suitable for all classes of organic compounds (including PAH's, PCB's, pesticides, and VOC's).

The samples, with lids screwed on tightly, must be kept cool (preferably refrigerated, otherwise in coolers out of the direct sunlight) until delivery to the analytical laboratory.

3.0 LABORATORY ANALYSIS

3.1 Laboratory Quality Management

Laboratories participating in the analysis of soil and land applied materials as required by the NMA are required to have a sound quality management program.

Quality Management (QM) is that aspect of the over-all management function that determines and implements the quality policy. International Standard ISO/IEC 17025 outlines management and technical requirements for implementing a laboratory quality management system.

Laboratory Accreditation Requirement

Laboratories analyzing soil for available nutrients as required by the NMA must be accredited for the applicable nutrient tests by the Ontario Ministry of Agriculture, Food and Rural Affairs (“OMAFRA”) under the OMAFRA Agronomic Test Accreditation Program.

Laboratories analyzing land applied materials for nutrients as required by the NMA must be accredited by OMAFRA under the OMAFRA Agronomic Test Accreditation Program, or by a body which accredits laboratories to ISO/IEC 17025 standards for analytical laboratories (e.g. the Standards Council of Canada through CAEAL).

Laboratories analyzing soil and land applied materials for metals and *E. coli* as required by the NMA must be accredited by a body which accredits laboratories to ISO/IEC 17025 standards for analytical laboratories (e.g. the Standards Council of Canada through CAEAL).

3.2 Laboratory Method

All laboratories participating in the analysis of soil and land applied materials for NMA activities must have a formal written method used for the analysis. Bench procedures must be documented in sufficient detail to ensure uniform application and must be readily available to technical staff.

Method Summary

A summary of the method used for such analysis may be required by the OMAFRA to review data. It will assist the OMAFRA in evaluating if the laboratory method/performance data is in compliance with the data quality requirements of this Protocol (Section 4.0).

A method summary should contain the following information as a minimum:

- Method Used, e.g., EPA 5030, MOE/LSB E3394 or your laboratory Reference Method.
- Method Principle – Brief description of sample preparation and instrumentation.
- Sample preservation if required.
- Sample storage temperature.
- Accreditation (laboratory/method) - Type of accreditation and name of accrediting body.
- Method performance characteristics – Provide such information in a tabular form. The example is given in Table 3-1.

Table 3-1 Method Performance Characteristics

Analyte	MDL	Accuracy	Precision		Method Linearity/Working Range
			Within-Run	Between-Run	
	Unit	% Recovery	% RSD*	% RSD	Unit

* RSD – Relative Standard Deviation

Provide the following information:

Accuracy: Material used for accuracy determination, e.g., in-house spiked matrix blank, CRM, or other and number of determinations used for this study.

Precision: Material used for precision determination, e.g., in-house spiked matrix blank, CRM, or other and number of determinations used for this study.

3.3 Method Detection Limit (MDL)

The method detection limit is a statistically defined method attribute. Measured results falling at or above this point are interpreted to indicate the presence of an analyte in the sample with a specified probability - usually greater than 99% - and assumes that sources of error in identification or biases in measurement are known and controlled.

Procedure for MDL Determination

Take a minimum of eight aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method.

If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed.

Calculate a result (x) for each sample/blank pair.

Calculate the standard deviation (S) of the replicate measurements as follows:

$$S = \sqrt{\left[\frac{\sum (x_i - \bar{x})^2}{(n - 1)} \right]}$$

where: x_i = the analytical results in the final method reporting units for the eight replicate aliquots (i = 1 to 8)

\bar{x} = the average of the eight replicate measurements

An alternative is to use historic within run replicate analysis data and calculate the standard deviation (S) of the replicate measurements as follows. This is suggested for soil samples.

$$S = \sqrt{\left[\frac{\sum (x_1 - x_2)_i^2}{(2 n)} \right]}$$

where:

x_1, x_2 = the two replicate results for each of the n replicate pairs
(minimum n = 40)

Compute the MDL as follows:

$$MDL = t_{(n-1, \alpha = 0.01)} S$$

where: $t_{(n-1, \alpha = 0.01)}$ is the Student's value appropriate for a 99% confidence level given the degrees of freedom n-1.

S = the standard deviation as determined above.

Table 3-2 Student's t Values at the 99 Per Cent Confidence Level

Number of Replicates	Degree of Freedom (n-1)	t (n-1)
7	6	3.143
8	7	2.998
9	8	2.897
10	9	2.821
11	10	2.764
16	15	2.603
21	20	2.528
26	25	2.485
31	30	2.457
∞	∞	2.369

3.4 Reporting Detection Limit (RDL)

This has been set at 1/10 of the maximum permissible contaminant concentration criteria or laboratory MDL, whichever is higher.

The Reporting Detection Limit requires laboratories to achieve MDL less than or equal to the RDL value.

Laboratories that achieve MDL less than RDL must therefore report results below RDL values.

3.5 Precision

Precision is the degree of agreement among independent measurements of the same quantity under specified conditions.

Both within-run and between-run precision must be established. This can be done by using replicate sample analysis (within-run) and analysis of spiked blank samples, in-house control or certified reference material, if and when available (between-run). Control limits for these should be established and maintained as part of the analytical performance criteria.

It is desirable to determine precision at $\approx 10\text{MDL}$.

Requirement - The precision requirement for each test is given in Section 4.

3.6 Accuracy and Recovery

Certified reference materials ("CRMs"), if and when available, should be used to assess laboratory accuracy. Accuracy is the degree of agreement of individual measurements with an accepted reference value. If a CRM of exactly the same type of material as the sample is unavailable, a similar CRM may be used. For example, a CRM of plant tissue or sludge may be used for manure analysis.

For metals, accuracy is based upon the analytical results compared to the listed values of the certified reference material. It is a certified value $\pm 20\%$ allowable error. For this program, certified reference material(s) are identified under each test (Section 4). Other CRMs may be used, provided they produce data within the above allowable range when subjected to the same method principle.

Recovery is the measured value of that portion of an analyte or surrogate added to a sample that is recovered by testing.

The accuracy/recovery requirement for each test is given in Section 4.

Participation in one or more proficiency testing ("PT") programs also demonstrates acceptable method performance.

