Protocol for the Sampling and Analysis of Industrial/Municipal Wastewater

Version: 2.0

January 1, 2016

STOPPING
WATER POLLUTION
AT ITS SOURCE

MISA
Municipal/Industrial Strategy for Abatement

Ontario

Protocol for the Sampling and Analysis Of Industrial/Municipal Wastewater

Version: 2.0

Ontario Ministry of the Environment and Climate Change
Laboratory Services Branch

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Table of Contents

1.0 Introduction

This section provides the user with an overall view of the intent, scope and limitations of this document.

1.1 Purpose

The purpose of this Protocol is to provide guidelines with respect to sampling, analysis and QA/QC procedures to be followed for Ministry of the Environment and Climate Change (MOECC) programs and to specify requirements for compliance with Ministry regulations and/or Environmental Compliance Approvals (ECA).The Protocol was originally written for the Effluent Monitoring and Effluent Limits (EMEL) regulations, but the procedures are not limited to these regulations.

This Protocol is specifically incorporated in the Effluent Monitoring and Effluent Limits regulations under the *Environmental Protection Act*. In all cases specific requirements imposed by the Effluent Monitoring and Effluent Limits regulations in respect of each industrial Sector take precedence over this Protocol if there is an inconsistency between those requirements and the Protocol. It is important, therefore, that the Effluent Monitoring and Effluent Limits regulations be read in conjunction with this Protocol. The nine regulations for which this protocol is incorporated are as follows:

Ontario Regulation 215/95 Effluent Monitoring and Effluent Limits – Electric Power Generation Sector

Ontario Regulation 561/94 Effluent Monitoring and Effluent Limits – Industrial Minerals Sector

Ontario Regulation 64/95 Effluent Monitoring and Effluent Limits – Inorganic Chemical Sector

Ontario Regulation 214/95 Effluent Monitoring and Effluent Limits – Iron and Steel Manufacturing Sector

Ontario Regulation 562/94 Effluent Monitoring and Effluent Limits – Metal Casting Sector

Ontario Regulation 560/94 Effluent Monitoring and Effluent Limits – Metal Mining Sector

Ontario Regulation 63/95 Effluent Monitoring and Effluent Limits – Organic Chemical Manufacturing Sector

Ontario Regulation 537/93 Effluent Monitoring and Effluent Limits – Petroleum Sector

Ontario Regulation 760/93 Effluent Monitoring and Effluent Limits – Pulp and Paper Sector

The MISA (Municipal and Industrial Strategy for Abatement) program was initiated with a series of sector specific monitoring regulations which referred to a common General Regulation (Effluent Monitoring Regulation, General: Ontario Regulation 695/88 as amended to 533/89). The General Regulation contained, among other things, the common requirements, guidelines, principles and protocols related to the sampling, preservation, storage and analysis of wastewater samples, the minimum numbers and types of field and laboratory quality control samples to be included and a general guideline for data recording and reporting. The General Regulation was replaced with the above listed nine sector-specific regulations during the period 1993–1995. Minor amendments were made to these nine regulations in 2007.

This Protocol may also be incorporated by reference into instruments issued under legislation administered by the Ministry, including in Environmental Compliance Approvals (ECA), other forms of approvals (e.g. Certificate of Approval), and/or Orders.

1.2 Scope

This Protocol contains much of the same information originally presented in the General Regulation. It includes direction on techniques for planned sampling of industrial/municipal wastewater, preservation of samples and their storage requirements, maximum storage times allowed prior to analysis, the most appropriate and where applicable alternate preparation and instrumental analysis protocols and the type and frequencies of field and laboratory QC samples. This document represents a synthesis of best available information from organizations including the Ontario Ministry of Environment and Climate Change (e.g. Brownfields), Environment Canada (e.g. CCME protocols), Standard Methods for the Examination of Water and Wastewater (Current edition, American Public Health Association), and the U.S. Environmental Protection Agency (Federal Register CFR40 part 136). It also incorporates the recommendations and conclusions reached through collaborative efforts of government, industrial and private laboratory personnel.

The techniques described here may be applicable to unplanned sampling events, but the sampling of unplanned events is beyond the scope of this document.

This document also defines the principles and protocols which must be followed by all laboratories handling samples collected under the Effluent Monitoring and Effluent Limits regulations. In some cases it intentionally stops short of stipulating any detailed procedures, methods or control techniques. While this approach can leave room for interpretation and uncertainty resulting in slight differences in sampling or analytical procedures, it also leaves room for improvement, analyst discretion and modernization of techniques which can improve the quality of environmental analytical data being generated.

Throughout the document, “Ministry” and “Ministry officials” refers to the Ontario Ministry of the Environment and Climate Change (MOECC) and its employees, unless indicated otherwise.

1.3 History of Revisions and Changes

This Protocol is reviewed on a regular basis. Changes are incorporated which represent an improvement, refinement or advancement in environmental science based on best scientific judgement and/or peer review.

1.3.1 Initial Publication

August, 1994.

1.3.2 Revision #1

January, 1999; reprinted August 1999

Additions: Sec.3.6 – Sampling Under Sewage Treatment Plant Regulations
ATG1b – Carbonaceous BOD
ATG12 – Mercury– Fluorescence detection added
ATG31 – Total Residual Oxidants: “(total residual chlorine)” added
ATG36 -NDMA, (n-nitrosodimethylamine)

Changes: Use of n-hexane for Solvent Extractables (ATG25) (See pages 25, 26, Section 4.6)
Sec. 9 – Appendix - Table 1 – - Analytical Test Groups Changes to RMDLs.

Clarifications: Sec. 5.3.1 – Laboratory QC Samples Sec. 5.4.1 – Field QC Samples

1.3.3 Revision #2

January 1, 2016

Additions: Sec. 2.1– Health and Safety
Provided more details for sampling Oil & Grease (section 2.5)
Sec. 2.6 – Toxicity Sampling
Added table of suggested analytical method sources for each ATG
ATG2d – Cyanide Amenable to Chlorination (Free cyanide)
ATG6a – Phosphorus (Soluble); Orthophosphate
Sec. 9.8.4 – Total Solids
Added sampling and analytical procedures for ATG21 and ATG22

Expanded description of TEQ calculations and moved Table 5 (renumbered to Table 2) to section 9.22 for ATG24
Sec. 9.27.4 – Bromide
Additional microbiological parameters in section 9.32
Sec. 9.33 – Toxicity Sample Collection and Analytical Procedures.
Sec. 9.34 – Additional Physical Analyses
Bibliography – Section 10

Changes:

Removed Section 2, Format and Content; included a summary in Section 1; renumbered subsequent sections
Expanded introductory paragraphs to include broader scope of application to non-industrial wastewater streams
Included reference to PAAM document as a guideline for method validation in section 3.5; added description of uncertainty calculation in 3.5.1
Removed reference to “regulations” for sewage treatment plant sampling in section 2.8 (formerly 3.8)
Updated national accreditation bodies, quality references and definitions of reference materials in Section 4
Replaced references to previous data reporting system (MIDES) with current system (MEWS) in Section 5
Combined sampling and analysis descriptions for ATG9a with ATG 9, and ATG17 with ATG16
Removed list of elements for ATG29 in RDL Table (Section 8) and replaced with more generic description
Modified low-level data qualifier reporting requirements in sections 5.1.4 and 5.2.1

Deletions:

Removed tables 2 and 3 from the appendices, as information was duplicated in the individual ATG descriptions
Removed Table 4 to allow more flexibility for laboratories
Removed Figure 1: Proposed QC Summary Table
Removed requirement to blank correct data (section 4.3.2)
Reduced requirement to prepare quarterly QC summaries to an annual report (section 5.3)
Removed the PCDD/F homologue group totals from ATG Table in Section 8 as they are not required for TEQ calculations.
Removed phrase “Required under the Effluent Monitoring and Effluent Limits Regulations” throughout document as repetitive (regulations stipulate that all requirements of the Protocol be followed).

2.0 Guidelines for Sampling, Preservation and Storage

See Section 9.0 for sampling, preservation and storage requirements for each analytical test group (ATG).

All samples obtained for analysis must be from a point in the wastewater stream that is representative of the whole stream composition. The volume of sample taken must be sufficient to allow for analysis of all required analytes plus associated quality control samples (e.g., field duplicate, laboratory replicate and spiked sample).

It is recommended that all automated and manual sampling devices and equipment, their containers and all tubing, valves and contact components be dedicated to a particular sampling site in order to minimize the possibility of cross contamination. As an alternate to this dedicated application it is the user's responsibility to demonstrate that the sampling equipment is clean, free from contamination and suited to the sampling and analysis needs at the next location. Generally, the cleaning and preparation of relocated equipment should include hot water, phosphate free detergent washing, hot and cold water rinsing, distilled water rinsing and, finally, multiple rinses with the actual wastewater being sampled. This is especially important where trace levels of contaminants are being analyzed.

2.1 Health and Safety Considerations

Prior to sampling in the field, become familiar with the appropriate sections of the Occupational Health and Safety Act and Regulations for Industrial Establishments, the site Safety Manual, and any other relevant safety manuals. When possible, seek guidance from experienced personnel for locating and avoiding possible hazards at the sampling site.

Wear the required personal protective equipment (PPE) as required by the facility. This may include, but is not limited to, coveralls, gloves, steel toed rubber safety boots, hard hat, hearing protection, face shield and/or safety glasses, and/or any other PPE specified by the site safety protocols. Follow all site-specific safety protocols.

Following sampling activities, wash hands with soap and water and clean contaminated clothing and equipment.

2.2 Sample Types and Techniques

See Section 2.5 for some ATG specific sampling requirements.

Wastewater samples are often obtained by the use of automated equipment capable of either flow or time proportional sub-sampling of a wastewater stream. These autosamplers must be mechanically and electrically suited to the environment in which they will operate and, in consideration of safety and accessibility, be physically located to facilitate routine use, maintenance and inspection by field staff and Ministry officials.

Sampling requirements for wastewater analysis can also be fulfilled by manual sampling using simple field equipment including buckets, funnels and suitable lengths of chain or dip poles. This equipment must conform to the same materials composition as outlined for automated equipment in *Section 2.2.4 (1*) (i.e. Teflon®, stainless steel, glass, etc.). The equipment must be suited to the sampling and analysis being performed.

2.2.1 Grab Samples

A grab sample is meant to represent the wastewater stream at a given point in time as opposed to a composite sample which represents the wastewater stream over a longer time period (24 hours).

Grab samples may be taken from a slipstream and valve: after purging the sample line, the samples should be collected into appropriate laboratory containers.

Grab sampling may also be conducted using an automated sampler in manual mode when the automatic function fails. If necessary, a pump may be used to draw the sample.

There are several methods of obtaining grab samples:

Grab 1: wastewater is collected in a clean container (e.g. bucket) and immediately transferred to the appropriate laboratory container(s), preserved as necessary and capped.

Grab 2: the appropriate laboratory sample container is submerged in the wastewater stream on a chain or pole until it is full; it is retrieved, preserved as necessary and capped. An automated sampler may also be used in manual mode to collect wastewater directly into the appropriate sample container which is preserved as necessary and capped.

Grab 3: the wastewater is collected in a container as for GRAB 1 and the appropriate clean (outside as well) laboratory container (e.g. volatiles vial) is held at an angle and submerged into the liquid until it is full and air bubbles have been expelled at which time it is carefully retrieved, preserved as necessary and capped. Care must be taken to avoid sample contamination from the outside of the laboratory container, label adhesives or the retrieval device.

Grab samples collected for analysis of compatible ATGs may be combined in a single large container and subdivided later, or they may be collected in several individual containers, each dedicated to a specific analysis.

2.2.2 Composite Samples

Composite samples can be collected either by automated or manual methods.

A manual composite sample consists of grab samples typically taken at equally spaced time intervals and combined (composited) once all sub-samples have been collected.

Automated composite samples can be taken either proportional to the wastewater stream flow (in which cases there must be flow sensing devices connected to the sampler) or on an equal volume/equal time basis. Both of these approaches require fully automated, programmable sampling devices.

Some sampling procedures specific to certain situations are described in Sections 2.5, 2.6 and 2.7, but severally composite samples are collected by the following techniques:

flow proportional:

AUTO 1 Automatic equipment collecting samples proportional to the wastewater stream flow at time intervals of 30 minutes or less over the sampling period, under typical flow conditions.

MANUAL 1 A minimum of eight grab samples taken at equally spaced time intervals over the sampling period (e.g., every three hours in a 24 hour period) combined in proportion to the wastewater stream flow.

equal time/equal volume:

AUTO 2 Automatic equipment collecting samples of equal volume at equally spaced time intervals of 15 minutes or less over the sampling period.

MANUAL 2 A minimum of eight grab samples taken at equally spaced time intervals over the sampling period (e.g., every three hours in a 24 hour period) combined in equal volumes.

MANUAL 3 *See Section 2.5 for specific uses*: A minimum of three grab samples taken at time intervals of at least six hours over the sampling period and combined prior to analysis, or analyzed individually and the mean reported.

MANUAL4 Three grab samples taken at time intervals of at least two hours over an eight hour sampling period.

2.2.3 On-line Analyzers

On-line analyzers offer an alternate approach to sampling and analysis for some parameters. See Section 3.2.

2.2.4 Automated Sampler Considerations

Three important characteristics of automated sampling devices are discussed in this section.

1) Materials Composition

All wettable surfaces that contact the wastewater sample must be inert (i.e., must not contaminate, absorb or adsorb chemicals required to be analyzed in the wastewater sample). This requirement can generally be met through consistent use of materials such as Teflon®, glass, stainless steel and, where dictated by sampler design and function (e.g., peristaltic type pumps, pinch valves, volume control tubes), short sections of surgical grade silicone rubber tubing. This type of tubing should be preferentially replaced by Teflon® or other chemically inert materials as far as possible without impairing the performance of the sampling device. Where surgical grade silicone rubber tubing is used the total length should be kept to an absolute minimum and it is generally accepted that this should be less than two metres. Particular care should be taken to ensure that this tubing and all other wettable parts are cleaned or replaced appropriately.

2) Temperature Stability

A requirement for autosamplers is that they maintain the sample storage environment at a temperature between the freezing point of the sample and 10°C. This will require cooling and/or heating capabilities depending on location and time of year. The temperature must be monitored daily during sample collection and storage and the readings documented. A min-max thermometer or other suitable device may be used for this purpose. Records must be maintained such that all data including repair, inspection, use, maintenance and temperature records be readily available for inspection.

3) Ability to Obtain a Representative Sample

The choice of autosampler design and capability will be dictated by specific sampling and analysis requirements. It is, however, essential that the autosampler take the sample from a location in a wastewater stream that will provide a representative sample. Sample at a point of thorough mixing with no excessive turbulence (loss of volatiles may occur) and at a point away from walls or surfaces of a pipe or channel that may cause insufficient mixing due to currents and eddies. The sampling location must conform to the requirements of Part II of each Effluent Monitoring and Effluent Limit regulation (as listed in section 1.1) or other instrument

issued under Ministry legislation (e.g. ECA) and be evaluated for the impact of any site specific turbulence and mixing phenomena.

The sampler must maintain the sample integrity when transferring effluent from the stream to the sample container, in particular by maintaining adequate velocities (1 metre/second) in the transport system to exceed the scour and settling velocities of the constituents of interest.

2.2.5 Compositing Techniques

Where a sample is collected in a large container and requires analysis for several groups of compounds, the wastewater must be transferred to appropriate laboratory containers. Teflon® or other suitable tubing and gravity suction is recommended for transfer of the wastewater to the individual laboratory container. A peristaltic pump may be used to transfer the aliquots into the appropriate laboratory containers, so long as the materials in contact with the sample conform to the requirements of Section 2.2.4, 1) Materials Composition. The sample may also be poured into the individual laboratory containers. Sample transfer must be accompanied by continuous mixing of the composite sample by using a mechanical stirrer, manual swirling or other appropriate means. Use of magnetic stirring bars should be avoided since they may adsorb suspended solids containing metals, thus affecting the sample integrity.

Where grab samples are collected as part of a composite for volatiles or sulphide (ATGs 15-18), i.e., by the MANUAL 3 technique, each individual sample container must be submitted to the laboratory for analysis. The laboratory has the option of analyzing each sample and recording the arithmetic mean or combining equal volumes of each grab and analyzing the resulting composite.

Where grab samples are collected as part of a composite for solvent extractables analysis (ATG 25), each sample container must be submitted to the laboratory as this analysis includes solvent rinsing of each container. The laboratory has the option of analyzing each sample and recording the arithmetic mean or combining the samples for a single analysis, ensuring adequate rinsing of the sample containers.

Another option for tests such as solvent extractables (ATG 25) or sulphide (ATG 15) is to collect three equal volumes of wastewater into a single pre-graduated laboratory container, which, for ATG 15, has been pre-charged with sufficient preservative to ensure alkalinity of the final solution.

2.2.6 Recommended Sample Volume(s)

See Section 9.0 for recommended minimum sample volumes for each ATG.

The minimum recommended sample volume for a grab is 100 mL except where samples are collected directly in the septum-capped glass vials (ATGs16-18), when sample volumes may be 25 or 40 mL.

A smaller volume may be collected and submitted to a laboratory for analysis if it is sufficient to meet all the analytical requirements including lab and field QC obligations. The volume used for analysis must also be sufficient for the laboratory to achieve its analytical method detection limit (MDL).

2.3 Preservation

See Section 9.0 for preservation requirements for each ATG.