3.7 Method Linearity

The linearity (working range) of the method for each analyte must be established and documented in the method. Linearity is the range over which the analytical system exhibits a linear or other well established relationship between the amount of material introduced into the analytical system and the instrument's response.

No sample result should be reported that is outside the calibration range of the method. If a result is too high, the sample should be diluted. If too low, a larger aliquot (portion) of sample must be analyzed to meet the requirements of the method detection limit.

3.8 Recommended Laboratory QC/QA Procedures

The following are recommended laboratory quality procedures:

Pre-service QC:

- lab-ware and reagent blanks
- instrument setup standard
- reference standard to validate in-house standards
- certified reference material to validate method recovery
- instrument detection limits (IDLs) and detector linearity curves (minimum of 3 point calibration)

In-service QC:

- baseline drift blanks
- standards
- instrument checks

Run quality QC and QA:

- method spiked blanks
- method blanks
- in-house matrix check material
- replicate sample (minimum of one set per run of 30 samples)
- spiked samples, if applicable.

Laboratories should maintain records of data to show that the analytical systems were in control at the time of analysis. The results of these quality control and performance-monitoring checks should be tabulated and summarized for ready retrieval, evaluation and auditing. A sample is shown in Table 3-3.

Table 3-3 Laboratory QC Data

Identify validation standards, in-house spiked matrix blank, CRM's, etc.

Analyte	Instrument Control		Run Control		
	Amount Injected (Unit)	Amount Recovered (Unit)	Blank (Unit)	Accuracy / Recovery (%)	Replicate Analysis (Sample #) (Unit)

a) Name/identify externally validated standard (s) used to verify calibration or validate in-house standards.

b) Name/identify material used for accuracy/recovery determination, e.g., in-house spiked matrix blank, CRM, other.

3.9 Data Acceptance Criteria

The basis for determining the acceptability of laboratory data should include the following:

- Method should be consistent with the principle as given under specific test (Section 4) has been applied.
- The performance characteristics (RDL, accuracy and precision) of a method used for NMA analysis should be within specifications as given under each test (Section 4).
- The results of all applicable quality control samples should be within the acceptable range. See specific tests (Section 4).
- The analytical system should be in control at the time of analysis.

3.10 Data Reporting

A laboratory's data-management system should establish and maintain direct links between sample information (such as source, field sample number or code, date and time sampled, tests required), and laboratory information (such as laboratory sample number or code, date and time analyzed, tests performed and identification of the analyst who did the work).

A properly recorded result shall include the test or analyte name or code, the units of measure, the method used for analysis and any qualifying remarks.

The number of digits following a decimal point should not exceed the number of digits after a decimal point appearing in the method detection limit.

Analytical results may be corrected to take into account any positive results of associated method blank for some specific analysis. A method blank result above the method detection limit is normally considered a positive result. The criteria or control limits for blank corrections should be determined by laboratories on the basis of historical data, and these should be documented. Otherwise, data should be reported without correction. If a correction is made, it should be clearly identified and described.

All data should be reported. Data below RDL should have remark as < RDL. Data below MDL should have remark as < MDL.

All data for soil and land applied materials (≥ 1 % solid) should be reported on a dry weight basis. Dry matter content should also be reported.

All data for dilute liquid land applied materials (< 1 % solid) should be reported on a volume basis.

4.0 DATA QUALITY REQUIREMENTS

Data quality requirements for the analysis of soil and land applied material for the Nutrient Management Act is given in this section.

Laboratories may use the methods that are referenced under specific tests or other validated methods that meet data quality requirements as given under each test.

4.1 Guidance on Selecting Laboratories for Analysis

A listing of laboratories accredited under the OMAFRA Agronomic Test Accreditation Program is available from the OMAFRA at any of its offices, in the crop production recommendation publications (e.g. OMAF publications 360, 363, 811), or from the OMAFRA website at www.omafra.gov.on.ca.

Laboratories may be accredited to ISO/IEC 17025 standards within Canada by either the Standards Council of Canada (SCC), or the CAEAL

A listing of SCC accredited labs can be obtained by contacting:

Standards Council of Canada

270 Albert Street, Suite 200

Ottawa ON, K1P 6N7

Telephone: (613) 238-3222

Fax: (613) 569-7808, or from their web site: www.scc.ca.

A listing of CAEAL accredited labs can be obtained by contacting:

Canadian Association for Environmental Analytical Laboratories

310-1565 Carling Avenue

Ottawa, ON K1Z 8R1

Telephone: (613) 233-5300

Fax: (613) 233-5501, or from their web site: www.caeal.ca

4.2 Soil Analysis

4.2.1 Soil pH

Matrix Soil

Analysis

This analysis is required at least once within the five years prior to nutrients being applied. Soil pH is measured in a saturated paste.

Method Principle

Soil pH is determined with a standard glass electrode pH meter in a saturated soil-water paste.

Sample Preparation

Samples must be air dried and crushed to pass a 2 mm sieve. Add sufficient distilled water to air-dried, crushed soil to make a saturated paste. There should not be any free water on top of the soil sample. Hand mix the sample well using a glass rod, and allow to stand for 15-20 minutes.

Instrumentation

Standardize the pH meter with both pH 7.00 and pH 4.00 buffers. Insert the pH electrodes into the paste and determine the pH while slowly moving the electrodes within the paste.

Laboratory QC Samples per Run

Calibrate the pH meter, according to manufacturer's directions, before each set of analysis.

Method Performance Criteria

Inter- and intra-lab precision must be within ± 0.3 pH units of the mean of samples from all accredited labs.

Reference Method

OMAFRA pH

4.2.2 Soil Buffer pH

Matrix Soil

Analysis

This analysis is required to determine the lime requirement of soil samples with a soil pH below 6.0. Buffer pH is measured into a sample of previously dried, crushed soil mixed with a Shoemaker-McLean-Pratt (SMP) buffer solution.

Method Principle

The reduction in pH of a standard buffer solution is measured to determine the amount of lime required to bring the soil pH of an acid soil into an acceptable range for crop production.

Sample Preparation

Samples must be air dried and crushed to pass through a 2 mm sieve. Combine one part air dried crushed soil with two parts SMP buffer in a disposable beaker. Shake for 10-15 minutes, let stand 15 minutes then determine pH.