Some samples require preservation to ensure stability of target compounds during transportation and storage or to eliminate substances which may interfere with the analysis. In some cases preservation of the sample is optional, and if selected, will allow for a longer storage period before analysis must be initiated.

Generally, samples requiring preservation must be preserved immediately or as soon as possible, upon collection, either at the end of the collection period for samples collected with an automated sampling device or after collection of each grab sample. See Section 2.5 for cases where the preservative must be pre-charged.

Where a composite sample is collected in a large container for analysis for several ATGs, some of which require preservation, the samples must be preserved immediately following their transfer into laboratory containers.

Where samples are to be preserved to a fixed set-point (pH, colour) care must be taken that the set point has been reached by using detection techniques such as confined range pH paper, pocket/portable pH metres, standard colour comparison charts etc. The use of these techniques and/or devices must not contaminate the sample.

It is recommended that the volume of preservative not exceed 1% of the total sample volume.

CAUTION: Acid preservation of samples suspected of containing cyanide or sulphide MUST be carried out in a well-ventilated area.

2.4 Storage and Shipping

See Section 9.0 for maximum storage times for each ATG.

Storage time is defined as the time interval between sample collection (typically at the end of the 24 hour composite sampling period) and the initiation of analysis. This includes the sample stabilization steps done by the laboratory. This may also be known as sample holding time.

All samples must be stored for as short a time interval as possible and under conditions that will minimize sample degradation.

Samples are to be maintained at temperatures above the freezing point of the wastewater and under 10°C, with minimal exposure to light. See Section 2.2.4, Temperature Stability.

Under the Effluent Monitoring and Effluent Limits regulations, sample pick up is defined for the purposes of collection, storage and transport to a laboratory for analysis (see Glossary). Regulated industries are given prescribed time periods for when samples are to be transferred to a laboratory for analysis.

Prior to shipping samples, every effort should be made to initiate cooling of the samples if they are above 10ºC when collected. Samples are to be transferred under conditions that will maintain their temperature above the freezing point of the wastewater and under 10°C. Upon receipt at the laboratory, data qualifiers/comments may be added when reporting data if samples are received at temperatures >10ºC.

The partial freezing or presence of slush in a sample submitted for toxicity analysis during the winter months must be noted upon sample receipt. The sample may still be analyzed (see 9.36).

2.5 Unique Sampling Requirements for Some ATGs

See Section 9.0 for sampling requirements for each ATG.

The characteristics of sampler composition can be reviewed and adapted to suit the nature and sensitivity of the chemicals to be analyzed and the testing protocols to be used. For example, if an autosampler were applied only to the collection of samples for phosphorus analysis, then wettable surfaces could include materials of a similar composition to the containers for that test (e.g. polyethylene terephthalate or linear polyethylene as described in Section 9.0). The use of a pre-charged container for other parameters not specified below may be used as appropriate.

Cyanide (ATG 2)

Samples collected for cyanide analysis using an automated sampler require a separate container which must be pre-charged with the appropriate preservative as described in Section 9.0.

Samples containing strong oxidizing agents (e.g., chlorine) should be neutralized as soon as possible after sample collection to prevent oxidation/degradation.

Alternate: The MANUAL 3 technique may be used for cyanide, in lieu of AUTO 1 or 2, when an automated composite sampler cannot deliver sufficient sample volume for all required analyses. Pre-charged containers are not required when using this technique.

pH (ATG 3)

Where the characteristics of the wastewater may lead to changes in pH over the sampling period, an on-line analyzer must be used or grab samples must be collected and analyzed as soon as reasonably possible.

Ammonia (ATG 4A)

Samples containing strong oxidizing agents (e.g., chlorine) should be neutralized as soon as possible after sample collection to prevent oxidation/degradation.

Phenolics (ATG 14)

It is recommended that MANUAL sampling techniques be used for phenolics to avoid contamination from silicone rubber parts in automated samplers. If an automated sampler is used, sample contamination may be avoided by using the last bottle in the collection sequence for the phenolics.

A sample collected for phenolics analysis using an automated sampler requires a separate container which must be pre-charged with the appropriate preservative. See Section 9.0.

Samples containing strong oxidizing agents (e.g., chlorine) should be neutralized as soon as possible after sample collection to prevent oxidation/degradation.

Alternate: The MANUAL 3 technique may be used for phenolics, in lieu of AUTO 1 or 2, when an automated composite sampler cannot deliver sufficient sample volume for all required analyses.

Sulphide and Volatiles: ATGs 15, 16, 17& 18

Grab samples must be collected for volatile organics and sulphide analysis and composite samples must be taken by manual sampling techniques.

A volatiles sample should be obtained at a location of quiescence and uniform concentration upstream of turbulence which might strip volatile constituents from the wastewater.

To minimize losses of target parameters, the sample should be collected directly into the laboratory container with no headspace and the container sealed, refrigerated and analyzed as soon as possible. Where the water collected is below 4°C, some headspace may be needed to accommodate increasing pressure within the sealed containers.

Solvent Extractables (ATG 25)

Samples for ATG 25 (oil and grease) must be collected directly into the laboratory container (GRAB 2) to minimize losses during transfer, unless direct retrieval is not practicable. Oil and grease will float on top of the wastewater and the sampler must take great care to ensure that the sample adequately

addresses the presence of immiscible liquids. The best practice is to choose a sampling location in the area of greatest mixing to ensure that a representative sample is collected. The sample container should not be rinsed, as the hydrophobic nature of the oil and grease will cause it to coat the inside of the sampling container resulting in inflated results which are not representative of the wastewater sampled.

Total Residual Oxidants (TRO): ATG 31

TRO must be sampled and analyzed using an on-line analyzer or by collecting a grab sample (GRAB 1, GRAB 2 or GRAB 3) and analyzing it as soon as reasonably possible (within 1 hour).

Escherichia coli (E. coli) (ATG 35)

E. coli samples must be collected by the GRAB 2 technique. Where disinfection is accomplished through the use of oxidizing agents (e.g., chlorine or sodium hypochlorite), sodium thiosulphate must be added to *E. coli* samples as soon as possible after sample collection(if the sample container is not pre-charged with sodium thiosulphate). Samples must not be frozen.

Changes in *sampling* techniques

Changes in sampling techniques should be kept to a minimum: once a valid mode of sampling has been selected, it must be maintained and changed only if necessary. Each change must be documented and reported to the MOECC or to the municipality in the case of Sewer Use applications.

2.6 Sampling for Toxicity

Toxicity samples are liquid samples collected from surface waters, leachates or industrial/municipal discharges for measuring the survival of rainbow trout and *Daphnia magna* (acute lethality testing). Fathead minnows and *Ceriodaphnia* may be used for chronic (sub-lethal) toxicity testing. They are collected as grab samples from the location(s) specified in the applicable Effluent Monitoring and Effluent Limits regulation or in an instrument such as an ECA.

Sample containers can be made of any clean, non-toxic material such as glass, polyethylene, polypropylene, polycarbonate, stainless steel, Nalgene® or Teflon®. Sample volumes are listed in section 9.36.

It is recommended that food-grade polyethylene liner bags be used to line the sample containers (pails) when collecting the large volumes required for rainbow trout and fathead minnow testing. Fill the bag lining the inside of the pail directly from the sample site, or fill the bag using another sampling device which has been thoroughly cleaned and then rinsed with the sample.

Squeeze the bag to expel all the air, and then apply a tie-wrap to seal. Check that the lid of the pail is tightly closed. Use a tag to identify the sample, complete

all required information (see section 4.2.3) and then attach to the handle of the pail.

When sampling directly into a container, rinse the container briefly with sample, discard, and then refill the container ensuring there is no or minimal air trapped in the container.

Samples for acute lethality testing MUST be analysed within 5 days of sampling. Ship samples by the quickest method available. Ensure all tags and submission sheets are filled out completely. **Samples must not be allowed to freeze solid during transport.** Frozen solid samples will not be tested. If a sample will be in transit for more than 2 days, attempt to keep the sample cool by placing cold packs or wet ice (wrapped in a separate sealed bag) inside the pail, but outside the sample bag. An option may be to double bag the sample to ensure the ice water or a leaking cold pack does not contaminate the sample.

Samples for sub-lethal testing (*Ceriodaphnia* and fathead minnow) must be tested within 3 days of sampling.

2.7 Sampling Under the Effluent Monitoring and Effluent Limits Regulations

The Effluent Monitoring and Effluent Limits regulations specify sampling location and frequency requirements. Requirements for different discharge types are outlined below. Reference must be made to the regulations for specific requirements.

Process Effluent

Flow proportional composite samples must be collected from process effluents (AUTO 1, MANUAL 1 for most ATGs, except MANUAL 3 for ATGs 15–18).

In cases of automated sampler malfunction, composite samples must be collected using the MANUAL 1 technique. If the malfunction affects only the flow proportional programming, the AUTO 2 sampling technique may be used.

The discharger must be able to demonstrate that the samples are being collected flow proportionally by recording the number and/or volume of samples, where possible.

In cases where the process effluent stream flow has been proven, to the Director's satisfaction, to be non-variable, equal volume/equal time composite samples may be collected (AUTO 2 or MANUAL 2 for most ATGs except MANUAL 3 for ATGs 15-18). The discharger must record the number and/or volume of samples, where possible.

Variable flow means a flow rate within a day which varies by more than plus or minus 15 percent of the daily mean flow rate for more than 10% of the time (more

than 150 minutes per operating day for more than 18 operating days in a six month period).

Sampling for pH

Where the Effluent Monitoring and Effluent Limits regulations require pH analysis, three grab samples must be collected over the sampling period at intervals of at least four hours and each GRAB analyzed as soon as reasonably possible. An on-line analyzer may be used and three readings taken at intervals of at least four hours must be recorded and reported.

Batch Discharges of Process Effluent

Where a process effluent is to be discharged in batches, a grab sample of the effluent must be collected. If the effluent is not representative of the process, e.g., thorough mixing is not possible or particulates are not completely re-suspended, a composite sample of the effluent must be collected using the AUTO 1 or 2 techniques (MANUAL 3 for ATGs 15–18). If conditions prohibit use of an automated sampler, three grabs must be collected from the effluent: one at the beginning, one halfway through, and one at the end of the discharge.

Cooling Water

Composite samples must be collected from cooling water streams and the AUTO 1 or 2 techniques are preferred, although the MANUAL 3 technique may also be used. In case of automated sampler malfunction the MANUAL 3 technique may be used.

Storm Water

Sampling requirements for storm water streams are outlined in the MOECC *Protocol for Conducting a Storm Water Control Study*, current version, as amended from time to time.

2.8 Sampling Under Environmental Compliance Approvals for Sewage Treatment Plants

The following requirements do not apply to pH (ATG 3) and TRO (ATG 31– total residual oxidants or total residual chlorine) which are best sampled and analyzed using on-line analyzers.

An alternate sampling method for these parameters is the collection of a grab sample which is then analyzed as soon as reasonably possible.

***Process effluent, secondary treatment plants and primary treatment plants*:**

The following sampling procedures apply to sewage treatment plant effluent monitoring for assessment of compliance with effluent limits set in their environmental compliance approvals (ECA) and other assessments that may be required by an ECA or by an Order. Consult the applicable ECA or Order for any

specific requirements, which would take precedence over this protocol. The design capacity, treatment process, and access restrictions of each site will also affect the selection of sampling technique.

A plant with a design capacity exceeding 4,600 cubic metres per day must collect from each process effluent stream a composite sample over a 24 hour period using automated sampling equipment and the AUTO 1 or AUTO 2 technique.

In cases of autosampler malfunctioning, composite samples should be taken by the MANUAL 1 or MANUAL 2 technique.

A plant with a design capacity of less than 4,600 cubic metres per day may collect from each process effluent stream a composite sample consisting of three grab samples taken at intervals of at least two hours over an eight hour period (MANUAL 4). The grabs may be combined prior to analysis or the laboratory may analyze each individual sample and report the arithmetic mean. Samples should be collected during peak influent flow periods to be representative of average operating conditions.

Lagoon Treatment Plants

A lagoon treatment plant which discharges continuously, must collect from the effluent stream a composite sample over a 24 hour period using automated equipment and the AUTO 1 or AUTO 2 technique. In cases of autosampler malfunctioning, composite samples should be taken by the MANUAL 1 or MANUAL 2 technique.

A lagoon treatment plant which discharges seasonally or annually over a period of one week or less, must collect three grabs, one at the beginning, one in the middle and one at the end of the discharge. When the seasonal or annual discharge period exceeds one week, the lagoon treatment plant must collect one sample for each week of discharge

Bypass Effluent

A sample may be collected from each bypass effluent stream as a single grab sample (GRAB1, 2 or 3) during each day of a bypass discharge. Each sample must be analyzed as soon as is reasonably possible after sample pick-up.

3.0 Guidelines for the Analysis of Samples

See Section 9.0 for analytical principles for each ATG.

3.1 Principles of Analysis

This section describes and provides guidance on the general principles and protocols to be followed in sample preparation, clean-up and instrumental analysis.

The analysis of wastewater samples can be a very demanding and complex activity depending on the type of sample, matrix problems, the presence of co-extractive or interfering materials etc. In this regard it is necessary that laboratory analysis be performed according to tenets of good laboratory practice as well as regulatory requirements.

A few key requirements that must be met are:

- analysis must be carried out by competent laboratory personnel in a properly equipped and maintained laboratory environment;
- analytical techniques must be appropriate for the sample matrix and must lead to adequate separation and accurate identification of the compounds to be analyzed;
- recovery of target parameters must be optimized;
- analytical procedures must comply with the principles and protocols of analysis listed in Section 9.0.

All wastewater samples must be analyzed according to the sample preparation and instrumental measurement principles listed for each ATG in Section 9.0. This includes elements related to container materials, container pretreatment and preservation.

Before an analytical procedure can be used, the laboratory method detection limit (LMDL) must be determined for each target parameter according to the procedure described in Section 6.0 and must be equal to or less than the regulatory method detection limit (RMDL) values listed in Section 8.0, Table 1.

All analyses must be initiated within the time frames listed as maximum storage times for each ATG in Section 9.0, except in unavoidable circumstances, in which case analytical results must be qualified by the remark code "OLD" as described in Section 5.2.5. Results of analyses must be made available as soon as reasonably possible.

Sufficient and appropriate QC samples must be included with each set of samples being analyzed. Section 9.0 lists the types of QC samples which apply

for each ATG. The types and frequency of QC samples are specified in Section 4.3.

3.2 Recommended and Alternate Techniques

Section 9.0 outlines recommended and any alternate principles of preservation and storage times, sample preparation and instrumental measurement.

The recommended instrumental measurement method principles are deemed to be the most suitable for a wide range of effluent matrices.

The alternate instrumental measurement method principles may be suitable for some effluent types.

3.2.1 Container Pre-treatment

Generally new containers do not need to be cleaned prior to use, but if they are re-used, recommended pre-treatment or washing procedures are identified in Section 9.0 for each ATG.

Each laboratory is responsible for ensuring that all glassware, reagents and equipment used for sampling and/or analysis are suitably clean and free from contaminants and interfering substances. The frequency and nature of cleanliness checks demonstrating acceptability of labwares is the responsibility of the laboratory.

3.2.2 Sample Preparation and Pretreatment

The task of preparation and/or pretreatment of wastewater samples prior to instrumental analysis can represent the majority of time and effort in the overall analysis scheme. Where preparation or pretreatment is required, principles and protocols to be followed are listed in Section 9.0 for each ATG. With the range of preparation/pretreatment techniques available, the main consideration is to treat the sample so that it will be suitable for the instrumental technique being employed and for the matrix being analyzed. Containers should be rinsed with the matrix to be analyzed prior to sample collection, unless the container has been pre-charged with a preservative.

3.2.3 Instrumental Analysis

Instrumental measurement methods must comply with the principles set out in Section 9.0 for each ATG.

3.2.4 Calibration

All analytical instruments must be calibrated in accordance with good laboratory practice. This includes periodic multiple point calibration (full calibration series) to establish response factors and linearity range. Daily calibration checks using a subset of the full calibration series are required

before each run and should be repeated at intervals during the run to verify system stability and control.

Calibration standards must be validated against a standard reference material, if available from a standards organization as described in Section 4.5.

A calibration curve must be established and confirmed periodically for each analytical procedure within the range normally encountered in samples of the type being analyzed.

3.3 On-Line Analyzers

On-line analyzers offer the capability to continuously monitor and report the presence and concentration of selected constituents in the wastewater stream. For an approved list of constituents (ATGs 3, 5a, 7, 16, 17, 18 and 31), these analyzers present an alternate approach to manual or automated sampling and subsequent laboratory analysis. An ECA may also approve the use of an on-line analyzer for other parameters.

The sampling equipment and instrumentation used must satisfy the requirements which are identified in Section 2.1.4. These include sampling equipment materials of composition, the ability to obtain a representative sample and assurance of temperature stability. They must also meet the criteria set out in Sections 3.0 and 4.0 in the analytical principles used for the test in question which include QA/QC practices such as establishing control limits and calibrating against reference standards.

An on-line analyzer should continuously monitor the wastewater and produce a continuous record over the sampling period; the continuous record should be composed of minute by minute or more frequent monitoring data. In the case of on-line GC analysis, the continuous record should be composed of data monitored at not more than two hour interval frequencies.

3.3.1 Use, Operation and Maintenance

On-line analyzers must be properly installed and operated according to good laboratory practice principles. Initially, on-line analyzers should be inspected and calibrated daily to determine the time interval during which the instrument continues to operate within reasonable control limits.

Subsequently the maintenance and calibration frequencies may be adjusted accordingly with a weekly interval as the minimum. These activities must be documented and be available upon request.

3.3.2 Recommendations for pH and Specific Conductance Analyzers

Electrodes must be cleaned regularly to maintain their accuracy and replaced when their performance becomes unacceptable. Experience has

shown that the need for calibration tends to be less frequent when the electrodes are replaced at regular intervals.

3.3.3 Performance Check

At least once a month the performance of each on-line analyzer must be checked to verify its continued proper functioning by verifying the operating system using an appropriate certified reference material. (See the Glossary for definition.)

The equipment used for these checks must meet the criteria set out in Sections 3.0 and 4.0 in the analytical principles used for the test in question including QA/QC practices such as establishing control limits and calibrating against reference standards.

3.3.4 Malfunction

When an on-line analyzer malfunctions samples may be collected by the AUTO 1 or 2 or the MANUAL 1 or 2 techniques.

3.4 Analytical Performance Criteria

3.4.1 Method Detection Limits (MDL)

See Section 8.0, Table 1 for RMDLs for each ATG.

To ensure that all laboratories performing wastewater analyses have the capability to perform these analyses at appropriate levels, they are required to determine a laboratory specific method detection limit (LMDL) for each parameter to be analyzed.

These LMDLs must be determined according to the MOECC protocol described in Section 6.0, using the sample volumes, preparation and instrumental analysis procedures which will be used for wastewater samples.

An analytical method must not be used for samples taken under Effluent Monitoring and Effluent Limit regulations or other instrument issued under Ministry legislation until all LMDLs have been demonstrated to fall at or below the higher of either one-fifth of the average level or limit typically found in the specific effluent stream being monitored, or the applicable Regulatory Method Detection Limit (RMDL) values listed in Section 8.0, Table 1.

The LMDLs are to be recorded using the number of significant digits used in recording subsequent sample data generated by that analytical method (usually 2 figures). This is further defined in Section 5.1.3.

It is recommended that LMDL determinations be repeated at least - annually for each parameter to be analyzed by a laboratory unless routine

QC data demonstrate that no significant change has occurred in the sensitivity or the precision of the analytical procedure. The LMDLs must be re-determined whenever a significant change is made to a method.

LMDLs should be determined using the routine sample aliquot and dilution factor that will be applied to "real" samples because the size of sample analyzed and associated changes in dilution will affect the LMDL value proportionately.

If a dilution factor is applied to the LMDL, a sample where the measurement is near or below this adjusted LMDL must be re-analyzed using a larger aliquot to meet the requirement to measure down to a LMDL which is less than the RMDL listed in Table 1.

If matrix interferences preclude target parameter detection near the LMDL the protocol described in Section 5.2.3 must be used.

Where matrix effects cause co-elution of compounds, the analytical method used for LMDL determinations and sample analyses is expected to resolve all target parameters (exceptions are listed in Table 1), but it is understood that there may be cases where interferences render resolution impossible. However, it is expected that the laboratory will make every reasonable effort to resolve and quantitate every required parameter. In the case where an effluent is known to contain interferences, e.g., chloride, a different detection method or additional clean-up must be used where possible.

3.5 Adoption of New Methods

The method principles recommended in Section 9.0, ATG Guide reflect the best known methods of analyzing effluent at the time of this revision. To facilitate the use of alternate methods of analysis, and to accommodate future analytical improvements, the MOECC recommends that a laboratory follow the principles outlined in *Protocol for Acceptance of Alternate Methods (PAAM)*, PIBS 5297e, as amended from time to time.

3.6 Method Validation

Any new method must be validated by the user prior to use and all methods must be re-evaluated periodically to ensure their continued validity.

The following are some suggestions which may be of assistance to anyone wishing to validate a method.

- Verify the calibration standards against appropriate reference materials, where available from a standards organization.

- A comparison of data from samples analyzed by an already valid method and the new method should be carried out to indicate ability of the new method to analyze the particular matrix involved for the required parameter.

- Criteria or control limits should be set and documented for acceptance or rejection of the calibration standards.

- Within run and between run precision should be determined in reagent water and samples which approximate the matrix routinely analyzed. Control limits should be set for each sample type.

- Documentation should be available demonstrating that the required QC samples are run with every batch of samples, that they are checked for conformance to predetermined performance levels (e.g., control limits) and that corrective action is taken when performance does not meet specifications.

- Uncertainty of measurement should be estimated and documented. There are several guidelines for the estimation of measurement uncertainty including those published by MOECC and EURACHEM/Cooperation on International Traceability in Analytical Chemistry (CITAC). Every possible source of uncertainty should be evaluated, but only those exceeding one-third the largest source need to be included in estimating combined uncertainty. If method performance data are used to estimate uncertainty, studies should be conducted such that the number and range of effects, concentrations and matrices are varied to ensure that the conditions encountered under normal use of the method are represented.

- The presence of a quality assurance system should also be demonstrated to ensure that the quality control procedures are continuously documented, monitored and controlled.

3.7 Special Considerations and Precautions

CAUTION: Acid preservation of samples suspected of containing cyanide or sulphide MUST be carried out in a well-ventilated area.

Test Specific Precautions

The following include some of the more important precautions to be followed in the sampling and analysis of certain parameters.

COD (ATG 1)

High chloride content in samples may cause severe interference problems in the analysis of COD.

Biochemical Oxygen Demand (5 day) (ATG 1a)

Where the option to use an oxygen electrode is selected for BOD_5 determination, the data must be verified by analyzing at least one sample or standard by an alternate technique and the oxygen electrode method (both results must be recorded). To avoid sample degradation samples must be analyzed immediately.

Carbonaceous Biochemical Oxygen Demand (5 day) (ATG 1b)

For the analysis of $CBOD_5$, a nitrification inhibitor must be added to the sample before analysis, either in the field or in the laboratory.

pH (ATG 3)

Where the characteristics of the wastewater may lead to rapid changes in pH an on-line analyzer should be used or grab samples collected and analyzed as soon as reasonably possible.

DOC/TOC (ATG 5)

High chloride content in samples may cause severe interference problems in the analysis of DOC/TOC.

Total and Soluble Phosphorus (ATG 6 & 6a)

The stannous chloride procedure must not be used due to linearity problems: increases in phosphorus concentration beyond a method-specific point are detected as decreases. Consequently, unexpectedly high phosphorus concentrations may not be detected.

Metals (ATGs 9, 10 and 12)

If the presence of cyanide or sulphide is suspected in the wastewater, care must be taken to ensure adequate ventilation while lowering the pH, and the sample container and submission sheets must contain adequate caution notes to alert laboratory staff to the presence of these chemicals.

When spiking samples, care must be taken to ensure that the presence of anions will not result in the formation of insoluble compounds.

Boron (ATG 9)

Glass containers must not be used when samples are to be analyzed for Boron due to the possibility of sample contamination from borosilicate.

Hydrides (ATG 10)

It is recommended that plastic bottles not be pre-charged with concentrated nitric acid to avoid false positives for antimony.

Mercury (ATG 12)

Hydrochloric acid is the preferred preservative for samples collected for mercury analysis.

Samples containing coloured materials, reducing agents and highly alkaline substances may require larger volumes of the previously recommended potassium dichromate solution and nitric acid as preservatives. These preservatives are still acceptable as an alternative. The amounts of preservatives to obtain coloured acidic samples should be determined and these volumes noted on the sample bottles so that an appropriate blank compensation can be done.

Preservatives are likely to become contaminated if stored in plastic vials/bottles close to mercury and its compounds. It is recommended that preservatives be stored in glass containers and away from mercury and its salts. A periodic test for mercury should be made to ensure preservatives are uncontaminated.

Volatile Organic Analysis (ATGs 16-18)

Grab samples composited in the laboratory must be handled carefully and quickly to avoid undue losses of target parameters.

Extractables, base-neutral (ATG 19)

Samples must not come into contact with any plastic or rubber material (such as disposable gloves) to avoid contamination by substances such as phthalate esters.

Extractables, acid (ATG 20)

Samples must not come into contact with phenolic resins, such as Bakelite®caps, to avoid sample contamination.

General Organics (ATGs 16-27 and 34)

Collection of duplicate samples is recommended for organics analyses (ATGs 16–27 and 34) in case problems are encountered necessitating re-analysis and to fulfil QC sample requirements including use as an alternate for laboratory replicate sample or spiked sample.

Dioxins/Furans (ATG 24)

Regulatory limits are set as total toxic equivalents (TEQ) in addition to individual limits on 2,3,7,8-TCDD and 2,3,7,8-TCDF. Analysis for the 17 most toxic congeners is now required, as opposed to the total congener group analysis. See Section 9.22 and Table 2.

Solvent Extractables (ATG 25)

The Ministry continues to designate n-hexane as the recommended solvent for extraction and residue characterization of industrial and municipal wastewaters. At this time, the use of dichloromethane as extraction solvent is assigned as the alternate procedure and Freons, as a group, are assigned as not recommended for the analysis of solvent extractable materials (also colloquially referred to as “oil and grease”).

PCBs (ATG 27)

The total PCB concentration calculated as an Aroclor or a mixture of Aroclors is required and laboratories doing congener-specific analysis should record these in addition to the required data. A trigger may be set requiring that PCB results above this concentration be confirmed by congener analysis to assist in determining the potential for toxic effects.

Fluoride (ATG 30)

High chloride content in samples may cause severe interference in the analysis of fluoride.

Some organic acids may interfere with ion chromatographic analysis of fluoride.

4.0 Quality Management

See Section 9.0 for QC requirements for each ATG.

"Quality Management: coordinated activities to direct and control an organization with regard to quality.” International Standards Organization, ISO9000:2005.

Environmental analysis requires a sound field and laboratory quality management program to ensure the quality of the analytical data produced. The laboratory management, in consultation with its customers, is responsible for ensuring that appropriate control activities and performance evaluation procedures are identified and performed, that the results are documented, and that appropriate action is taken in a dependable, timely and economic manner.

A good Quality Management (QM) program includes activities such as the development of a quality documentation system, including a Quality Manual, regular use of external reference materials, participation in inter-laboratory (round-robin) comparison studies, and accreditation by an independent party (such as the Canadian Association for Laboratory Accreditation [CALA] or the Standards Council of Canada [SCC]). Accreditation does not preclude the possibility of inspections to evaluate compliance with regulatory requirements.

The standard CAN-P-4E (as amended from time to time), Canada’s adoption of ISO/IEC Standard 17025:2005 (as amended from time to time), outlines the requirements associated with documenting and implementing appropriate systems for managing staff, methods, equipment, samples and data.

4.1 Quality Assurance and Quality Control (QA/QC)

"Quality Assurance: part of quality management focused on providing confidence that quality requirements will be fulfilled." International Standards Organization, ISO9000:2005.

Quality assurance (QA) encompasses those activities which define the level of quality required, the critical system components which may impact quality, the procedures whereby quality status will be determined, and the nature and timing of any remedial action required. A comprehensive QA program will ensure that the quality of the process and its product is monitored, documented, and controlled on a continuing basis.

"Quality Control: part of quality management focused on fulfilling quality requirements." International Standards Organization, ISO9000:2005.

Quality control (QC) encompasses those activities which specifically monitor and control discrete laboratory tasks or systems to produce the information that is required to verify and demonstrate that they meet predefined operating criteria or to substantiate the need for remedial action.

Performance Evaluation encompasses activities which evaluate and document the overall control status of the process and determine the need for long-term remedial action.

Good Laboratory Practice (GLP) is a fundamental level of activities in the quality management of a laboratory. It encompasses elements of good housekeeping, cleanliness, quality and consistency of supplies, availability of standard operating procedures for all routine analysis activities, application of good technique based on proper education and training, as well as appropriate documentation of organizational and experimental purpose, tasks, procedures, observations, conclusions or results.

The establishment and maintenance of GLP and QM in a laboratory can be accomplished through the adoption of a standard code of practice such as those defined in CAN-P-4E/ISO/IEC 17025:2005.

4.2 Documentation/Record Keeping

An essential element of QA/QC is documentation and record keeping for all facets of sample handling and analysis.

4.2.1 Methods/Bench Procedures

An authorized, formal written description of the method used to analyze samples is necessary. Bench procedures must be documented in sufficient detail to ensure proper uniform application and must be readily available to technical staff. When modifications are required because of sample matrix or other factors, they must be noted and appended to the appropriate analytical records. Bench procedures should include sample pretreatment/preparation, instrumental measurement methods and data reporting procedures. QC activities documented in the bench procedures should include instrument calibration standardization, standards preparation and validation, frequency of use of reference standards and materials, as well as the sources of all standards and standard solutions. Bench procedures and methods should be reviewed periodically to ensure their continued applicability to the matrices of interest.

4.2.2 Analytical Control Status

Protocols must be established to demonstrate that analytical systems are in control.

Control limits must be established and maintained for calibration and method blanks and should also be determined for replicate or duplicate precision, reference material accuracy and target parameter recovery.

Records must be kept of corrective actions taken when control elements are exceeded.

Control charting is a highly recommended method to demonstrate control status. The number of analytes being monitored and charted for control will depend on the individual behaviour of each analyte in a given laboratory setting. However, it is usual practice to demonstrate control of all analytes for a period of at least one year after which time a few selected, representative analytes can be monitored and charted for control of an entire group. The pertinent data for the remaining parameters must be recorded and stored for future use, if necessary.

Parameters limited under a regulation or other instrument issued under Ministry legislation must be demonstrated to be under control; selection of other representative analytes for control charting is at the analyst's discretion.

The use, monitoring and charting of reference materials is an additional external verification of performance. The frequency of analysis and types of certified or standard reference materials will vary between laboratories depending on availability and analysis capabilities, but should generally represent 10% of routine in-house QC efforts.

4.2.3 Sampling Records

Records of sampling and sampler maintenance must be kept current and accessible for review.

Records must include:

- date and time of all sampling activity including grab and toxicity samples and performance check samples for on-line analyzers, etc;
- temperature stability records;
- sample identification, e.g., wastewater stream, control point etc.;
- sample collection method, e.g., autosampler, 24 hour composite, grab, etc.;
- identification of sampling staff;
- malfunctions and corrective action taken;
- maintenance log including frequency and type of maintenance performed, e.g., tubing changes, cleaning, reprogramming, programmer repairs etc.;
- calibration, cleaning, repair log for on-line analyzers;
- sample condition; this may include the presence of slush and/or ice chips during the winter
- any other relevant information.

Any sampling malfunctions/problems which may impact sample analysis must be communicated to the laboratories performing the analysis.

4.2.4 Analytical Records

Formal data recording and reporting practices must be established to ensure that the quality of a reported result is known and that it is traceable back to the raw information on which it is based.

Analytical results must be recorded and archived along with the information required to ensure traceability to all associated procedural, quality control and performance evaluation records. An archiving policy should be established to ensure retention of analytical and QA/QC records for a minimum of three years.

An electronic database/spreadsheet format is recommended to enter, store and display data as tables or graphs.

4.2.5 QC Sample Records

Laboratories must maintain all records necessary to show that the analytical systems used were in control at the time of analysis. The results of these QC and performance monitoring checks should be separately tabulated and summarized for ready retrieval, evaluation and audit. They must be retained in a secure manner for review. A protocol should be established for data correction and any corrections should be made in such a manner that the original data is legible. QC records include results of all analyses of laboratory and field QC samples, as well as spiking concentrations for both the spiking solutions and spiked samples.

It is recommended that a protocol be established for the frequency and content of a statistical summary of QC sample data to facilitate data review by the analyst and clients. This summary should include all QC sample types and present a statistical review for each individual test such as number of samples, range of values observed, average or mean, standard deviation, plus any other relevant mathematical or statistical summary.

4.3 Laboratory QC Samples

See Section 9.0 for laboratory QC samples which apply to each ATG.

4.3.1 Types and Frequency

Four types of laboratory QC samples must be collected and/or prepared and analyzed with each analytical run. For a few special cases such as pH only one QC sample, (duplicate or replicate) need be analyzed. Section 9.0 lists the QC samples required for each ATG. An analytical run means a group of samples which are processed together through each step of an analytical procedure.

A set of laboratory QC samples comprises the following:

i) A method blank sample which is an uncontaminated sample of reagent water which is free of the target parameters and of any substance which may interfere with that analysis. It undergoes sample processing identical to that carried out for the test samples.

ii) A replicate sample which is an additional or second aliquot (portion) of a randomly selected sample in the analytical run. If there is insufficient sample volume for replicate analysis for ATGs 19–23, 25–27, a duplicate sample must be collected and analyzed.

Note: for ATG-16–18, the replicate sample requirement may be fulfilled by the collection and analysis of duplicate samples (defined in Section 4.4.1), unless the sample injection system allows for replicate analysis of the original sample.

Whether a replicate or a duplicate sample is analyzed must be specified when recording and reporting results

iii) A spiked blank sample is a method blank sample to which known (and recorded) quantities of each target parameter have been added; the concentrations added should be 5-10 times the individual RMDLs. This may also be referred to as a laboratory control sample.

iv) A spiked sample is a randomly selected sample in the analytical run to which known (and recorded) quantities of each target parameter has been added. Where there is insufficient sample volume, a duplicate sample must be collected, spiked and analyzed in lieu of a replicate. The recommended spiking concentration is two to three times the typical concentration in the effluent. The difference between the spiking concentration and the sample concentration should exceed the method precision.