Instrumentation

Read the pH on a standardized pH meter, calibrated to both pH 4.00 and 7.00 buffer solutions, while electrodes are slowly moved within the suspension.

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Inter- and intra-lab precision must be within ± 0.3 pH units of the mean of samples from all accredited labs.

Reference Method

OMAFRA BpH

4.2.3 Available Nutrients - Phosphorus

Matrix Soil

Analysis

This analysis is required at least once within the five years prior to nutrients application. Plant available phosphorus is measured using the 0.5 M sodium bicarbonate method.

Method Principle

A portion of previously dried, crushed and sieved (< 2 mm), sample is extracted with a dilute alkaline solution, and P concentration is determined in the extract.

Sample Preparation

Samples must be air dried and crushed to pass a 2 mm sieve. Shake one part air-dried crushed soil for 30 minutes with 20 parts of 0.5 M sodium bicarbonate extracting solution, then let settle and filter. Determine P concentration in extract in auto-analyzer and calculate mg P/L of soil.

Instrumentation

Set up the Autoanalyzer to develop the colour reaction by the molybdate – ascorbic acid method. Read the sample absorbance at a wavelength of 820 nm.

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Inter- and intra-lab precision must be within $\pm 15\%$ of the mean of samples from all accredited labs.

Reference Method

OMAFRA P

4.2.4 Available Nutrients - K, Mg and Ca

Matrix Soil

Analysis

Analysis of available potassium is required at least once within the five years prior to nutrients application. Analysis of available magnesium is not required as part of a NMP, but is very useful in determining the requirement for magnesium fertilizers for crop production. Some labs may also determine the calcium content of the soil from the same extract. Plant available cations are measured using the 1 M ammonium acetate method.

Method Principle

A portion of previously dried, crushed and sieved (< 2 mm), sample is extracted with a dilute ammonia acetate solution, and analyzed using a spectrometric technique.

Sample Preparation

Samples must be air dried and crushed to pass a 2 mm sieve. Shake one part of air dried crushed soil with 10 parts of neutral 1 M ammonium acetate solution for 15 minutes. Let settle and then filter. Determine concentrations in extract on atomic absorption spectrophotometer.

Instrumentation

Potassium (K) is determined by atomic absorption spectrometry (AAS) in the emission mode at a wavelength of 766 nm.

Magnesium (Mg) is determined on the same extract at a wavelength of 285.2 nm AAS. If the sample reads over 400 absorbance units, it is diluted 1:9 with ammonium acetate and the results multiplied by a factor of 10.

Calcium (Ca) is read on same extract as Mg and K, but all samples are initially diluted 1:9 with ammonium acetate. Ca concentration is determined by AAS at a wavelength of 422.7 nm.

ICP may also be used to measure the concentration of cations in the extract.

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Inter- and intra-lab precision of the K analysis must be within $\pm 15\%$ of the mean ($\pm 20\%$ for Mg) of samples from all accredited labs.

Reference Method

OMAFRA Cations

4.2.5 Available Nutrients – Zn, Zn Index

Matrix Soil

Analysis

This analysis is not required as part of a NMP, but can be useful in determining whether a zinc deficiency might occur in crops. Soil zinc content is measured using the DTPA method. Results from this analysis are combined with soil pH to produce an index of zinc availability in agricultural soil.

Method Principle

A portion of previously dried, crushed and sieved (< 2 mm), sample is extracted with a DTPA solution and the concentration of zinc is determined on an Atomic Absorption Spectrophotometer. Zinc content and soil pH are used in a formula to produce an index of Zn availability.

Sample Preparation

Samples must be air dried and crushed to pass a 2 mm sieve. Shake one part air dried crushed soil with 2 parts of DTPA extracting solution for 1 hour. Samples are allowed to settle and then filtered.

Instrumentation

Zinc is read by AAS in the emission mode at 213.9 nm.

ICP may also be used to measure the concentration of ions in the extract.

Zinc is reported by index using formula:

$203 + 4.5 \text{ DTPA ext in mg/L} - 50.7 \text{ soil pH} + 3.33 (\text{soil pH})^2$.

Note: A small error in pH will cause a major change in the zinc index. E.g. if you take values for soil A as 4.8 paste and 5.2 (25 mL water), the resulting values if the Zn reading is 2 mg/L, are 50.3 and 43.44 respectively – a rather large error.

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Inter- and intra-lab precision of the calculated index must be within $\pm 15\%$ of the mean of samples from all accredited labs.

Reference Method

OMAFRA Zn

4.2.6 Available Nutrients – Mn, Mn Index

Matrix Soil

Analysis

This analysis is not required as part of the NMP, but is useful in determining whether manganese deficiency may occur in crops. Soil manganese content is measured using the 0.5 M phosphoric acid method. Results from this test are combined with soil pH to produce an index of manganese availability.

Method Principle

A portion of previously dried, crushed and sieved (< 2 mm), sample is extracted with a dilute phosphoric acid solution, and analyzed using an atomic absorption spectrophotometer.

Sample Preparation

Samples must be air dried and crushed to pass a 2 mm sieve. Shake one part air dried crushed soil with 8 parts 0.5 M phosphoric acid extracting solution for 10 minutes. Let settle, and then filter.

Instrumentation

The manganese is read on an atomic absorption spectrophotometer at 279.5 nanometers in the A.A. mode. ICP may also be used to measure the concentration of ions in the extract.

Manganese index is reported using the formula:

$$498 - 137 \text{ soil pH} + 0.248 \text{ extracted Mn} + 9.64 (\text{soil pH})^2.$$

A small change in pH affects the index greatly.

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Inter- and intra-lab precision of the calculated index must be within $\pm 15\%$ of the mean of samples from all accredited labs.

Reference Method

OMAFRA Mn

4.2.7 Available Nutrients – Nitrate N

Matrix Soil

Analysis

This analysis is not required in a NMP, but can be used to refine the nitrogen fertilizer application rates on corn or barley. Nitrate nitrogen is measured using the 2 M potassium chloride extraction.

Method Principle

A portion of previously dried, crushed and sieved (< 2 mm), sample is extracted with a dilute potassium chloride solution, and the concentration of nitrate in the extract determined using a colourimetric technique.

Sample Preparation

Take frozen or air dried soil (if frozen allow to thaw approximately 2 hours at room temperature), and sieve through 2 or 4 mesh screen. Take smaller particles for nitrate analyses. Clay samples or extremely wet samples will not sieve properly, you may have to cut sample into smaller pieces, using a knife or spatula.

Shake one part fresh or air dried soil with 5 parts of 2 N KC1 extracting solution for 30 minutes. Let settle and then filter.

Take a sample of rest of soil (5-15 g) for moisture analyses. Dry at 105°C overnight and calculate soil moisture.

Instrumentation

Nitrate is determined on an auto-analyzer using the cadmium reduction technique to reduce the nitrate to nitrite, followed by reaction with a colour agent and measurement of the absorbance at 520 nm.

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Inter- and intra-lab precision must be within $\pm 15\%$ of the mean of samples from all accredited labs.

Reference Method

OMAFRA NO3

4.2.8 Total Metals - Cd, Cr, Co, Cu, Pb, Mo, Ni, and Zn

Matrix Soil

Analysis

Soils in fields that will be receiving non-agricultural source material must be analyzed for each of the above metals. Sampling and analysis frequencies are given in Section 1.3.1. Non-agricultural source material may not be applied to soil where any of the metal concentrations in soil are equal to or greater than those given in Tables 1-1 and 1-2.

Method Principle

A portion of previously dried, ground and sieved (< 0.355mm), sample is extracted with a heated, strong mixed acid solution, brought to volume with pure de-ionized water and analyzed using a spectrometric technique.

Sample Preparation

- 1 Air-dry the sample, disaggregate and pass through a 2.0 mm sieve.
- 2 Grind an aliquot of the above sample until the whole sample passes through a 0.355 mm sieve.
- 3 Digest a portion of the sample (< 0.355 mm) with concentrated Nitric acid/ Hydrochloric acid mixture (1:3) by heating at 125°C for a minimum of 2 hours.

Instrumentation ICP/OES

DCP, ICP/MS, flame AAS and graphite furnace AAS with suitable matrix modifiers may be used.

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Analyte	RDL	Accuracy* (Recovery)	Precision (Between-Run)
	µg/g	Acceptable Range (%)	Acceptable Deviation (%)
Cadmium	1	80-120	± 20
Chromium	12	80-120	± 20
Cobalt	2.5	80-120	± 20
Copper	10	80-120	± 20
Lead	10	80-120	± 20
Molybdenum	2.5	N/A	N/A
Nickel	3.2	80-120	± 20
Zinc	25	80-120	± 20

* Accuracy is based upon the certified reference material, such as, EPA 287.

Reference Method
MOE/LSB - E3073

4.2.9 Mercury

Matrix Soil

Analysis

Soils in fields that will be receiving non-agricultural source material must be analyzed for mercury. Sampling and analysis frequencies are given in Section 1.3.1. Non-agricultural source material may not be applied to soil where mercury concentration in soil is equal to or greater than that given in Tables 1-1 and 1-2.

Method Principle

Mercury in the sample is converted to the inorganic form by the acid digestion process. The inorganic mercury in aqueous solution is then reduced with stannous chloride, and analyzed by Cold Vapour Flameless Atomic Absorption (CV AAS.)

Sample Preparation

- 1 Air-dry the sample, disaggregate and pass through a 2.0 mm sieve.
- 2 Grind an aliquot of above sample until the whole sample passes through a 0.355 mm sieve.
- 3 Digest a portion of the sample (< 0.355 mm) with concentrated sulphuric acid/nitric acid (4:1) by heating within a temperature range of 215 °C to 235 °C for a minimum of 12 hours.

Instrumentation

CV-AAS

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Analyte	RDL	Accuracy* (Recovery)	Precision (Between-Run)
	µg/g	Acceptable Range (%)	Acceptable Deviation (%)
Mercury	0.05	80 - 120	±20

* Accuracy is based upon the certified reference material, such as, National Research Council Sediment - PACS-1 or NIST 1646 sediment.

Reference Method

MOE/LSB - E3059

4.2.10 Arsenic and Selenium

Matrix Soil

Analysis

Soils in fields that will be receiving non-agricultural source material must be analyzed for arsenic and selenium. The sampling and analysis frequencies are given in Section 1.3.1. Non-agricultural source material may not be applied to soil where concentrations of arsenic and selenium in soil are equal to or greater than those given in Tables 1-1 and 1-2.

Method Principle

A portion of sample is digested in an oxidizing acid mixture to convert all forms of arsenic and selenium to arsenate (AsO_4)³⁻ and selenate (SeO_4)²⁻ respectively. The arsenate and selenate are then reduced with sodium borohydride to arsine and hydrogen selenide which are then analyzed by flameless AAS.

Sample Preparation

- 1 Air-dry the sample, disaggregate and pass through a 2.0 mm sieve.
- 2 Grind an aliquot of above sample until the whole sample passes through 0.355 mm sieve.
- 3 Digest a portion of the sample (< 0.355 mm) with concentrated Nitric acid/Sulphuric acid/Perchloric acid (6:3:1) at 200°C for 16 hours.

Instrumentation

Hydride - Flameless Atomic Absorption Spectrophotometry (HYD-FAAS).

ICP/MS and graphite furnace AAS with suitable matrix modifiers may be used.

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Analyte	RDL	Accuracy* (Recovery)	Precision (Between-Run)
	µg/g	Acceptable Range (%)	Acceptable Deviation (%)
Arsenic	1.4	80 - 120	± 20
Selenium	1	80 - 120	± 20

* Accuracy is based upon the certified reference material, such as, NIST 2709 San Joaquin soil.

Reference Method
MOE/LSB - E3245

4.2.11 Boron - Hot Water Extraction

Matrix Soil

Analysis

The OMAFRA may require analysis of soils where application of materials high in boron is planned, on a case-by-case basis.

Method Principle

A 25 g portion of previously dried, ground (< 2 mm) sample is extracted with a weak calcium chloride solution and analyzed using a spectrometric technique.

Sample Preparation

- 1 Air-dry the sample, disaggregate and pass through a 2.0 mm sieve.
- 2 Combine a 25 g portion of the air dried sample with 50 mL 0.01 M CaCl₂ solution. Boil for 5 minutes, then cool and filter.

Instrumentation

ICP (AAS or DCP may be used)

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control, Calibration Check and Sample Replicate.