Each of these QC samples must be processed through each step of the analytical procedure. The number of QC samples which must be analyzed depends on the number of samples in the analytical run.

Where a run consists of 20 samples or fewer, a single set of four QC samples must be analyzed at the beginning of the run. Where a run contains 21 to 40 samples, two sets of QC samples must be run, one at the beginning of the run and a second set after 20 samples. If there are 41 or more samples in a run, a minimum of three sets of QC samples must be run, one at the beginning, one in the middle and one at the end of the run.

4.3.2 Use of Laboratory QC Data

Laboratory QC sample analysis will serve to monitor the performance of the methods, the instrumentation and the analyst.

All QC activities must be documented and detailed records must be retained for review.

QC sample results are generally expected to fall within established control limits. If this is not the case, the impact and data quality of associated samples must be reported using appropriate remark codes or in a covering letter.

Replicate sample analysis will provide an indication of within-run precision.

Analysis of spiked blank samples will provide an indication of the efficiency of the method to recover and accurately quantify target parameters.

Results of spiked sample analysis will indicate the presence of matrix-specific interferences which may hinder accurate target parameter recovery and quantification.

Method blank sample results will establish a baseline response and indicate the presence of contamination in glassware and equipment, and cross contamination from samples containing high concentrations of target parameters or interfering substances. Should method blank sample results fall outside the established control limits, results must be reviewed and validated or the samples in that particular run must be re-analyzed accompanied by method blank samples which fall within the established control limits.

Results for all QC samples must be closely monitored and reviewed periodically by responsible staff to ensure that out-of-control situations are identified and corrected. The protocols for definition and reaction to such situations must be documented and available to laboratory staff.

It is recommended that sufficient sample volume be collected for repeat analysis if needed. However, if the sample volume is insufficient for re-analysis, a new set of samples must be collected and analyzed, accompanied by a controlled method blank sample.

Data are not normally corrected for method recovery (e.g., surrogates) except when isotope dilution is used as in dioxin analysis.

4.4 Field QC Samples

Field QC samples indicate sampling variability and the presence of field contamination. This is especially relevant to sampling in areas where the risk of cross-contamination is often high.

4.4.1 Types and Frequency

i) A duplicate sample is one of two separate samples collected at the same time in a manner that minimizes differences. When an

autosampler is used, samples collected in separate bottles may be considered to be duplicates, otherwise duplicate samples must be collected using two automated samplers installed at the same sampling location. Samples collected by manual grab methods must be taken simultaneously or sequentially. The duplicate sample must be correctly identified and recorded so as to facilitate data evaluation.

ii) A travelling blank is a sample of uncontaminated reagent water free of the analytes of interest. It is prepared by the laboratory performing the analysis, brought to the sampling site, opened at least as long as the manual sampling interval, (or while sampler bottles are being changed), preserved as necessary, then returned to the lab for analysis. A travelling blank is not required where an on-line analyzer is used unless the monthly performance check sample is transported to a laboratory for analysis; then a travelling blank sample should be prepared and analyzed quarterly. This may also be known as a field blank.

iii) A travelling spiked blank is a sample of uncontaminated reagent water free of any interfering substances to which a known amount of standard solution and appropriate preservative have been added by the laboratory performing the analysis. The travelling spiked blank must be prepared within *24 hours* of accompanying the sample containers to the sampling location. The travelling spiked blank is brought to the field and returned, unopened, to the same laboratory for analysis. The travelling spiked blank must be spiked with solutions containing all the target parameters required to be analyzed.

It is **required** that at least once a year, a duplicate sample must be analyzed from at least one process effluent stream for which limits have been set, for which the frequency of monitoring is weekly or quarterly. As well, a travelling blank and a travelling spiked blank must be analyzed in accordance with this Protocol for each sample for which a duplicate is being analyzed. These requirements do not apply to 2,3,7,8--tetrachlorodibenzo-para-dioxin, 2,3,7,8-tetrachlorodibenzofuran, or other 2,3,7,8-substituted dioxin and furan congeners.

It is *recommended* that a set of the above field QC samples be analyzed for every effluent stream once a month for parameters which are monitored daily, once a quarter for weekly parameters, semi-annually for monthly and quarterly parameters, and annually for semi-annual parameters, to ensure and demonstrate control of the sampling process, and effluent quality.

Duplicate samples should be collected for all ATGs. Travelling blank samples should be prepared and analyzed for all ATGs except ATGs 3, 8, 24, and 25, at the frequencies listed above. When on-line analyzers are

used, field QC samples need not be collected and analyzed. However, if the monthly performance checks are analyzed in a laboratory as opposed to using instantaneous field measurement, the performance check sample should be collected and analyzed in duplicate.

Travelling spiked blanks should be prepared and analyzed only for organic analyses, ATGs 16–23, 26, 27, 33 and 34.

When recording field QC results, the proper sample type codes must be used to correctly identify the samples for data evaluation.

4.4.2 Field QC Data Application

Each of the field QC samples provides different information about the quality of the effluent samples collected and indicates possible field contamination.

A duplicate sample provides a measure of the reproducibility of the sampling, handling and analytical techniques used.

A travelling blank sample will provide an indication of any problems with sample contamination due to extraneous volatile fractions of contaminants in the atmosphere and any contaminants introduced by handling of the sample containers.

A travelling spiked blank sample should provide an indication of the degree of degradation of the target parameters from the time of sampling to analysis.

Field QC data is an integral part of the database. All records associated with the field QC analysis, as well as the associated laboratory QC samples must be accessible for review.

4.5 Reference Materials

A reference material (RM) is defined as a “material, sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in measurement or in examination of nominal properties**”** (VIM, ISO/IEC Guide 99:2007, 5.13).

A certified reference material (CRM) is a “reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures.” (VIM, ISO/IEC Guide 99:2007, 5.14). Examples of sources of CRMS are the National Research Council of Canada, the National Institute of Standards and Technology, or other international standards organizations.

Calibration standards should be validated against reference materials if available from a standards organization. RM/CRMs are used as an independent check of a system calibration. Frequency of RM/CRM analysis will depend on the nature

and historical data for the analytical system of interest. Well established, traditional, stable methods/standards may require use of RM/CRMs on a less frequent basis, while experimental methods or highly variable or perishable standards may need more frequent RM/CRM analysis.

When a suitable RM/CRM is not available, calibration standards should be validated against a traceable second (different) source of standards.

Results of RM/CRMs and the associated QC samples should be documented and summarized. Control limits for RM/CRMs may be established and performance reports prepared indicating the accuracy of RM/CRM analysis.

5.0 Analytical Data Recording

This section presents guidelines and requirements with respect to recording results for all analytical test groups (ATGs). Whether or not there is a requirement to report data to the MOECC, there is a requirement to record and maintain an appropriate data management system by any regulated organization and within the laboratory providing the analytical services. This system must ensure that records are readily accessible for audit by the MOECC upon request.

The following sections address the determination of: analytical repeatability (S_w), method detection limit (MDL), the smallest reporting increment (SRI) and truncation or round-off of measurements. They describe the use of remark codes, particularly for indicating low-level results and the definition and use of method codes.

Test codes and units of measure codes to be used to report data to the Ministry are found in the Ontario Ministry of the Environment and Climate Change Wastewater System (MEWS) software. Information on the use of MEWS for reporting data electronically to the MOECC is obtained in the *MEWS User Guide for industrial officers and staff*, as amended from time to time, which addresses the specific details (e.g., sample type codes) and procedures required for both effluent and field QA/QC data. The MEWS User Guide is available electronically at MEWS Industrial User Guide.

The *MEWSXML Format Electronic File Transfer for industrial officers and staff*, as amended from time to time, provides guidelines for electronic data transfer to MEWS, and is available electronically at MEWS Electronic File Transfer.

5.1 Routine Data Recording – General

A laboratory's data management system will establish and maintain direct links between the sample information (such as source, field sample number/code, date/time sampled, tests required, etc.) and laboratory information (such as lab sample number/code, date/time analyzed, tests performed, analyst, etc.).

A properly recorded result will include the test/analyte name/code, the units of measure, the method used and appropriate qualifying remarks. The result will include an adequate number of significant digits (based on the analytical repeatability of the method used).

This protocol specifies:

a) analytical principles, to ensure general data comparability; and,

b) analytical sensitivity, based on pre-determined criteria for analytical detection capability, to ensure a consistent ability to measure at the levels required to ensure achievement of the regulatory and/or program's goals.

The imprecision (noise) associated with analytical measurements ultimately affects the analyst's ability to differentiate between a sample containing some small amount of the target analyte and a sample presumed to contain none of the

target analyte (a blank). The imprecision of the analytical method also affects the ability to define `zero', and to discern bias (a systematic difference between results from different analysts and/or methods). It also impacts on the analytical operating range.

To enhance the comparability of data from different laboratories, the MOECC established a target value for analytical performance based on a tabulated Regulation Method Detection Limit (RMDL) for each analyte. In general, laboratories can achieve this level of performance by making adjustments to the amount of sample analyzed and the relative dilution or concentration factors used within the selected method.

For general purposes analytical measurement results below RMDL are considered to be low-level values. The Ministry requires that all low-level measurements be recorded, and reported to the MOECC as required.

A variety of remark codes are provided to discriminate between various types of low-level and "less-than" data. Their use is described in Section 5.1.4 and their interpretation in Section 5.2.1.

For the purposes of reporting under the Effluent Monitoring and Effluent Limit regulations (as listed in section 1.1) or as specified in any other instrument issued under Ministry legislation, an electronic data reporting system was developed to facilitate transfer of data from the laboratory, to the discharger and to the MOECC. The MISA Data Entry System (MIDES) has been replaced by the Ontario Ministry of the Environment and Climate Change Wastewater System (MEWS) for data transfer. In addition to various codes defining sample locations and sample types (including QC sample types), its reporting structure for each field sample test result depends on, a test code, a result field, a unit of measure code and a remark code. The reporting structure is individually defined for each company profile file. The remark codes are available from a pop-up menu in MEWS when data is reported. The following sections of this document provide detailed information on data recording practices and requirements.

Definitions:

Test Code: A six character alphanumeric field. The first two characters identify a chemical element (e.g., nitrogen = NN, lead = PB, etc.) or a group of related organic compounds often within the same chromatographic scan (e.g., halogenated compounds group 1 = X1). The remaining four characters clarify the type of test or the test name. They tend to be mnemonic. Thus PPO4FR is phosphate (a phosphorus compound) performed on a filtered (fractionated) sample to recover whatever reacts under the test conditions. CUUT is copper performed on the entire (unfractionated/unfiltered) sample to recover the total amount (subject to the method used). B2BENZ is benzene.

Units of Measure: Used to identify the concentration units used (e.g. mg/L, μg/L, etc.) and how the result was calculated (e.g., report as N, as SO_4, as P, as PO_4, etc.). These are defined in the MEWS User Manual.

Remark Code: A three-character alphanumeric code provided in the MEWS data reporting system. It is used for indicating low-level or less-than data, for qualifying results, or to explain the absence of a result.

5.1.1 Method Codes

This code was originally used under the Effluent Monitoring Regulation to identify laboratories and methods of analysis. Although it is not required under current regulations it remains a convenient tool for the identification of the laboratory doing the analysis and the method used.

The laboratory must list each of its methods for the analytical tests for which it is responsible and should assign a unique method code for each of the variations/combinations of sample preparation, analysis, detection, and measurement procedures it may use.

The documentation for the method code of an analytical method used to determine one or more test results might include:

CODE Brief Description

ID003A	(sample prep).....entire sample (analytical workup).....acid digestion (detection system).....AAS

The forms used under the Effluent Monitoring and Effluent Limits regulations are an example for keeping records of method codes and LMDLs.

Required: The company must provide to the Ministry, on request, the names of its laboratories (including sub-contractors), contact information and the analytical method used with the corresponding LMDL for each test required.

The laboratory must follow the test methodologies it has selected, and must maintain a complete procedural description, including the associated control practices, for review by Ministry staff on request. Laboratories are required to apply the quality assurance and quality control practices as listed in Section 4.0.

Any significant changes to the method which might affect the precision, accuracy, or recovery of the method must be documented by the laboratory and be available to the Ministry, on request, along with new estimates of the LMDL.

5.1.2 Laboratory Method Detection Limit (LMDL)

Definitions:

Analytical repeatability: Ability to obtain a similar result for each of a sequence of replicate applications of a method carried out by the same analyst within the same analytical batch/run. It can be estimated at various concentration levels by the procedure provided for calculating the within-run standard deviation (S_w) in Section 6.6.5. This estimate does not include the effect of analytical biases/mistakes or unpredictable sample matrix effects.

Method detection limit (MDL): MDL is a statistically defined decision point. It marks the detection level above which one can conclude that a measured result indicates the probable presence of analyte in the sample, with a stated risk that this conclusion is false. This estimate is based on the analytical repeatability, within-batch standard deviation (S_w) for samples processed through the entire method with a risk of less than 1% that the conclusion is false.

Regulation MDL (RMDL): The upper limit permitted for the LMDL value for analytes required under the Effluent Monitoring and Effluent Limits regulations and any other applicable instrument, such as an ECA or an Order. RMDL values are listed in Section 8.0, Table 1.

Laboratory MDL (LMDL): A laboratory specific estimate of the method detection limit calculated using the procedure described in Section 6.0.

The relatively low number of replicates (8) required to estimate MDL yields a highly variable estimate. It should be recognized that the LMDL estimate is typically uncertain by as much as a factor of two.

When different LMDL estimates (between-day, among analysts, between methods, or between sample types) agree within about a factor of two, they are not considered statistically different.

The fact that the LMDL is not greater than the RMDL must be demonstrated at least once. If the method is altered or significantly changed a new LMDL must be determined. It is recommended that the LMDL be verified approximately every 12 months unless routine QC data demonstrate that no significant change has occurred in the sensitivity or the precision of the analytical procedure.

To provide confidence that the actual LMDL on any given day will be below the RMDL, it is desirable that the LMDL estimate be about 1/2 of the RMDL. Improvements in analytical procedures may allow for lower levels of the LMDL to be obtained. For the purposes of the Effluent Monitoring and Effluent Limits regulations, the LMDL does not need to be lower than 1/10th the RMDL.

The analyst should demonstrate reliable precision before estimating the LMDL. The test samples must be processed individually through the entire method. The analytical method must be defined rigorously enough to

ensure that replicate measurements will be more or less `normally distributed' e.g., clustered together. Anomalous values should not be included in the calculation of analytical repeatability.

The size of sample analyzed, and associated changes in dilution or concentration factors, will affect the LMDL value proportionately. Therefore the LMDL should be determined using the routine sample aliquot and dilution factor that will be applied when analyzing actual samples.

If the concentrations of analyte found in routine samples are typically off-scale, a smaller sample aliquot may be taken for routine measurement purposes. This dilution factor will cause a proportional change to the operational LMDL. *BUT*, when the measurement is near or below this adjusted LMDL, the sample must be re-analyzed using a larger aliquot to meet the requirement to measure down to an LMDL which is less than RMDL.

The statistical procedure and concepts on which the detection limit is based do NOT incorporate allowance for errors or bias in measurement due to sample matrix effects or otherwise. The analyst is expected to prevent or control errors. If the result for a specific sample is suspect because of sample matrix effects, the analyst may use one of several remark codes to indicate this. If these effects prevent measurement of an analyte, the analyst must estimate the level at which the interference prevents analysis. See Sections 6.2.3 and 6.2.4.

The LMDL must be calculated for each regulated analyte using the procedure described in Section 6.0.

The measured LMDL must not exceed the required value of the RMDL.

The value of the LMDL for each regulated analyte must be recorded, along with an identification of the test procedure used. See Section 5.1.1, Method Codes.

5.1.3 Routine Data Recording – Significant Digits

Definitions:

Significant Digits: Any digit/figure in a recorded value which is at, or to the left of the same decimal position as the left-most digit of the estimated within-run standard deviation (S_w) of the analytical method, excluding leading zeros.

Estimate the analytical repeatability by calculating the within-run standard deviation (S_w) by one of the alternatives provided in Section 6.0.

Smallest Reporting Increment (SRI): Describes the size of the interval between adjacent results. It is chosen to be smaller than S_w when S_w has been estimated at or near the MDL.

Procedure for SRI determination: The SRI value is based on S_w:

e.g., SRI = S_w rounded down to nearest 1, 2 or 5 with due regard for decimal position.

Thus, if the first (left most) digit of S_w is:

5 to 9;	SRI = 5 (adjusted for decimal position)
2 to 4;	SRI = 2
1;	SRI = 1

Example:

S_w	SRI
570	500 **
293	200 **
134	100 **
8.9	5
0.93	0.5 (or 1) ***
0.038	0.02
0.013	0.01
0.0088	0.005

** Right hand zeros may not be `significant'. They also indicate the inferred decimal position.

*** Borderline cases can be chosen to reflect the most typical SRI for other analytes in the scan.

Record results in multiples of SRI or to retain at least two significant digits. Three significant digits should be retained if the first digit on the left is "1".

e.g., if SRI = 0.2, then results are recorded in steps of 0.2, thus ..., 6.4, 6.6, 6.8, ...

e.g., The result 35.8 can be rounded off (to 36). The result 13.4 should not be rounded off.

Ensure that the units of measure are correct. Add any remark codes considered appropriate.

For the purposes of the MOECC reporting requirements, only two significant digits need be used, although three significant digits are preferable if the first digit on the left is a "1". This avoids introducing bias.

Results should be recorded in steps not larger than the SRI, unless at least two significant digits can be retained. The laboratory is free to record results in increments smaller than SRI.

Estimates of standard deviation, and therefore of LMDL and SRI, are affected by the size of the sample aliquot and any additional dilution or concentration factors. Thus, if SRI =0.002 and a 100x dilution of sample is taken, then the SRI becomes 0.2.

When several analytes are being measured together, SRI values can be adjusted slightly if the S_w value is just below a 1, 2, or 5 boundary, and other similar analytes in the `scan' have S_w values just above the same boundary.

Laboratories must record all results for regulated samples. A result must be recorded for all regulated analytes down to the level of SRI. Censoring of results below LMDL is not permitted. Results should be recorded with at least two significant digits.

5.1.4 Routine Data Recording – Low-Level and "Less Than" Data

Definitions:

In the following examples assume RMDL = 25, LMDL = 7.3, SRI = 2.

Low-Level: Below RMDL but not below LMDL – results in this range may be qualified as low-level by use of the remark code <T. e.g., 12 <T or 12 <RMDL.

Very Low-Level: Below LMDL but not below SRI – there are two options for qualifying these results. Results below LMDL but not below 1/10th (10%) of the RMDL should be qualified as very low-level by using the remark code <LMDL. Results that are below 1/10th (10%) of the RMDL should be qualified <DL. e.g., 4 <LMDL Note that for this example the value of 4 is > than 1/10th the RMDL of 25.

Less Than: Below SRI – Results below SRI represent `analytical zero'. Generally there will be no observable response. These are recorded by indicating the measured value, usually the value of SRI qualified by the remark code <W. e.g., 2 <W or ND.

Less Than: Over-estimate (Interference) – When a result cannot be estimated due to gross sample matrix interference, etc., estimate the amount due to the effect of the interference. Record estimate and qualify it by the remark code <, e.g., 150 <.

The recorded value is usually a definite over-estimate. The actual amount present is unknown. It may, or may not be, a low-level data point. See also "Remark Codes – Approximate/Unreliable".

All results above RMDL may be accompanied by an appropriate explanatory remark code.

The use of the remark code <T for results at or above LMDL is entirely optional. It does serve to flag low-level trace/tentative values.

Results below one-tenth RMDL are considered to be very low and they will be considered as "analytical zeros" for the purpose of estimating loadings under the Effluent Monitoring and Effluent Limits regulations. The company/laboratory must record such measurements by recording the measured value, usually of SRI qualified by a remark code, e.g. <W or ND.

When the analyte cannot be measured because of interference from other matrix constituents, the analyst should provide an estimate of the maximum amount (although it may be present at a much lower level) of analyte that might be present. This estimate is accompanied by the remark code <.

In the absence of a result the analyst must record an explanation for the lack of a result by an attached report, and/or by use of an accepted remark code. See Section 5.2.2.

5.2 Remark Codes – General

While analysts make every effort to control and prevent analytical and measurement errors, certain samples may introduce analytical problems due to the presence of other matrix constituents. These may affect the quality and interpretation of the reported result. Remark codes provide a means to bring these concerns to the attention of the data user.

There are several classes of remark codes. Their codes and interpretation are discussed in the following sections. Many of the remark codes described below are optional. Their use does not preclude the acceptance and use of the reported value by the MOECC.

Definitions:

Attached Reports: Written statements explaining the reason why a result has not been recorded for situations not adequately covered by a remark code.

For uniformity, it is recommended that all laboratories/companies use the same system for recording and qualifying data as described in this section and in the MEWS User Guide for reporting data to the MOECC.

All analytical results must be recorded for all regulated analytes. When no result is available, a written explanation must be provided.

5.2.1 Low-Level Data – Remark codes

The interpretation of low-level data requires a consistent approach to the use of the < sign and the low-level remark codes. Section 5.1.4 discusses their application for the MOECC requirements. This section describes their interpretation.

The remark codes < and > are discussed separately in the section "Remark Codes – Approximate/Unreliable"

Code	Name	Comments
<T	TENTATIVE LOW-LEVEL RESULT; LMDL =< RECORDED VALUE <RMDL	Recorded value = measured value. Value is at or greater than LMDL but below RMDL. It is a tentative low-level result. The value will be used to calculate a loading for regulatory purposes. The use of this code is optional. Such data requires verification against other related data. Even when results exceed the LMDL, other QA/QC information may indicate the presence of biases which will affect data interpretation.
<LMDL	LOW LEVEL RESULT; LMDL > RECORDED VALUE ≥ 0.1 (10%) OF RMDL (see <DL)	Recorded value = measured value. It is a very low-level result The value is below the LMDL but will be used to calculate a loading for regulatory purposes. Sufficient data of this type may help distinguish between analytes which are consistently not present from those which tend to be found at low levels. This is important when evaluating the trace presence of analytes of concern, particularly when the levels are comparable to the blank. Conclusions are subject to evaluation of QA/QC blank and spike recovery data.
<DL	RESULT < 0.1 (10%) OF RMDL Note: this code has replaced the historical use of the code <RL	Recorded value = measured value. The value is below 0.1 of the RMDL ($1/10^{th}$) and may be below the LMDL. It is a very low-level result. For the Effluent Monitoring and Effluent Limits regulations, the value “0” will be substituted for a loading calculation.
<W Or ND	NO MEASURABLE RESPONSE (ZERO): < RECORDED VALUE	The recorded value is the smallest observable response. The use of this code is optional. Either no response was observed and the measured result was `analytically zero', or the response is negligible (below SRI). Sufficient data of this type suggests the absence of analyte at levels above the recorded SRI value, subject to evaluation of QA/QC spike recovery data.

5.2.2 Missing Data and Attached Report

Missing results can occur because of sampling or analytical problems. An attached report, which can be done in MEWS, is always required to explain missing results. The following codes are used when there is no result to report in the result field, or when the result is textual rather than numeric. Use of the following remark codes will assist data users who may not have ready access to the file of explanatory textual notes.

Code	Name	Comments
?	LATE DATA: DATA NOT YET AVAILABLE : SEE TEXT	All available data must be recorded within the specified deadline in order to be in compliance. If some data is not yet available from the laboratory this must be explained.
!	NO DATA WILL BE RECORDED: SEE TEXTUAL REPORT	Field or laboratory accidents may prevent analysis for one or more analytes. Whenever possible sufficient sample volume must be taken to allow for re-analysis.
!N	NO DATA: INSUFFICIENT VOLUME DUE TO INSPECTION	When the MOECC inspectors remove some or all of the routine sample, the company is not required to re-sample.
!NM	NO EFFLUENT – NO SAMPLE AVAILABLE	If there is no effluent there can be no data.
AR	ATTACHED REPORT	If there is need to explain data, or the lack of data, in more depth than permitted by the use of remark codes, an attached report can be useful. This can be done in MEWS for each result, using up to 2000 alphanumeric characters.

5.2.3 Sample Matrix Effects/Interference

Sample matrix effects are often suspected, but can be difficult to confirm. Information from the analyst which flags suspect data may assist in the data interpretation.

Sample matrix problems (particulates, multi-phase, heterogeneity, etc.) can introduce analytical problems. Colour and the multiplicity of other sample constituents present in waste can interfere, increasing or decreasing the observed vs. real concentrations of the target analytes. Certain types of interference are characteristic of specific methods. The analyst will often be able to explain the effect of the interference on data interpretation. If the effect is severe enough the analyst may elect not to report a result.

The following codes are used when the measured result is recorded but is considered to be somewhat suspect.

Code	Name	Comments
IS	INTERFERENCE SUSPECTED	The nature of the sample, problems during sample preparation or analysis, etc., lead the analyst to question the result. Do not use indiscriminately.
IB	INTERFERENCE: BACKGROUND	Often relates to problems setting background correction, baseline, etc., due to noise or adjacent interfering peaks.
IC	INTERFERENCE: COLOUR	Certain colourimetric tests may yield high results on coloured samples.
IM	INTERFERENCE: SAMPLE MATRIX	May relate to other materials being present in the effluent that affects the analysis.
MP	MULTIPHASE SAMPLE: RESULT MAY BE SUSPECTED	The presence of fine and coarse particulates (or biomaterial, wood chips, etc.) and/or an oily phase may prevent the acquisition of a representative sample.

5.2.4 Approximate/Unreliable Data

The nature of waste samples (non-homogeneity or perishability) is such that a proper representative aliquot may be difficult to obtain for analysis. The ability of the analyst to flag this assists in the data interpretation. In some cases the estimate may still be adequate for determining compliance with an effluent limit.

Code	Name	Comments
A	APPROXIMATE VALUE	The nature of the sample prevents proper representative aliquotting. The result is less precise or less accurate than usual.
AIS	APPROXIMATE VALUE: INSUFFICIENT SAMPLE	Smaller than routine aliquots degrade the precision and reliability of measurements.
The following codes are used when the measured value is felt to represent an upper or lower limit for the amount of target analyte actually present in the sample. The value recorded may be the actual number obtained, or it may be an indication of a limitation of the method for this particular sample.		
<	ACTUAL RESULT LESS THAN RECORDED	This remark code indicates that the recorded value is an over-estimate. The analyst suspects that the response has been enhanced (e.g., by severe matrix interference) or has increased due to sample perishability effects. The estimate is accompanied by the remark code <.
>	ACTUAL AMOUNT PROBABLY GREATER THAN RECORDED	The analyst suspects that the response is suppressed by severe interference effects, or has decreased due to sample perishability. The estimate is accompanied by the remark code >.
The following codes indicate a larger than usual range of uncertainty for the accompanying result, often because of difficulty obtaining a representative aliquot, or because of related sample or QC problems. The result may be okay, but the analyst is unwilling to report an unqualified result.		

Code	Name	Comments
UCR	DATA UNRELIABLE: COULD NOT CONFIRMBY REANALYSIS	When a suspicious result is obtained, the analyst will often repeat the analysis when there is sufficient sample. This code indicates inability to perform the required re-analysis
UNF	DATA UNRELIABLE: CONTENTS NOT FILLED TO TOP	Tests for many organics require a completely filled container to avoid target analyte losses into the headspace. Results will tend to be low.
UQC	DATA UNRELIABLE: POSSIBLE LAB QC PROBLEM(S)	Tests for some analytes require use of the entire sample. Therefore a repeat analysis is not possible in the event that a QC problem was detected. A duplicate sample should be collected to allow for re-analysis when needed.
USD	DATA UNRELIABLE: SAMPLE DECOMPOSITION NOTED	May be used when sample decomposition has occurred during transit which might affect the analytical result.

5.2.5 Miscellaneous

Certain codes are required to note sample problems related to field procedures, or inability to comply completely with regulatory requirements. There is also a set of codes required to explain how PCB data has been quantified.

Code	Name	Comments
OLD	OLD: SAMPLE EXCEEDS MAXIMUM STORAGE TIME	The protocol specifies a maximum storage time before analysis. Exceeding this time may not affect chemistry results which must be recorded and reported, accompanied by the remark code **"old"**.
SD	SAMPLE DUPLICATES DIFFER IN APPEARANCE	Duplicates are required under the Effluent Monitoring and Effluent Limits regulations and any other applicable instrument to monitor the variability and reliability of sampling. When the samples look different upon arrival at the laboratory, there may have been problems with sampling, transportation or sample preservation.
SID	SAMPLE IDENTIFICATION QUESTIONABLE	The sample bottle labels don't match the submission form or the sample appears to be different than expected for the specified source.
SIP	SAMPLE IMPROPERLY PRESERVED	The protocol specifies the type of sample preservation required. Analyses may have been performed on an incorrectly preserved or unpreserved sample, because of misadventure to the proper sample. Coding should be done where there is reason to believe that the result will be significantly affected.
Txx	TIME: x HOUR BETWEEN SAMPLING AND ANALYSIS	These codes are primarily used when recording microbiological data.
Pxx	PCB RESEMBLED (MIX OF) AROCLOR xxxx (and xxxx)	These codes are used to identify the chromatographic “fingerprint” as resembling an Aroclor type. Pop-up menu Table for Pxx is included

Code	Name	Comments
		in MEWS.
NC	NO CALCULATION	This is a system-generated code. It is added when a discharger provides analytical data but no flow value, so that a loading cannot be calculated.

5.3 Laboratory Quality Control

The validity of analytical data depends on the application of a well-documented methodology by trained, expert staff, using an analytical detection system which has been properly calibrated and which is maintained in a state of statistical control. A competent laboratory will include a variety of check procedures and check samples.

Definitions:

Laboratory Quality Control: Activities are undertaken to evaluate the suitability of a process or component for its intended purpose. These may include **pre-service** checks of reagent quality, instrument stability, staff expertise, etc. They also include **in-service** checks of system performance to ensure performance criteria are being met and that the system is stable. Most analytical systems include `bench procedures' such as sample preparation, sample cleanup and analytical work-up. The system also includes some form of measurement device through which one or more `batches' of prepared samples are `run'.

Quality control: Implies the existence of an expected value and predetermined statistically defined criteria for determining acceptability. **Bench QC** includes: method blank(s), certified reference materials (in natural matrix), `spiked samples', and `replicate samples', etc. **Run QC** includes: calibration checks, standard reference materials (in laboratory solvent), baseline checks, sensitivity checks, curvature checks, etc.

QC Summaries: A table or chart showing expected value, limits, observed values, and notes concerning action taken when observed values exceeded the predetermined limits.

Reference Materials (RMs): Pure materials obtained from a recognized agency (such as NIST, NRC, or others delegated by them) and certified for the purpose of making standard solutions of known purity and concentration, or prepared and certified solutions of one or more analytes in a laboratory solvent prepared by such agencies. These are used for validating in-house standards prepared from commercial or other sources of materials.

Certified Reference Materials (CRMs): Naturally occurring materials (biota, vegetation, soil, etc.) which have been certified by a recognized agency (as listed above) to contain specified levels of selected constituents, when measured by specified standard procedures. These are used for validating the performance of a method (recovery, specificity, selectivity, repeatability).

Standard Reference Material (SRM): Acronym used by NIST to describe either type of material provided by them, irrespective of function.

Every laboratory must be able to demonstrate regular use of RMs and CRMs as appropriate and as available from a standards organization, and must maintain a record of results obtained for inspection by the MOECC regional or laboratory staff.

Also the MOECC must be able to readily access bench level and run QC data for the purpose of database evaluation, and to ensure appropriate response to effluent data variability.

Every laboratory providing results for the purposes of complying with the Effluent Monitoring and Effluent Limits regulations and any other applicable instrument must prepare a summary report of its bench and run QC data on an annual basis. All reports and the supporting original QC data must be available for review by the MOECC regional or laboratory staff on request. This summary should include at least the following information for each of the QC sample types (blank, spiked blank, spiked sample, replicate sample) required under the regulation:

- number of actual samples analyzed
- concentration of test analyte found routinely
- minimum, maximum, average, standard deviation
- number of QC samples (of each type) analyzed
- for spiked blank and spiked sample, the design (expected) value
- minimum, maximum, average recovery
- for replicate samples, data should be segregated by concentration level, e.g., bottom 10% of operating range, 10 to 50% of range, 50 to 100% of range, off- scale
- the standard deviation and mean for each interval should be calculated from the differences (D) between replicates as follows:

$$s = \sqrt{\frac{\left(\sum D_i^2\right)}{(2n)}}$$

where: i varies from 1 to n
n is the number of samples in the interval

The process for setting statistical limits should avoid data which indicates chronic drifting or sudden changes in the observed values. *Control charts* provide a particularly useful mechanism for demonstrating control status over an extended period of time and assist in assessing long-term performance (trends, sudden changes, bias, etc.). A well-controlled system will approach a `normal' or `Gaussian' distribution.

Analysts should participate in relevant inter-laboratory comparison studies, as available, to substantiate the overall validity of their method.

6.0 Estimation of Analytical Method Detection Limits (MDL)

6.1 Introduction

This protocol has been established to ensure a consistent approach to the development of method detection limit (MDL) estimates for Ministry programs based on the use of fortified reagent (blank) water or evaluation of available routine within-run duplicate analyses. The Effluent Monitoring and Effluent Limits regulations has established criteria for maximum permitted laboratory MDLs (LMDLs), which are referred to as Regulation MDLs (RMDLs) and are shown in Section 8.0, Table 1.

It should be noted that when MDL estimates are developed using clean samples (e.g., reagent (blank) water) they represent an optimum achievable value. LMDLs obtained in this fashion are very useful for establishing performance criteria and allowing comparison of inter-laboratory method capabilities, but may not be applicable in defining the quantitation capability for other samples which introduce matrix effects.

The following protocol represents a modification to that documented in the Federal Register/Vol. 49, No. 209/Friday, October 26, 1984/Appendix B to Part 136 – Revision 1.11.

This modification restricts the options listed in the original document and gives more direct instructions at other option points.

6.2 Definition

The method detection limit (MDL) is a statistically defined decision point such that measured results falling at or above this point are interpreted to indicate the presence of analyte in the sample with a specified probability, and assumes that there are no known sources of error in identification or biases in measurement.

For the purposes of this protocol, the MDL is defined as having a confidence limit of 99%. This confidence limit defines the multiplication factor used from Student's *t*-tables relating MDL to the analytical precision. This Student's *t*-value depends on the amount of data used to calculate the analytical precision. In general, analytical precision will depend on the analytical conditions and the sample matrix. When possible, precision will be determined by replicate analysis of typical low-level samples, with sufficient replication to provide a reasonable estimate.