Method Performance Criteria

Accuracy and precision data are under review.

Reference Method

MOE/LSB - E3073

Note

This method can identify contaminated sites, but is not sensitive enough to identify potentially deficient sites for crop production.

4.3 Analysis - Land Applied Materials

4.3.1 Hydrogen Ion (pH)

Matrix Land Applied Materials (Non-agricultural source materials)

Analysis

Non-agricultural source materials with pH less than 6.0 unit or pH greater than 8.5 units, should not be applied to crops when they are being grown.

Method Principle

pH is determined with a standard glass electrode pH meter.

Sample Preparation

Solid

Prepare aqueous slurry in the ratio of 1g sample: 9 mL water. Stir or shake for approximately 20 minutes, allow suspension to settle and then determine pH of liquid fraction.

Liquid/Slurry

Decant, filter or centrifuge a portion of sample, then determine the pH of the liquid fraction.

Instrumentation

pH electrode and pH meter compensated to 25°C. Accuracy and reproducibility to 0.2 pH unit with a range of 0 - 14 and equipped with temperature compensation.

Laboratory QC Samples per Run

3 Buffer Checks, Sample Replicate and In-House Matrix Check.

Method Performance Criteria

Accuracy: ± 0.2 pH units

Precision: ± 0.2 pH units

Reference Method MOE/LSB - E3137 (solid)
MOE/LSB - E 3218 (liquid/slurry)

Notes

- 1 Sample preservation - store samples in refrigerator (4 - 10°C).
- 2 Maximum sample storage time: 14 days.

4.3.2 Electrical Conductivity

Matrix Land Applied Materials (Non-agricultural source materials)

Analysis

Method Principle

Conductivity, a measure of the capacity of a liquid to convey an electric current at a specific temperature, is defined as the reciprocal of water's electrical resistance, measured between two electrodes one square centimetre in area and one centimetre apart. The conductivity test requires introducing the sample to the conductivity cell and recording the conductivity.

Sample Preparation

Solid (low organic matter)

Prepare aqueous slurry in the ratio of 10g sample: 20 mL water. Stir or shake for approximately 30 minutes, allow suspension to settle for 30 minutes then determine conductivity on the material.

Liquid/Slurry

Decant, filter or centrifuge a portion of sample and then perform conductivity determination on the liquid fraction.

Instrumentation

Conductivity meter compensated to 25°C.

Laboratory QC Samples per Run

2 Conductivity Standards, Blank and Sample Replicate.

Method - Performance Criteria

Accuracy: $100 \pm 10\%$

Precision: $\pm 10\%$

Reference Method MOE/LSB - E3218 (liquid/slurry)
MOE/LSB - E3138 (solid)

Notes

- 1 Sample preservation - store samples in refrigerator (4 – 10°C).
- 2 Maximum sample storage time: 14 days.

4.3.3 Total Dry Matter

Matrix Land Applied Materials

Analysis

Accurate determination of the dry matter content of land-applied materials is necessary to calculate application rates on a moist basis.

Method Principle

A portion of sample is weighed as received, dried for 16 hours at $105 \pm 5^\circ\text{C}$, cooled and reweighed. The percent total solid is determined.

Sample Preparation

Disaggregate the sample and pass through a 2 mm sieve. Take subsamples (10 - 25 g) of this mixture, and dry in an oven at $105 \pm 5^\circ\text{C}$ for 16 hours to a constant weight. Cool and reweigh sample to determine total solids as a percent of the fresh weight.

Instrumentation

Balance, capable of weighing ± 0.01 g.

Laboratory QC Samples per Run

Calibration Check and Sample Replicate.

Method - Performance Criteria

Accuracy: $100 \pm 10\%$

Precision: $\pm 10\%$

Reference Method

MOE/LSB-3139

4.3.4 Total Volatile Solids (Organic Matter)

Matrix Solid or Liquid Land Applied Materials

Analysis

Method Principle

A portion of ground sample is dried for 16 hours at $105^{\circ}\text{C} \pm 5^{\circ}\text{C}$, then muffled at $475^{\circ}\text{C} \pm 25^{\circ}\text{C}$ for 4 hours. The weight loss, and percent ash are determined.

Sample Preparation

1. Disaggregate the sample and pass through a 2 mm sieve, then take and grind a subsample to pass through a 0.355 mm sieve.
2. Heat the subsample in a muffle oven at $475^{\circ}\text{C} \pm 25^{\circ}\text{C}$ for 4 hours.
3. Determine the weight loss, and per cent ash.

Instrumentation

Muffle furnace

Balance, capable of weighing ± 0.01 g.

Laboratory QC Samples per Run

Calibration Check and Sample Replicate.

Method - Performance Criteria

Accuracy: $100 \pm 10\%$

Precision: $\pm 10\%$

Reference Method

MOE/LSB-3139

4.3.5 Total Kjeldahl Nitrogen

Matrix Land Applied Materials

Analysis

Total nitrogen in land applied materials is determined to provide a basis for calculating the organic nitrogen portion of the material (by subtracting the ammonium N from the total). The required sampling frequency is specified in Sections 1.3.2 and 1.3.3.

Method Principle

Amino nitrogen in organic materials is converted to ammonium by digestion in the presence of strong acid, salt and a catalyst. Ammonium content, which will also include ammonia and ammonium in the sample before digestion, is determined by colourimetry, ammonia selective electrode or titration.

Sample Preparation

Test the samples as received. Determine the dry matter content of the material separately.

Sample is mixed with H₂SO₄, K₂SO₄, and cupric sulphate (catalyst), and heated to 400 °C to convert organically bound nitrogen to NH₄.

Instrumentation

Autoanalyzer, colourimeter

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Inter- and intra-lab precision must be within $\pm 10\%$ of the mean of samples from all accredited labs.

Reference Method

AOAC 978.02

Notes

- 1 Sample Preservation - Store samples in refrigerator (4 - 10°C). If extended storage is required (>10 days), freeze the samples.
- 2 Method does not completely account for oxidized forms of nitrogen such as nitrate, nitrite, or nitrogen in heterocyclic ring compounds. Nitrogen determination by combustion (Dumas method) may give better results in materials with significant contents of these forms of nitrogen.