6.3 Scope and Application

This protocol is designed for application to a wide variety of sample types ranging from reagent (blank) water fortified with a known concentration of analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The protocol requires a complete, specific, and well

defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

Since the MDL procedure was designed for application to a broad variety of physical and chemical methods, it was made device or instrument independent.

There are four options available for estimating the analytical precision:

a) accumulation of a large number of in-run replicate analyses of typical samples at levels not exceeding 10 times the estimated MDL;

b) accumulation of in-run replicate analyses of laboratory reagent quality water spiked with a known amount of the target analyte(s) at levels not exceeding 10 times the estimated MDL;

c) analysis of eight replicate aliquots of a typical low level sample at levels not exceeding 10 times the estimated MDL;

d) analysis of a series of eight replicate aliquots of laboratory reagent quality water spiked with a known amount of the target analyte(s) at a level not exceeding 10 times the estimated MDL.

When applied for the Effluent Monitoring and Effluent Limits regulations, the appropriate RMDL shall be used in place of the 'estimated MDL' in the above options.

6.4 Organic Analytes (Analytical Test Groups 16–27, 33 and 34)

This protocol requires that option d) in Section 6.3 be used. The fortification of laboratory reagent (blank) water with a known level of analyte is required to standardize the protocol for all laboratories and minimize the problems associated with analyzing duplicate or replicate samples or finding a standard “matrix” for organics analysis. The analytical precision is established based on eight replicate analyses and the estimated MDL is derived from a combination of these measurements and the appropriate value from t-test tables. This option is not intended to assess the effect of the matrix on the values obtained but rather to define a standardized approach in the development and application of inter-laboratory performance criteria for the program.

6.4.1 To determine the MDL, proceed as follows:

Make an estimate of the MDL using one of the following:

- the concentration value that corresponds to an instrument signal/noise ratio of 3:1;
- the concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water;

- that region of the standard curve where there is a significant change in sensitivity, e.g., a break in the slope of the standard curve;
- instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

6.4.2 Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference-free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent).The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix. The use of commercially obtained or laboratory prepared organic free water is acceptable but clearly indicate what was used.

6.4.3 Prepare a laboratory standard (analyte in reagent water) at a concentration which is at least five times, but not to exceed 10 times the estimated method detection limit. Proceed to Section 6.6.1.

6.5 Conventionals, Metals and Inorganics (ATGs 1–15, 25 and 30)

This protocol allows any of the options a), b), c) or d) in Section 6.3 to be used. For options a) and b) the laboratory should review recent data on in-run replicates (data accumulated within the preceding 12-month period or less) and apply the formula as outlined in Section 6.6.3 to at least 40 data pairs. This procedure also applies to the parameters included in section 9.34.

6.5.1 For option c) proceed as follows:

a) When a "real" sample is being used for the MDL determination, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated method detection limit proceed to Section 6.6.

b) If the measured level of analyte is less than the estimated method detection limit, add a known amount of analyte to bring the level of analyte between one and ten times the estimated method detection limit.

c) If the measured level of analyte is greater than five times the estimated method detection limit, there are two options:

- Obtain another sample with a lower level of analyte in the same matrix if possible;

- The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

Proceed to Section 6.6.1.

6.5.2 For option d) proceed as in Section 6.4.

6.6 Procedure for LMDL Determination

6.6.1 Take eight aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units.

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.

6.6.2 For option c) and d), 8 replicates of a typical low level sample or spiked reagent water, calculate the standard deviation (*S*) of the replicate measurements as follows:

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

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

6.6.3 For option a) and b), assessment of historic within run replicate analysis data, calculate the standard deviation (*S*) of the replicate measurements as

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

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

6.6.4 Compute the MDL as follows:

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

where: $t_{(\ n-1,\ \alpha\ =\ 0.01\ )}$ is the Student's *t*-value appropriate for a 99%confidence level given the degrees of freedom n-1.

S = the standard deviation as determined above.

Tables of Student's t-Values at the 99 Percent Confidence Level		
Number of Replicates	**Degree of Freedom (n-1)**	**t (n-1)**
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
∞	∞	2.326

6.7 Recording

Record the calculated MDL to two significant figures (e.g., 0.032). The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount of analyte was used for this determination, also record the mean recovery.

6.8 Treatment of Outliers

Single Analyte Methods:

If one of the results can be shown to be an 'Outlier' by the Dixon test (described below), AND the LMDL calculated for the remaining seven replicates (3.143 times S) is less than RMDL, this latter estimate of LMDL will be accepted.

Scans:

Certain methods permit analysis of several analytes within a single 'scan'. The MDL for each analyte in the scan must be less than the corresponding RMDL. When the LMDLs tend to bracket the RMDLs, the overall method is not sensitive enough and the LMDLs will not be considered acceptable.

However, if only a few of the LMDLs in a 'scan' exceed their respective RMDLs, there may be outliers within the set of eight replicates for these non-complying analytes. If this can be confirmed, as described above, for each of the non-complying analytes, then the LMDL based on seven replicates (3.143 times *S*) will be accepted for those few analytes.

To forestall the possibility that one replicate sample may be an outlier for all or most analytes in the scan, and that the calculated LMDLs therefore will be greater than RMDL for several analytes, the analyst may choose the following option:

- perform eleven replicates (rather than eight);
- for each analyte, note which replicate gives the highest and the lowest results;
- reject the sample replicate containing the greatest number of high results;
- reject the sample replicate containing the greatest number of low results;
- reject the sample with the greatest number of high and low results; and
- calculate LMDLs for each analyte using the remaining eight replicate samples.

If this procedure fails to indicate an LMDL for each analyte which is below the respective RMDL, redefine the method (for example, larger sample aliquot, different range expansion, etc.), retrain staff, and repeat the entire procedure for estimating RMDL for all analytes in the scan. Discard all previous replicate data.

Outlier procedure: Dixon's Test for sample size; n = 8 to 10.

i) sort the replicate values from lowest to highest r_1, r_2,.....$r_{(n-1),}$ $r_{n;}$

ii) determine the difference between the suspect value and its nearest neighbour $r_1 - r_2$ (or $r_n - r_{(n-1),}$);

iii) determine the difference between the suspect value and the next to last value at the opposite end of the sorted list of values $r_1 - r_{(n-1),}$ (or $r - r_2$);

iv) calculate the ratio of ii) divided by iii);

v) if the ratio is greater than 0.55 the value r_1 (or r_n) is considered to be an outlier (<5% risk of error).

Natrella, M.G. "Experimental Statistics", NBS Handbook 91, (1966) USGPO, Washington, D.C.

7.0 Glossary and Acronyms

Glossary

Analytical run	A group of samples processed together through each step of an analytical procedure
AUTO	Refers to sampling technique where an automated sampling device is used
Autosampler	Device to collect samples automatically either in proportion to the wastewater flow or as equal volumes at equal time intervals; automated sampler; automatic sampling device;
Bakelite®	Trademark of The Dow Chemical Company (including the former Union Carbide Canada Ltd) for phenol formaldehyde resin
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	Volume of waste water made up of sub-samples or aliquots which have been combined automatically or manually or obtained from a slip-stream by an on-line analyzer
Certified Reference Material (CRM)	A reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities using valid procedures (ISO/IEC GUIDE 99:2007)
Duplicate	Duplicate sample: one of two samples collected at a sampling point at the same time in a manner that minimizes differences between the samples. The duplicate samples are carried through all steps of sampling and analytical procedures in an identical manner.
Grab Sample	Volume of effluent of at least 100 mL (except for volatiles), collected over a period not exceeding 15 minutes and immediately transferred to an appropriate laboratory sample container, see Section 2.1.1
Effluent Monitoring and Effluent Limits (EMEL) regulations	The nine sector-specific Effluent Monitoring and Effluent Limits (EMEL) regulations made under the Environmental Protection Act (Ontario), as listed in section 1.1 of this Protocol
Inspection sample	Sample collected by a provincial officer from a sampling point of a discharger
Manual	Refers to sampling technique where a number of grab samples are collected then combined either in proportion to flow or in equal volumes to form a composite sample

Glossary

Method Blank	A blank sample which undergoes sample processing identical to that carried out for the test samples. Method blank results are used to assess contamination from the laboratory environment and reagents
Nalgene®	Trademark for a manufacturer of containers made from a variety of different resins, including polyolefins.
On-line analyzer	Device directly connected to a sampling point which can sample and analyze water automatically
Parameter	Refers to a compound or analyte listed in an ATG
Pick up	As defined in the EMEL regulations, pick up in relation to a sample, means pick up for the purpose of storage, including storage within an automatic sampling device, and transportation to and analysis at a laboratory
Pre-charged	Refers to the addition of preservative to an autosampler container prior to sample collection
Recording	Refers to record keeping and documentation of information and data pertaining to sampling, analysis, QA/QC procedures, equipment maintenance and any other relevant information
Replicate	One of two aliquots taken from a sample for analysis
Reporting	Submission to the MOECC, as required, of analytical data and other information (with the exception of the technical term "smallest reporting increment")
Regulatory Method Detection Limit (RMDL)	Regulatory method detection limit listed in Table 1. The RMDL is the maximum allowable value for a LMDL under the Effluent Monitoring and Effluent Limits regulations
Routine	Refers to analyses performed frequently (e.g., daily, thrice-weekly or weekly), as opposed to characterization, open characterization or other analyses performed at less frequent time intervals
Run	Same as analytical run: a group of samples processed together through each step of an analytical procedure
Sample Storage Time (Holding Time)	Period of time between sample collection (e.g., end of twenty-four hour time–sample collection period) and initiation of sample analysis; also known as holding time; maximum allowable sample storage times are listed for each ATG in Section 9.0
Target parameter	Compound of interest to be analyzed individually or as part of an analytical test group
Teflon®	Registered trademark of E.I. Du Pont de Nemours &

Glossary

	Company. Where Teflon® is specified other chemically inert fluorocarbon resins may be used such as polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), perfluoroalkoxy (PFA) resins, chlorotrifluoroethylene (CTFE), co-polymers of ethylene with tetrafluoroethylene (ETFE) or chlorotrifluoroethylene (TCTFE)

Acronyms

AA or AAS	atomic absorption or atomic absorption spectrophotometry
ATG	Analytical Test Group (as listed in Table 1)
CALA	Canadian Association for Laboratory Accreditation
CAS	Chemical Abstract Service of the American Chemical Society
DCP	direct current plasma
ECA	Environmental Compliance Approval (formerly known as a Certificate of Approval [CofA]) issued under the Environmental Protection Act
ECD	electron capture detector
ELCD	Hall electrolytic conductivity detector
FID	flame ionization detector
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
GLP	good laboratory practice
IC	ion chromatography
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma-atomic emission spectrophotometer
ICP-MS	inductively coupled plasma-mass spectrometry
HPLC	high performance liquid chromatography
LaSB	Laboratory Services Branch of the Ontario Ministry of the Environment and Climate Change
LMDL	laboratory method detection limit
MDL	analytical method detection limit or minimum concentration of a parameter necessary to infer its presence in a sample with a level of confidence greater than 99 percent
MEWS	Ministry of the Environment and Climate Change Wastewater System

Acronyms

MISA	Municipal and Industrial Strategy for Abatement of the MOECC: program evolved into the Effluent Monitoring and Effluent Limits regulations
MOECC	Ministry of the Environment and Climate Change (Ontario)
NATO	North Atlantic Treaty Organization
NIST	National Institute for Standards and Technology (US)
NRC	National Research Council of Canada
PCDD/DF	polychlorinated dibenzo-p-dioxin/dibenzofuran
PET	polyethylene terephthalate
PID	photo ionization detector
QA	quality assurance
QC	quality control
QM	quality management
RMDL	regulatory method detection limit
SCC	Standards Council of Canada
SRI	smallest reporting increment (see section 5.1.3)
TEF	toxic equivalency factor
TEQ	toxic equivalent
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

8.0 Table of Analytical Test Groups, Parameters and Detection Limits

Table 1: Analytical Test Group Numbers, Parameters and Regulatory Method Detection Limits					
Analytical Test Group Number & Name		**Parameters**	**CAS #**	**RMDL**	**Units**
1	Chemical Oxygen Demand	Chemical Oxygen Demand (COD)	N/A *	10	mg/L
1a	Biochemical Oxygen Demand (5 day)	Biochemical Oxygen Demand (5 day)	N/A *	2.0	mg/L
1b	Carbonaceous Biochemical Oxygen Demand (5 day)	Carbonaceous Biochemical Oxygen Demand (5 day)	N/A *	2.0	mg/L
2	Total Cyanide	Total Cyanide	57-12-5	0.005 as HCN	mg/L
2a	Weak Acid Dissociable Cyanide	Weak Acid Dissociable Cyanide	N/A *	0.005	mg/L
2b	Cyanate	Cyanates	N/A *	5	mg/L
2c	Thiocyanate	Thiocyanate	N/A *	5	mg/L
2d	Cyanide Amenable to Chlorination	Cyanide Amenable to Chlorination	N/A *	0.005	mg/L
3	Hydrogen ion (pH)	Hydrogen ion (pH)	N/A *	N/A	pH units
4a	Nitrogen	Ammonia plus Ammonium	N/A *	0.25 as Nitrogen	mg/L
4a	Nitrogen	Total Kjeldahl Nitrogen	N/A *	0.25 as Nitrogen	mg/L
4b	Nitrogen	Nitrate + Nitrite	N/A *	0.25 as Nitrogen	mg/L
5a	Organic Carbon	Dissolved Organic Carbon (DOC)	N/A *	0.5 as Carbon	mg/L
5b	Organic Carbon	Total Organic Carbon (TOC)	N/A *	2 as Carbon	mg/L
6	Total Phosphorus	Total Phosphorus	N/A *	0.1 as Phosphorus	mg/L
6a	Phosphorus (Soluble)	Orthophosphate	N/A *	0.1 as Phosphorus	mg/L
7	Specific Conductance	Specific Conductance at 25°C	N/A *	5	µS/cm
8	Suspended Solids	Total Suspended Solids (TSS)	N/A *	3	mg/L
		Volatile Suspended Solids (VSS)	N/A *	3	mg/L
8a	Dissolved Solids	Dissolved Solids	N/A *	10	mg/L
9	Metals	Aluminum	7429-90-5	0.03	mg/L
		Beryllium	7440-41-7	0.01	mg/L
		Boron	7440-42-8	0.05	mg/L
		Cadmium	7440-43-9	0.002	mg/L
		Chromium	7440-47-3	0.01	mg/L

Table 1: Analytical Test Group Numbers, Parameters and Regulatory Method Detection Limits					
Analytical Test Group Number & Name		**Parameters**	**CAS #**	**RMDL**	**Units**
		Cobalt	7440-48-4	0.01	mg/L
		Copper	7440-50-8	0.01	mg/L
		Lead	7439-92-1	0.02	mg/L
		Lithium	7439-93-2	0.05	mg/L
		Molybdenum	7439-98-7	0.01	mg/L
		Nickel	7440-02-0	0.02	mg/L
		Silver	7440-22-4	0.01	mg/L
		Strontium	7440-24-6	0.02	mg/L
		Thallium	7440-28-0	0.03	mg/L
		Vanadium	7440-62-2	0.02	mg/L
		Zinc	7440-66-6	0.01	mg/L
9a	Additional Metals	Iron	7439-89-6	0.02	mg/L
		Uranium	7440-61-1	0.02	mg/L
		Magnesium	7439-95-4	0.02	mg/L
10	Hydrides	Antimony	7440-36-0	0.005	mg/L
		Arsenic	7440-38-2	0.005	mg/L
		Selenium	7782-49-2	0.005	mg/L
11	Chromium (Hexavalent)	Chromium (Hexavalent) (Note 1)	18540-29-9	0.01	mg/L
12	Mercury	Mercury	7439-97-6	0.0001	mg/L
13	Total Alkyl Lead	Tetra-alkyl Lead (Note 2)	N/A *	0.005 as Lead	mg/L
		Tri-alkyl Lead (Note 2)	N/A *	0.005 as Lead	mg/L
14	Phenolics (4AAP)	Phenolics (4AAP)	N/A *	0.002 as Phenol	mg/L
15	Sulphide	Sulphide as H_2S	N/A *	0.02 as H_2S	mg/L
16	Volatiles, Halogenated	1,1,2,2-Tetrachloroethane	79-34-5	1	µg/L
		1,1,2-Trichloroethane	79-00-5	0.6	µg/L
		1,1-Dichloroethane	75-34-3	0.4	µg/L
		1,1-Dichloroethylene	75-35-4	1	µg/L
		1,2-Dichlorobenzene	95-50-1	0.5	µg/L
		1,2-Dichloroethane (Ethylene Dichloride)	107-06-2	0.5	µg/L

Table 1: Analytical Test Group Numbers, Parameters and Regulatory Method Detection Limits					
Analytical Test Group Number & Name		**Parameters**	**CAS #**	**RMDL**	**Units**
		1,2-Dichloropropane	78-87-5	0.5	µg/L
		1,3-Dichlorobenzene	541-73-1	0.5	µg/L
		1,4-Dichlorobenzene	106-46-7	0.5	µg/L
		Bromodichloromethane	75-27-4	0.8	µg/L
		Bromoform	75-25-2	2	µg/L
		Bromomethane	74-83-9	3	µg/L
		Carbontetrachloride	56-23-5	0.8	µg/L
		Chlorobenzene	108-90-7	0.5	µg/L
		Chloroform	67-66-3	0.5	µg/L
		Chloromethane	74-87-3	2	µg/L
		cis-1,3-Dichloropropylene	10061-01-5	0.5	µg/L
		Dibromochloromethane	124-48-1	0.8	µg/L
		Ethylene dibromide	106-93-4	0.5	µg/L
		Methylene chloride (Dichloromethane)	75-09-2	1.3	µg/L
		Tetrachloroethylene (Perchloroethylene)	127-18-4	0.5	µg/L
		trans-1,2-Dichloroethylene	156-60-5	0.5	µg/L
		trans-1,3-Dichloropropylene	10061-02-6	0.5	µg/L
		Trichloroethylene	79-01-6	0.5	µg/L
		Trichlorofluoromethane	75-69-4	1	µg/L
		Vinyl chloride (Chloroethylene)	75-01-4	2	µg/L
17	Volatiles, Non-Halogenated	Benzene	71-43-2	0.5	µg/L
		Ethylbenzene	100-41-4	0.5	µg/L
		Styrene	100-42-5	0.5	µg/L
		Toluene	108-88-3	0.5	µg/L
		o-Xylene	95-47-6	0.5	µg/L
		m-Xylene and p-Xylene (Note 3)	108-38-3 & 106-42-3	0.5	µg/L
18	Volatiles, Water Soluble	Acrolein	107-02-8	4	µg/L
		Acrylonitrile	107-13-1	4	µg/L

Table 1: Analytical Test Group Numbers, Parameters and Regulatory Method Detection Limits					
Analytical Test Group Number & Name		**Parameters**	**CAS #**	**RMDL**	**Units**
19	Extractables, Base Neutral	Acenaphthene	83-32-9	1	µg/L
		5-Nitroacenaphthene	602-87-9	3	µg/L
		Acenaphthylene	208-96-8	1	µg/L
		Anthracene	120-12-7	0.6	µg/L
		Benz[a]anthracene	56-55-3	0.5	µg/L
		Benzo[a]pyrene	50-32-8	0.6	µg/L
		Benzo[b]fluoranthene	205-99-2	0.7	µg/L
		Benzo[g,h,i]perylene	191-24-2	0.7	µg/L
		Benzo[k]fluoranthene	207-08-9	0.7	µg/L
		Biphenyl	92-52-4	0.6	µg/L
		Camphene	79-92-5	2	µg/L
		1-Chloronaphthalene	90-13-1	1	µg/L
		2-Chloronaphthalene	91-58-7	1	µg/L
		Chrysene	218-01-9	0.3	µg/L
		Dibenz[a,h]anthracene	53-70-3	1.3	µg/L
		Fluoranthene	206-44-0	0.4	µg/L
		Fluorene	86-73-7	1	µg/L
		Indeno[1,2,3-cd]pyrene	193-39-5	1.3	µg/L
		Indole	120-72-9	1.5	µg/L
		1-Methylnaphthalene	90-12-0	2.2	µg/L
		2-Methylnaphthalene	91-57-6	1.5	µg/L
		Naphthalene	91-20-3	1	µg/L
		Perylene	198-55-0	1	µg/L
		Phenanthrene	85-01-8	0.4	µg/L
		Pyrene	129-00-0	0.4	µg/L
		Benzylbutylphthalate	85-68-7	0.6	µg/L
		Bis(2-ethylhexyl)phthalate	117-81-7	2.2	µg/L
		Di-n-butylphthalate	84-74-2	1	µg/L
		Di-n-octylphthalate	117-84-0	1	µg/L
		4-Bromophenyl Phenyl Ether	101-55-3	0.3	µg/L

Table 1: Analytical Test Group Numbers, Parameters and Regulatory Method Detection Limits					
Analytical Test Group Number & Name		**Parameters**	**CAS #**	**RMDL**	**Units**
		4-Chlorophenyl Phenyl Ether	7005-72-3	0.9	µg/L
		Bis(2-chloroisopropyl)ether	108-60-1	1	µg/L
		Bis(2-chloroethyl)ether	111-44-4	2	µg/L
		Diphenyl ether	101-84-8	0.4	µg/L
		2,4-Dinitrotoluene	121-14-2	0.8	µg/L
		2,6-Dinitrotoluene	606-20-2	0.7	µg/L
		Bis(2-chloroethoxy)methane	111-91-1	1	µg/L
		Diphenylamine (Note 4)	122-39-4	10	µg/L
		N-nitrosodiphenylamine (Note 4)	86-30-6	10	µg/L
		N-nitrosodi-n-propylamine	621-64-7	1.5	µg/L
20	Extractables, Acid (Phenolics)	2,3,4,5-Tetrachlorophenol	4901-51-3	0.4	µg/L
		2,3,4,6-Tetrachlorophenol	58-90-2	1.5	µg/L
		2,3,5,6-Tetrachlorophenol	935-95-5	1	µg/L
		2,3,4-Trichlorophenol	15950-66-0	0.6	µg/L
		2,3,5-Trichlorophenol	933-78-8	1	µg/L
		2,4,5-Trichlorophenol	95-95-4	1	µg/L
		2,4,6-Trichlorophenol	88-06-2	1	µg/L
		2,4-Dimethylphenol	105-67-9	5	µg/L
		2,4-Dinitrophenol	51-28-5	42	µg/L
		2,4-Dichlorophenol	120-83-2	1	µg/L
		2,6-Dichlorophenol	87-65-0	1	µg/L
		4,6-Dinitro-o-cresol	534-52-1	24	µg/L
		2-Chlorophenol	95-57-8	2	µg/L
		4-Chloro-3-methylphenol	59-50-7	1	µg/L
		4-Nitrophenol	100-02-7	1.4	µg/L
		m-Cresol	108-39-4	2	µg/L
		o-Cresol	95-48-7	2	µg/L
		p-Cresol	106-44-5	2	µg/L
		Pentachlorophenol	87-86-5	1	µg/L
		Phenol	108-95-2	1.5	µg/L

Table 1: Analytical Test Group Numbers, Parameters and Regulatory Method Detection Limits					
Analytical Test Group Number & Name		**Parameters**	**CAS #**	**RMDL**	**Units**
21	Extractables, Phenoxyacid Herbicides	Note 5			µg/L
22	Extractables, Organochlorine Pesticides	Note 6			µg/L
23	Extractables, Neutral-Chlorinated	1,2,3,4-Tetrachlorobenzene	634-66-2	0.01	µg/L
		1,2,3,5–Tetrachlorobenzene	634-90-2	0.01	µg/L
		1,2,4,5-Tetrachlorobenzene	95-94-3	0.01	µg/L
		1,2,3-Trichlorobenzene	87-61-6	0.01	µg/L
		1,2,4-Trichlorobenzene	120-82-1	0.01	µg/L
		2,4,5-Trichlorotoluene	6639-30-1	0.01	µg/L
		Hexachlorobenzene	118-74-1	0.01	µg/L
		Hexachlorobutadiene	87-68-3	0.01	µg/L
		Hexachlorocyclopentadiene	77-47-4	0.01	µg/L
		Hexachloroethane	67-72-1	0.01	µg/L
		Octachlorostyrene	29082-74-4	0.01	µg/L
		Pentachlorobenzene	608-93-5	0.01	µg/L
24	Chlorinated Dibenzo-p-dioxins and Dibenzofurans	2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6	3.9	pg/L
		1,2,3,7,8-Pentachlorodibenzo-p-dioxin	40321-76-4	14	pg/L
		1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	39227-28-6	7	pg/L
		1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	19408-74-3	27	pg/L
		1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	57653-85-7	6	pg/L
		1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	35822-46-9	8	pg/L
		Octachlorodibenzo-p-dioxin	3268-87-9	70	pg/L
		2,3,7,8-Tetrachlorodibenzofuran	51207-31-9	6	pg/L
		2,3,4,7,8-Pentachlorodibenzofuran	57117-31-4	5	pg/L
		1,2,3,7,8-Pentachlorodibenzofuran	57117-41-6	10	pg/L
		1,2,3,4,7,8-Hexachlorodibenzofuran	70648-26-9	6	pg/L
		1,2,3,7,8,9-Hexachlorodibenzofuran	72918-21-9	12	pg/L
		1,2,3,6,7,8-Hexachlorodibenzofuran	57117-44-9	11	pg/L

Table 1: Analytical Test Group Numbers, Parameters and Regulatory Method Detection Limits					
Analytical Test Group Number & Name		**Parameters**	**CAS #**	**RMDL**	**Units**
		2,3,4,6,7,8-Hexachlorodibenzofuran	60851-34-5	9	pg/L
		1,2,3,4,6,7,8-Heptachlorodibenzofuran	67562-39-4	23	pg/L
		1,2,3,4,7,8,9-Heptachlorodibenzofuran	5567-89-7	10	pg/L
		Octachlorodibenzofuran	39001-02-0	30	pg/L
25	Solvent Extractables	Oil and Grease	N/A *	1	mg/L
26	Fatty and Resin Acids	Abietic Acid	514-10-3	5	µg/L
		Chlorodehydroabietic Acid	57055-38-6	5	µg/L
		Dehydroabietic Acid	1740-19-8	5	µg/L
		Dichlorodehydroabietic Acid	57055-39-7	5	µg/L
		Levopimaric Acid	79-54-9	5	µg/L
		Neoabietic Acid	471-77-2	5	µg/L
		Oleic Acid	112-80-1	5	µg/L
		Pimaric Acid	127-27-5	5	µg/L
27	Polychlorinated Biphenyls (PCBs)	PCBs (Total)	N/A *	0.05	µg/L
28a	Open Characterizaton – Volatiles		N/A *	10^{1} against 1,3-dichlorobutane	µg/L
28b	Open Characterization – Extractables		N/A *	10^{1} against D_{10} Phenanthrene	µg/L
29	Open Characterization – Elemental	Note 7	Note 7	0.05^{1}	mg/L
30	Anions	Chloride	N/A *	2.0	mg/L
		Sulphate	N/A *	5.0	mg/L
		Fluoride	16984-48-8	0.1	mg/L
31	Total Residual Oxidants	Total Residual Oxidants	N/A *	0.01 as Chlorine	mg/L
32	Fibrous Chrysotile Asbestos	Fibrous Chrysotile Asbestos	N/A *	0.04	million fibres per L
33	Adsorbable Organic Halide	Adsorbable Organic Halide	N/A *	0.05 based on 2,4,6-trichlorophenol	mg/L
34	Miscellaneous Organics	Diethanolamine	111-42-2	0.1	mg/L

Table 1: Analytical Test Group Numbers, Parameters and Regulatory Method Detection Limits					
Analytical Test Group Number & Name		**Parameters**	**CAS #**	**RMDL**	**Units**
34a		N-nitrosodimethylamine (NDMA)	62-75-9	1.0	ng/L
35	Microbiological Parameters	*Escherichia coli (E. coli)*	N/A	1	CFU/100 mL

CAS # - Chemical Abstracts Service Number
N/A * - Not Applicable
1 – Semi-quantitative

Note 1: Analyze for hexavalent chromium only if total chromium is greater than 1.0 milligram per litre.
Note 2: Analyze for alkyl leads only if total lead is greater than 1.0 milligram per litre, unless required by the MOECC.
Note 3: m-Xylene and p-xylene often co-elute in the analysis. A single combined result may be reported as m-xylene.
Note 4: Diphenylamine & N-nitrosodiphenylamine often co-elute in the gas chromatography/mass spectrometry (GC/MS) analysis. A single combined result may be reported as diphenylamine.
Note 5: Parameters for ATG 21 are specified under an Environmental Compliance Approval
Note 6: Parameters for ATG 22 that are considered organochlorine pesticides are specified under an Environmental Compliance Approval
Note 7: All elements of the periodic table as determined semi-quantitatively. May included speciated elements as appropriate to the effluent stream.
RMDL: The RMDL values listed are the maximum allowable values for a LMDL under the Effluent Monitoring and Effluent Limits Regulations.

9.0 Guidelines for Analytical Test Groups (ATGs)

This section is presented as a series of tables which contain all the information related to sampling, analysis and quality control (QC) for each analytical test group (ATG).

The information is presented in the form of guiding principles and protocols related to each component of sampling, analysis and quality control. The required RMDL applies to both the recommended and alternate analytical procedures. In some cases, there are entries that indicate a sampling or analytical approach that is not appropriate. An additional table of recommend analytical method sources has been provide, but laboratories may reference other method sources, providing they can demonstrate that they meet the regulatory method detection limit (RMDL) listed in Table 1 in section 8.0.The recommended methods are the current versions as of the time of publication of this protocol and does not preclude using methods developed by the recommended agencies after the date of publication of this document. Older versions of published methods may also be used, as long as the method continues to meet the analytical principles and the RMDLs described in this protocol. Definitions of sampling techniques are described in section 2.0. Definitions of quality control requirements are described in section 4.0.

Information is also provided for parameters frequently found in site-specific Environmental Certificates of Approval (ECA). These parameters are grouped with existing ATGs where applicable. While no RMDL is provided, laboratories are recommended to develop an LMDL that is one tenth of the applicable limit in the ECA.

9.1 ATG #1 – Oxygen Demand

The discharge of an effluent or wastewater into a receiving body places a demand on the utilization of available oxygen in the receiving body. The principle procedures used to assess the levels of oxygen demand are chemical oxygen demand (COD), biochemical oxygen demand using a defined laboratory consumption period, usually five days (BOD_5), and carbonaceous biochemical oxygen demand ($CBOD_5$).

9.1.1 Chemical Oxygen Demand (COD)– ATG 1

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	25 mL	None; protect from light	Unpreserved: 4 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	H_2SO_4 to pH between 1.5 and 2 after sampling	Preserved: 30 days
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate followed by reflux	Colourimetric measurement of trivalent chromium or back titration	10 mg/L
Alternate	Oven digestion at 150°C in presence of oxidizing reagents	n/a	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
	Adjust pH of unpreserved sample to 6–6.5, prior to adding 1:1 ratio of electrolyte to sample	UV irradiation to oxidize the sample in presence of photo-catalyst with an electrode detection system	
Not Recommended	n/a		
Precautions/Notes	High chloride content in samples may cause severe interference problems in the analysis of COD		

Recommended Method Sources			
MOECC	E3246 (2012)	E3515	
AWWA	5220 B	5220 C	5220 D
USEPA	410.2, Rev 2	410.4, Rev 2.0	410.1
ASTM	D1252-06 (2012)e1		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.1.2 Biochemical Oxygen Demand – 5 day (BOD_5) – ATG 1a

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	500 mL	None; protect from light	4 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only				Analysis should be initiated as soon as possible after sample collection.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate; i.e., destruction of chlorine, neutralization of pH, stabilization of samples to 20°C. Preparation of seed & dilution water as appropriate. Dilution of sample to provide adequate oxygen depletion during 5 day period.	Dissolved oxygen determination by oxygen electrode.	2 mg/L
Alternate	n/a	Dissolved oxygen determination by Winkler method	
Not Recommended	n/a	n/a	
Precautions/Notes	If carbonaceous BOD is required, a nitrification inhibitor is necessary. See section 9.1.3.		

Recommended Method Sources	
MOECC	E3182
AWWA	5210 B
USEPA	405.1

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable (see note)	Applicable (see note)	Applicable
NOTE: For each analytical run performed a BOD_5 test on a seeded dilution water, and a BOD_5 test on the seeded dilution water spiked with one or more organic compounds; i.e. glucose and glutamic acid. It is recommended that the results of the seeded dilution water be used to correct seeded sample results and that the spiked seeded dilution water be used as a recovery check against established control limits.				
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.1.3 Carbonaceous Biochemical Oxygen Demand – 5 day ($CBOD_5$) – ATG 1b

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	500 mL	None; protect from light	4 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only				Analysis should be initiated as soon as possible after sample collection.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate; i.e., destruction of chlorine,	Dissolved oxygen determination by oxygen electrode.	2 mg/L

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
	neutralization of pH, stabilization of samples to 20°C. Preparation of seed & dilution water as appropriate. Dilution of sample to provide adequate oxygen depletion during 5 day period. Addition of an appropriate nitrification inhibitor to the BOD bottle prior to taking dissolved oxygen (DO) reading on day one.		
Alternate	n/a	Dissolved oxygen determination by Winkler method	
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources	
MOECC	E3182
AWWA	5210 B
USEPA	405.1

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable (see note)	Applicable (see note)	Applicable
NOTE: For each analytical run performed a $CBOD_5$ test on a seeded dilution water, and a $CBOD_5$ test on the seeded dilution water spiked with one or more organic compounds; i.e. glucose and glutamic acid. It is recommended that the results of the seeded dilution water be used to correct seeded sample results and that the spiked seeded dilution water be used as a recovery check against established control limits.				
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.2 ATG #2 – Cyanides

Cyanide is considered inorganic cyanide in water. Various forms of cyanide and anionic complexes of cyanide have differing degrees of toxicity to aquatic life. The ASTM document D6696-14, Standard Guide for Understanding Cyanide Species, may be consulted for further discussion on cyanide species.