4.3.6 Ammonia and Ammonium - Nitrogen

Matrix Land Applied Materials

Analysis

Ammonium nitrogen in land applied materials (which includes both ammonium and ammonia nitrogen) is determined to provide an estimate of plant available nitrogen, as well as a basis for calculating the organic nitrogen portion of the material (by subtracting the ammonium N from the total). The required sampling frequency is specified in Sections 1.3.2 and 1.3.3.

Method Principle

Ammonium plus ammonia nitrogen is extracted from the sample in a KCl solution. Ammonium content in the extract is determined by colourimetry, using a modified Berthelot reaction.

Sample Preparation

Test the samples as received. Determine the dry matter content of the material separately.

Sample is mixed with 2M KCl solution, shaken, and then centrifuged or filtered.

Instrumentation

Autoanalyzer, colourimeter

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Inter- and intra-lab precision must be within $\pm 10\%$ of the mean of samples from all accredited labs.

Reference Method

USEPA 352.2

Notes

Ammonia specific electrode may be used as an alternate method, and will be less subject to interference from discolouration of the extract.

4.3.7 Nitrate and Nitrite - Nitrogen

Matrix Land Applied Materials

Analysis

Samples are analyzed for nitrate nitrogen and nitrite nitrogen to assess the nitrogen immediately available to plants. Some non-agricultural source materials may contain significant amounts of nitrate and nitrite nitrogen.

Method Principle

Samples are analyzed using an automated colourimetric procedure which entails converting nitrate to nitrite, and then analyzing the sample for nitrite.

Nitrate is reduced to nitrite by heating an aliquot of sample with hydrazine in alkaline media; this reaction is catalyzed by the addition of cupric ion. Subsequently, an azo dye is formed in acid media by diazotizing sulphanilamide with nitrite and coupling the product with N (1-naphthyl) ethylenediamine dihydrochloride. The absorbance of the light red azo dye is measured at 520 nm and the concentration of nitrate nitrogen plus nitrite nitrogen is determined by comparison with a similarly treated series of mixed Standards.

Sample Preparation

Liquid/Slurry

A supernatant of the settled sample is used for this analysis. Samples (if frozen) are thawed to room temperature prior to analysis. Highly turbid samples should be filtered to prevent clogging of the analyser fittings. Sewage sludge samples should be centrifuged prior to analysis.

Solid

Under Development

Instrumentation

Colourimeter

Laboratory QC Samples per Run

Method Blank, In-House Standard, Calibration Check and Sample Replicate.

Method Performance Criteria

Accuracy: $100 \pm 10\%$

Precision: 10%

Reference Method

MOE/LSB - E3366

Notes

1. Store samples in a refrigerator (4 – 10°C).
2. Maximum storage time, 7 days.

4.3.8 Organic Nitrogen

Matrix Land Applied Materials

Analysis

The organic nitrogen portion of the material is calculated by subtracting the ammonium N from the total N contents of the sample. The required sampling frequency is laid out in Sections 1.3.2 and 1.3.3.

Method Principle

Ammonium plus ammonia nitrogen, as determined in a KCl extract of the manure sample, is subtracted from the Total Kjeldahl Nitrogen in the sample. The difference is the organic N.

Sample Preparation

Extraction as defined for ammonium and total N.

Instrumentation

As defined for ammonium and total N.

Laboratory QC Samples per Run

As defined for ammonium and total N.

Method Performance Criteria

As defined for ammonium and total N.

Method Reference

N/A

Notes

If the total N content of the material has been determined by combustion (dumas method) rather than wet digestion, the nitrate content of the material should also be determined and the nitrate as well as the ammonium content should be deducted from the total N to determine the organic N.

4.3.9 Metals - Cd, Cr, Co, Cu, Pb, Mo, Ni, and Zn

Matrix Land Applied Materials (Non-agricultural source materials)

Analysis

This analysis is required for non-agricultural source material only. The sampling and analysis frequencies are given in Table 1-3. Non-agricultural source material may not be applied to soil where any of the metal concentrations in such material are equal to or greater than those given in Tables 1-1 and 1-2.

Method Principle

A portion of sample is extracted with a heated, strong mixed acid solution, brought to volume with pure deionized water and analyzed using a spectrometric technique.

Sample Preparation

Solid (i.e. dewatered sludge, filter cake - Method E3071)

Digest a portion of previously air dried, ground and sieved sample with concentrated Nitric acid/Hydrochloric acid mixture (1:3) by heating at 50°C for 1 hour and then at 95°C for another 3 hours. Adjust volume with pure deionized water, decant/filter and then analyze.

Liquid/slurry (i.e. liquid sludge, likely 1% to 10% solids - Method E3071)

Weigh an aliquot of homogenized sample. Digest with concentrated Nitric acid/Hydrochloric acid mixture (1:3) by heating at 50°C for 1 hour and then at 95°C for another 3 hours. Adjust volume with pure deionized water, decant/filter and then analyze. Report results on dry weight basis.

Clear Liquid (i.e. supernatant, less than 1% solids - Method E3094)

Digest an aliquot of sample with concentrated Nitric acid/Hydrochloric acid mixture (1:3) by heating at 50°C for 1 hour and then at 95°C for another 3 hours. Adjust volume with pure deionized water, decant/filter and then analyze.

Instrumentation

ICP/AES

DCP, ICP/MS, flame AAS and graphite furnace AAS with suitable matrix modifiers may be used.

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Analyte	RDL	Accuracy* (Recovery)	Precision (Between-Run)
	µg/g	Acceptable Range (%)	Acceptable Deviation (%)
Cadmium	2.0	80 - 120	± 20
Chromium	106	80 - 120	± 20
Cobalt	15	N/A	N/A
Copper	76	80 - 120	± 20
Lead	50	80 - 120	± 20
Molybdenum	2.5	N/A	N/A
Nickel	18	80 - 120	± 20
Zinc	185	80 - 120	± 20

* Accuracy is based upon the certified reference material, such as, WWS-26 from Environmental Resource Associate or EPA Quality Control Sample, municipal digested sludge (SPL # 2900).

Reference Method

MOE/LSB - E3071 for liquid/slurry and solid; MOE/LSB - 3094 for Clear Liquid.

Notes

- 1 Sample Preservation
Clear Liquid Samples - Preserved with nitric acid to less than pH 2.
Solid/Slurry/Solid Sample - Store samples in refrigerator (4 - 10°C).
- 2 Maximum Sample Storage Time: 60 days

4.3.10 Mercury

Matrix Land Applied Materials (Non-agricultural source materials)

Analysis

This analysis is required for non-agricultural source material only. The sampling and analysis frequencies are given in Table 1-3. Non-agricultural source material may not be applied to soil where mercury concentration in such material is equal to or greater than that given in Tables 1-1 and 1-2.

Method Principle

Mercury in the sample is converted to the inorganic form by acid digestion process. The inorganic mercury in aqueous solution is then reduced with stannous chloride, and analyzed by CV AAS.

Sample Preparation

Solid (e.g. dewatered sludge, filter cake - Method E3058)

Digest a portion of previously air dried ground and sieved sample with 50% v/v Aqua Regia (hydrochloric acid/Nitric acid - v/v 3:1) in the presence of potassium permanganate by heating within a temperature range of 90°C to 110°C for 1 hour and 15 minutes. Treat excess permanganate with hydroxylamine sulphate. Reduce inorganic mercury with stannous chloride prior to analysis. Adjust volume with pure deionized water, decant/filter and then analyze. Report results on dry weight basis.

Liquid/Slurry (e.g. liquid sludge, likely 1% to 10% solids - Method E3058)

Digest weighed aliquot of homogenized (well mixed) sample with 50% v/v Aqua Regia (hydrochloric acid/Nitric acid - v/v 3:1) in the presence of potassium permanganate by heating within a temperature range of 90°C to 110°C for 1 hour and 15 minutes. Treat excess permanganate with hydroxylamine sulphate. Reduce inorganic mercury with stannous chloride prior to analysis. Adjust volume with pure deionized water, decant/filter and then analyze. Report results on dry weight basis.

Clear Liquid (e.g. supernatant, less than 1% solids - Method E 3301)

Digest an aliquot of homogenized (well mixed) sample with concentrated sulphuric acid/nitric acid (1.2:0.5) in the presence of potassium persulphate and potassium dichromate for 2 hours at 87°C ± 3°C. Adjust volume with pure deionized water, decant/filter and then analyze.

Instrumentation

Cold Vapour Flameless Atomic Absorption (CV-FAAS)

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

	RDL	Accuracy* (Recovery)	Precision (Between-Run)
Analyte	µg/g	Acceptable Range (%)	Acceptable Deviation (%)
Mercury	0.5	80 - 120	±20

* Accuracy is based upon the certified reference material, such as, CRM 145R (sewage sludge mixed origin) or BE - 1 (sewage sludge).

Reference Method MOE/LSB - E3301 (clear liquid), MOE/LSB E3058 (slurry and solid)

Notes

Sample Preservation

- 1 Clear Liquid Sample - Preserve 250 mL sample with 0.5 - 1.0 mL concentrated nitric acid and 5 - 10 drops of 5% potassium dichromate solution. This should lower pH to below 2.0 and give the sample a permanent yellow colour.
Liquid Slurry/Solid Sample - Store samples in refrigerator (4 - 10°C).
- 2 Maximum Sample Storage Time: 15 days.

4.3.11 Arsenic and Selenium

Matrix Land Applied Materials (Non-agricultural source materials)

Analysis

This analysis is required for non-agricultural source material only. The sampling and analysis frequencies are given in Table 1-3. Non-agricultural source material may not be applied to soil where arsenic and selenium concentrations in such material are equal to or greater than that given in Tables 1-1 and 1-2.

Method Principle

A portion of sample is digested in oxidizing acid mixture to convert all forms of arsenic and selenium to arsenate (AsO_4)³⁻ and selenate (SeO_4)²⁻ respectively. The arsenate and selenate are then reduced with sodium borohydride to arsine and hydrogen selenide which are then analyzed by flameless AAS.

Sample Preparation

Solid - (e.g. dewatered sludge, filter cake - Method E3091)

Digest a portion of previously air dried ground and sieved sample and sample with concentrated Nitric acid/Sulphuric acid/Perchloric acid (6:3:1) at 200°C for minimum of 16 hours. Adjust volume with pure deionized water, decant/filter and then analyze.

Liquid/Slurry (e.g. liquid sludge, likely 1% to 10% solids - Method E3091)

Digest a weighed aliquot of sample with concentrated Nitric acid/Sulphuric acid/Perchloric acid (6:3:1) at 200°C for minimum of 16 hours. Adjust volume with pure deionized water, decant/filter and then analyze. Report results on dry weight basis.

Clear Liquid (e.g. supernatant, less than 1% solids) (Method E

3302) Digest an aliquot of liquid with a 6:3:1 mixture of Nitric:sulphuric:perchloric acids at 140°C for about 16 hours. Adjust volume with pure deionized water, decant/filter and then analyze

Instrumentation

Hydride - Flameless Atomic Absorption Spectrophotometry (HYD-FAAS)

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Analyte	RDL	Accuracy* (Recovery)	Precision (Between-Run)
	µg/g	Acceptable Range (%)	Acceptable Deviation (%)
Arsenic	7.5	80 - 120	± 20
Selenium	1.4	80 - 120	± 20

* Accuracy is based upon the certified reference material, such as, CRM 145R (sewage sludge mixed origin) or BE - 1 (sewage sludge).

Reference Method

MOE/LSB - E3302 (clear liquid), MOE/LSB E3091 (liquid/slurry and solid)

Notes

- 1 Sample Preservation
Clear Liquid Sample - Preserve sample with nitric acid
Liquid/Slurry/Solid Sample - Store samples in refrigerator (4 - 10 °C)
- 2 Maximum Sample Storage Time: 30 days.

4.3.12 Total Phosphorus, Potassium, Sodium and Boron

Matrix Land Applied Materials

Analysis

Total phosphorus and potassium content of land applied materials are determined to estimate the amount of plant available nutrient being applied to land. The required sampling frequency is laid out in Sections 1.3.2 and 1.3.3. Sodium or boron content may need to be determined for land applied materials suspected of containing high concentrations of these elements, on a case by case basis.

Method Principle

A portion of sample is extracted with a heated, strong mixed acid solution, brought to volume with pure deionized water and analyzed using a spectrometric technique.

Sample Preparation

Solid

Digest a portion of previously dried and homogenized sample with concentrated Nitric acid/Hydrochloric acid mixture (1:3) by heating at 50°C for 1 hour and then at 95°C for another 3 hours. Adjust volume with pure deionized water, decant/filter and then analyze.

Liquid/slurry

Weigh an aliquot of homogenized (well mixed) sample and then digest with concentrated Nitric acid/Hydrochloric acid mixture (1:3) by heating at 50°C for 1 hour and then at 95°C for another 3 hours. Adjust volume with pure deionized water, decant/filter and then analyze.

Instrumentation

ICP/AES

Laboratory QC Samples per Run

Method Blank, Matrix Matched In-House Control or CRM, Calibration Check and Sample Replicate.

Method Performance Criteria

Inter- and intra- lab precision must be within $\pm 10\%$ of the mean of samples from all accredited labs.

Reference Method

Under development

4.3.13 *E. coli* (Only Sewage Biosolids)

Matrix Sewage Biosolids

Analysis

Municipal sewage sludge is required to be sampled and analyzed at least as frequently as set out in Table 1- 2. Such material may not be applied to soil where concentrations of *E-coli* exceeds 2×10^6 CFU/g of total solid (dry wt.).

Method Principle

A volume of buffered dilution water is added to a weighed amount of biosolids and processed with a Stomacher™ or equivalent. Serial dilutions are then prepared using the supernatant. Serial dilutions are then plated out on mFC-BCIG agar (or other selective agar) and incubated.

Sample Preparation

Add an amount of buffered dilution water to a weighed mass of biosolids material. Process in the Stomacher™ for 2 minutes. Decant off supernatant.

Instrumentation

Classical microbiological techniques - selective agar, biochemicals for confirmation.

Laboratory QC Samples per Run

Positive and negative controls run with each set of samples, plus spiked samples for recovery.

Method Performance Criteria

Under development

Reference Method

MOE/LSB - E3433

Notes

- 1 Sample storage - ice bath/temperature
- 2 Analysis must be performed within 48 hours.

5.0 ACRONYMS

AAS	Atomic Absorption Spectrophotometry
CRM	Certified Reference Material
CV-AAS	Cold Vapour - Atomic Absorption Spectrophotometry
DCP	Direct Current Plasma
US-EPA	Environmental Protection Agency (U.S.A.)
GPS	Global Positioning System
HYD-FAAS	Hydride Flameless - Atomic Absorption Spectrophotometry
ICP	Inductively Coupled Plasma Spectroscopy
ICP/AES	Inductively Coupled Plasma Spectroscopy - Atomic Emission Spectroscopy
ICP/MS	Inductively Coupled Plasma Spectroscopy - Mass Spectrometry
ICP/OES	Inductively Coupled Plasma Spectroscopy - Optical Emission Spectroscopy
MOE/LSB	Ministry of the Environment (Ontario), Laboratory Services Branch
MPN	Most Probable Number
NIST	National Institute of Standards and Technology (Gaitersburg, MD U.S.A.)
RSD	Relative Standard Deviation

6.0 GLOSSARY

Ammonium Nitrogen:	Means ammonia nitrogen plus ammonium nitrogen.
Analytical Run:	A group of samples processed together through each step of an analytical procedure.
Analytical Standard:	A series of chemical standards of the target analytes, used to set the relationship between instrument response and concentration.
Blank, Method Blank:	Pure Water or other type of blank (i.e., acid or solvent) used to monitor for contaminated reagents, glassware and method processes.
Composite Sample:	A sample that is made up of a number of grab samples that have been thoroughly mixed together.
Contaminant:	Means any solid, liquid, gas, odour, heat, sound, vibration, radiation or combination of any of them resulting directly or indirectly from human activities that may cause an adverse effect.
CRM:	Certified reference material; matrix sample containing analytes at concentration values which have been certified by multiple laboratory analysis.
Duplicate Sample:	One of two samples collected at a sampling point at the same time in a manner that minimizes differences between the samples.
Geo-Reference:	A specific set of coordinates within a numeric system of grid references (e.g., latitude/longitude or UTM (Universal Transverse Mercator)) used to precisely identify a geographic location.
Global Positioning System	Method of determining geo-reference using a GPS receiver.
Grab Sample:	A single sample taken directly from the material being sampled, sub sample or a portion of a composite sample.
Internal Standard:	A compound, representative of the compound(s) of interest and not expected to be found in the matrix, spiked into every sample extract and solution analyzed. It monitors losses/gains due to the analytical procedure. Data may or may not be corrected based on the calculated recovery.

Matrix:	Any type of material, (e.g., soil, manure, sewage sludge).
Matrix Check Material:	Matrix check materials are, typically, natural materials subjected to method processes in order to monitor method recovery. They are often in-house sample composites that have an established value and characteristics
NMAN	A computer program of that name prepared by OMAFRA for the purpose of preparing NMPs, as well as the workbook that can be used to prepare plans manually.
Nitrate Nitrogen:	Means nitrate nitrogen plus nitrite nitrogen.
Nutrient:	A compound or element that is absorbed and utilized by plants in the process of their growth and reproduction.
Nutrient Management Plan:	A plan for the application of materials containing nutrients to land in such a way that agronomic requirements of crops are met, and environmental impacts are minimized.
Nutrient Unit:	The amount of nutrients that give the fertilizer replacement value of the lower of 43 kilograms of nitrogen or 55 kilograms of phosphate.
Quality Management System:	A set of interrelated elements (e.g., policies and objectives) that direct and control the way a facility operates with regard to quality.
Replicate Analyses:	Natural samples may be split in the laboratory and analyzed together in the same run. Replicates are taken through the entire method process. This data can be used to assess the within-run precision of the analysis or sample matrix homogeneity.
Replicate Sample:	An additional or second aliquot (portion) of a randomly selected sample in the analytical run.
Representative Sample:	A sample of material that has been taken so that it has essentially the same composition and characteristics of the source material.

Spiked Samples: Analyte(s) of interest is spiked into the sample matrix in order to monitor recovery from the sample matrix using the method or parts of the method.

Spiked Water/Solvent: Analyte(s) of interest is spiked into reagent water/solvent to monitor recovery because of changes in the method or parts of the method.

Standard Additions The addition of known quantities of the analyte of interest to one or more split portions of a single sample can be used to determine the presence and possible effect of interference by various matrix constituents on the analytical method.