9.2.1 Total Cyanide – ATG 2

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	500 mL	NaOH (cyanide free) to raise pH to 12.	14 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only	If high cyanide is suspected, sample containers must be labelled "HAZARDOUS"	Samples containing strong oxidizing agents (e.g. chlorine) should be neutralized with sodium thiosulphate or sodium arsenite, as soon as possible after sample collection to prevent oxidation or degradation.	For Auto 1 or 2, sampler bottles must be pre-charged with preservative. The volume of preservative may be estimated based on the expected cyanide concentration.	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Acid distillation/Ultraviolet digestion	Colourimetry	0.005 mg/L as HCN
Alternate	n/a	Specific ion electrode (ISE); Polarography via the method of standard addition in the presence of suitable electrolyte	
Not Recommended	n/a	n/a	
Precautions/Notes	Manual distillation must be used where the sample contains significant thiocyanate levels unless the lab can demonstrate that the method used effectively removes thiocyanate. The presence of strong oxidizing agents (e.g. chlorine) may affect the result.		

Recommended Method Sources			
MOECC	E3015		
AWWA	4500-CN^-B 4500-CN^-E 4500-CN^- O	4500-CN^- C 4500-CN^- F	4500-CN^- D 4500-CN^- N
USEPA	335.4, Rev 1.0 SW-846, 9010C SW-846, 9213	335.2 SW-846, 9012B	335.3 SW-846, 9014
ASTM	D2036-09 A D7511-12	D6994-10 D7365-09a	D7284-13

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.2.2 Weak Acid Dissociable (WAD) Cyanides – ATG 2a

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	500 mL	NaOH (cyanide free) to raise pH to 12.	7 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only	If high cyanide is suspected, sample containers must be labelled "HAZARDOUS"	Samples containing strong oxidizing agents (e.g., chlorine) should be neutralized with sodium thiosulphate or sodium arsenite, as soon as possible after sample collection to prevent oxidation or degradation.	For Auto 1 or 2, sampler bottles must be pre-charged with preservative. The volume of preservative may be estimated based on the expected cyanide concentration.	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Acid distillation under slightly acidified conditions (pH 4.5 to 6.0)	Colourimetry	0.005 mg/L as HCN

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Alternate	n/a	Specific ion electrode (ISE) Titration Polarography via the method of standard addition in the presence of suitable electrolyte	
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources			
MOECC	n/a		
AWWA	4500-CN^- B 4500-CN^- E 4500-CN^- O	4500-CN^- C 4500-CN^- F	4500-CN^- D 4500-CN^- I
USEPA	n/a		
ASTM	D2036-09 C D7365-09a	D4282-02 (2010)	D7237-10

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.2.3 Cyanate – ATG 2b

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	100 mL	2 drops of 10N NaOH (cyanide free) per litre for IC analysis;	7 days

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
					NaOH (cyanide free) to pH to 12 for colourimetry.	
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only	If high cyanide is suspected, sample containers must be labelled "HAZARDOUS"	Samples containing strong oxidizing agents (e.g., chlorine) should be neutralized with sodium thiosulphate or sodium arsenite, as soon as possible after sample collection to prevent oxidation or degradation.	For Auto 1 or 2, sampler bottles must be pre-charged with preservative. The volume of preservative may be estimated based on the expected cyanide concentration.	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate	Ion selective electrode	5 mg/L
Alternate	n/a	Colourimetry	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
		Ion chromatography(IC)	
Not Recommended	n/a	n/a	
Precautions/Notes	Special care must be taken to minimize chloride interferences during IC analysis.		

Recommended Method Sources	
MOECC	n/a
AWWA	4500-CN^- L
USEPA	n/a
ASTM	n/a

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.2.4 Thiocyanate – ATG 2c

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	100 mL	None; If both cyanates & thiocyanates are to be analyzed, then preserve as for cyanates (section 9.2.4)	7 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene,	Wash with detergent if necessary,	Volume required to meet RMDLs and analyze all	Preserve to pH<2 with mineral acid	

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
		PET	distilled water rinses	applicable QC samples	and refrigerate.	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only	If high cyanide is suspected, sample containers must be labelled "HAZARDOUS"	Samples containing strong oxidizing agents (e.g., chlorine) should be neutralized with sodium thiosulphate or sodium arsenite, as soon as possible after sample collection to prevent oxidation or degradation.	.	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate	Colourimetry	5 mg/L
Alternate	n/a	Ion chromatography(IC)	
Not Recommended	n/a	n/a	
Precautions/Notes	Special care must be taken to minimize chloride interferences during IC analysis.		

Recommended Method Sources	
MOECC	n/a
AWWA	4500-CN^- M
USEPA	n/a

ASTM	D4193-08 (2013)e1

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.2.5 Cyanide Amenable to Chlorination – ATG 2d

Sampling Procedures	**Sampling Type**	**Container**	**Container Pretreatment**	**Sample Volume**	**Preservation**	**Maximum Sample Storage time**
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	500 mL	NaOH (cyanide free) to raise pH to 12.	14 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only	If high cyanide is suspected, sample containers must be labelled “HAZARDOUS”	Samples containing strong oxidizing agents (e.g. chlorine) should be neutralized with sodium thiosulphate or sodium arsenite, as soon as possible after sample collection to prevent oxidation or	For Auto 1 or 2, sampler bottles must be pre-charged with preservative. The volume of preservative may be estimated based on the expected cyanide concentration.	

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
				degradation.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Acid distillation	Colourimetry	0.005 mg/L as HCN
Alternate	n/a	Specific ion electrode (ISE); Polarography via the method of standard addition in the presence of suitable electrolyte	
Not Recommended	n/a	n/a	
Precautions/Notes	Manual distillation must be used where the sample contains significant thiocyanate levels unless the lab can demonstrate that the method used effectively removes thiocyanate. The presence of strong oxidizing agents (e.g. chlorine) may affect the result.		

Recommended Method Sources			
MOECC	E3015		
AWWA	4500-CN^- B	4500-CN^- G	4500-CN^- H
USEPA	OIA-1677 (report EPA-821-R-04-001)		
	SW-846, 9010C	SW-846, 9012B	SW-846, 9014
	SW-846, 9016	SW-846, 9213	335.1
ASTM	D2036-09 B	D2036-09 D	D4282-02 (2010)
	D6888-09	D7237-10	D7365-09a

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.3 ATG #3 – Hydrogen Ion (pH)

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	On-line analyzer AUTO 1 or 2	Glass or Plastic	Generally none for new containers	50 mL	None	4 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes	When an on-line analyzer malfunctions, samples may be collected by AUTO 1 or 2 or Manual 1 or 2 techniques.	If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.			.	When the characteristics of the wastewater may lead to rapid changes in pH, an on-line analyzer must be used or grab samples must be collected and analyzed as soon as reasonably possible.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate	On-line analyzer; pH electrode and pH meter	n/a
Alternate	n/a		
Not Recommended	n/a	n/a	
Precautions/Notes	pH may be analyzed from the same sample bottle as ATG 7 or ATG 8		

Recommended Method Sources	
MOECC	E3218
AWWA	4500-H^+ B
USEPA	150.1 150.2
ASTM	D1293-12 D6569-14

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	n/a	n/a	n/a	Applicable *
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	Applicable *	

* not required for on-line analyzers

9.4 ATG #4 – Nitrogen

There are several forms of nitrogen that are of environmental interest for effluents/wastewater and the receiving water.

9.4.1 Ammonia plus Ammonium (Dissolved) – ATG 4a

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	100 mL	None	Unpreserved: 3 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	H_2SO_4 to pH between 1.5 to 2	Preserved: 14 days
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.		Samples containing strong oxidizing agents (e.g., chlorine) should be neutralized as soon as possible after sample collection to prevent oxidation or degradation.		Analysis should be initiated as soon as possible after sample collection.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate (e.g., distillation)	Colourimetry Ion selective electrode Titration	0.25 mg/L as N

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
		Ion chromatography (IC)	
Alternate	n/a	n/a	
Not Recommended	Nesslerization	n/a	
Precautions/Notes	High chloride content in samples may cause severe interference problems in the analysis of ammonia plus ammonium. Chlorinated municipal wastewater samples should be neutralized prior to analysis, by use of an appropriate chlorine buffer.		

Recommended Method Sources			
MOECC	E3364		
AWWA	4500-NH_3 B 4500-NH_3 E 4500-NH_3 H	4500-NH_3 C 4500-NH_3 F	4500-NH_3 D 4500-NH_3 G
USEPA	350.1, Rev 2.0	350.2, Rev 1	350.3
ASTM	D1426-08 D6919-09		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.4.2 Total Kjeldahl Nitrogen – ATG 4a

The Kjeldahl methods determine nitrogen in the trinegative state. Kjeldahl nitrogen (TKN) is the sum of organic nitrogen and ammonia nitrogen.

The value for TKN can also be calculated by determining the total nitrogen present in the sample and subtracting the amount of oxidized nitrogen (NO_2 + NO_3). (Alternate method)

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	100 mL	None	Unpreserved: 3 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	H_2SO_4 to pH between 1.5 to 2	Preserved: 14 days
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.		Samples containing strong oxidizing agents (e.g., chlorine) should be neutralized as soon as possible after sample collection to prevent oxidation or degradation.		Analysis should be initiated as soon as possible after sample collection.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Kjeldahl type digestion	Colourimetry Ion selective electrode Titration Ion chromatography (IC)	0.25 mg/L as N
Alternate	UV/Persulfate Digestion & Oxidation	Colourimetry plus calculation	
Not Recommended	Nesslerization	n/a	
Precautions/Notes	High chloride content in samples may cause severe interference problems in the analysis of ammonia plus ammonium. Chlorinated municipal wastewater samples should be neutralized prior to analysis, by use of an appropriate chlorine buffer.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
	Use of the alternate method involves the following calculation: TKN = Total Nitrogen – Oxidized nitrogen (NO_2 + NO_3)		

Recommended Method Sources			
MOECC	E3368 (2012) E3516		
AWWA	4500-N_{org} B 4500-N B	4500-N_{org} C 4500-N C	4500-N_{org} D
USEPA	351.1, Rev 2 351.4	351.2, Rev 2.0	351.3, Rev 2
ASTM	D3590-11		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.4.3 Nitrate plus Nitrite – ATG 4b

This is the sum of the oxidized forms of nitrogen in a sample.

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	50 mL	None	5 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples		
Not		Contact with metal foil				

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended						
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.				

Nitrate ion (NO_3^-) plus nitrite ion (NO_2^-) may be determined analytically as one value, or may be determined by separate techniques and the values added together. The following tables include both options.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate	Colourimetry Ion selective electrode Ion chromatography (IC)	0.25 mg/L as N
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	Results and LMDLs to be reported as the sum of Nitrate plus Nitrite.		

Recommended Method Sources			
MOECC	E3364		
AWWA	4110 B 4500-NO_3^- D 4500-NO_3^- H	4110 C 4500-NO_3^- E 4500-NO_3^- I	4500-NO_2^- B 4500-NO_3^- F
USEPA	300.0, Rev 2.1 353.1, Rev 1 354.1 SW-846, 9216A	300.1, Rev 1.0 353.2, Rev 2.0 SW-846, 9056A SW-846, 6500	352.1 353.3 SW-846, 9210A
ASTM	D4327-11 D7781-14	D3867-09	D6508-10

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.5 ATG #5 – Organic Carbon

The measurement of the amount of organic carbon in an effluent or receiving body provides an expression of the total organic content of the material and is independent of the oxidation state of the organic matter.

9.5.1 Dissolved Organic Carbon (DOC) – ATG 5a

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2 On-line analyzer	Glass or Plastic	Generally none for new containers	100 mL	None; protect from light	Unpreserved: 3 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	Filter (see note in Analytical procedures), then add H_2SO_4 to pH between 1.5 to 2	Preserved: 10 days
Not Recommended		Contact with metal foil				
Precautions/ Notes	When an on-line analyzer malfunctions, samples may be collected by AUTO 1 or 2 or MANUAL 1 or 2 techniques.	If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate, followed by filtration through glass	Quantitative conversion of carbon to CO_2 by one of:	0.5 mg/L as carbon

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
	fibre filter or analysis of the supernatant of a settled sample. Where volatile/Purgeable organic carbon may represent a major portion of the DOC (i.e., more than 25%) use preparation and measurement techniques which favour inclusion of this portion in DOC results.	i) ultraviolet/persulfate digestion ii) combustion at >800°C with a catalyst iii) combustion at >1100°C, catalyst optional, followed by infrared or colourimetric detection	
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	DOC may be determined directly following filtration by using a sample free of inorganic carbon or as the difference between total carbon and inorganic carbon, following filtration. If a filter is used for dissolved organic carbon, use a 0.45 micron size filter as per Standard Methods. High chloride in samples may cause severe interference problems in the analysis of DOC/TOC. When on-line analyzers are used, the monthly performance check sample should be taken as a single grab and the result compared to the on-line reading at the time of sampling (see section 3.2.3).		

Recommended Method Sources	
MOECC	E3370
AWWA	5310 C
USEPA	n/a
ASTM	n/a

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable *	Applicable *	Applicable *	Applicable *
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable *	n/a	Applicable *	

* when on-line analyzers are used QC samples need not be analyzed

9.5.2 Total Organic Carbon (TOC) – ATG 5b

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	100 mL	None; protect from light	Unpreserved: 3 days
Alternate	MANUAL 1 or 2	Polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	H_2SO_4 to pH between 1.5 to 2	Preserved: 10 days
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate. A representative sampling including particles must be introduced into the measurement system in a form (i.e., homogenized) which ensures effective processing by the measurement system. Particles may be separated from the liquid with subsequent exclusive analysis of both phases. Where volatile/purgeable organic may represent a major portion of the TOC (i.e., more than 25%),	Quantitative conversion of carbon to CO_2 by one of: iv) ultraviolet/persulfate digestion v) combustion at >800°C with a catalyst vi) combustion at >1100°C, catalyst optional, followed by infrared or colourimetric detection	2 mg/L as carbon

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
	use preparation and measurement techniques which favour inclusion of this portion in TOC results.		
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	TOC may be determined directly following filtration by using a sample free of inorganic carbon or as the difference between total carbon and inorganic carbon. Confirm effective processing of samples using option i) UV/persulfate digestion, by comparing results from the analysis of samples with TOC levels and concentrations of particles close to the maximum expected for the effluent/matrix, to results from the analysis of the same samples using an appropriate technique. Repeat comparison whenever higher TOC levels or particle concentrations are expected. High chloride in samples may cause severe interference problems in the analysis of DOC/TOC.		

Recommended Method Sources			
MOECC	E3247		
AWWA	5310 B	5310 C	5310 D
USEPA	415.1 SW-846, 9060A	415.3, Rev 1.2	
ASTM	D4839-03 (2011) D5904-02 (2009)	D4129-05 (2013)	D7573-09

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.6 ATG #6 – Phosphorus

Phosphorus occurs in the environment predominantly as phosphates. Phosphorus is essential to the growth of organisms and may be the nutrient that limits the primary productivity of a body of water. Discharges of effluents or wastewaters with excessive levels of phosphates may stimulate the growth of aquatic organisms in nuisance quantities.

9.6.1 Total Phosphorus – ATG 6

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	75 mL	None	Unpreserved: 14 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with phosphate free detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	H_2SO_4 to pH between 1.5 to 2	Preserved: 30 days
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate followed by digestion with 5:1 ratio of nitric acid to sulphuric acid or Kjeldahl	Colourimetry	0.1 mg/L as P

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
	equivalent mixture		
Alternate	Perchloric acid digestion Persulphate digestion Aqua regia digestion Persulphate oxidation/UV digestion	ICP	
Not Recommended	n/a	Stannous chloride colourimetric procedure	
Precautions/Notes	H_2SO_4 preservation is not suitable for ICP analysis H_2SO_4 and Kjeldahl digestion are not appropriate for ICP analysis. Persulphate oxidation/UV digestion is alternate preparation for colourimetry only.		

Recommended Method Sources			
MOECC	E3516 E3368 (2012)		
AWWA	4500-P B 4500-P H	4500-P E 4500-P I	4500-P F 4500-P J
USEPA	365.1 Rev 2.0 365.4	365.2 Rev 2.0 200.7 Rev 4.4	365.3 SW-846, 6010C

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.6.2 Orthophosphate – ATG 6a

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	75 mL	None	7 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density	Wash with phosphate free	Volume required to		

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
		polyethylene, polystyrene, PET	detergent if necessary, distilled water rinses	meet RMDLs and analyze all applicable QC samples		
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate	Colourimetry Ion chromatography	0.1 mg/L as P
Alternate	n/a	n/a	
Not Recommended	n/a	Stannous chloride colourimetric procedure	
Precautions/Notes			

Recommended Method Sources			
MOECC	E3364		
AWWA	4500-P C 4500-P G	4500-P E 4110 B	4500-P F 4110 C
USEPA	300.0 Rev 2.0 365.2 Rev 2.0 SW-846, 6500	300.1 Rev 2.0 365.3	365.1 Rev 2.0 SW-846, 9056A
ASTM	D4327-11	D6508-10	

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.7 ATG #7 – Specific Conductance

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	On-line analyzer AUTO 1 or 2	Glass or Plastic	Generally none for new containers	75 mL	None	4 days
Alternate	MANUAL 1 or 2	Polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes	When an on-line analyzer malfunctions, samples may be collected by AUTO 1 or 2 or Manual 1 or 2 techniques.	If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.			.	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate	On-line analyzer; Conductivity meter and cell measured at 25°C or conductivity meter with temperature compensation	5 µS/cm
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Precautions/Notes	Measurement at 25°C may be achieved by used of a jacketed cell, a water bath for samples, or preparation of a curve comparing measured conductivity with temperature (to establish a correction factor if required) for each sample matrix. When on-line analyzers are used, the monthly performance check sample should be taken as a single grab and the result compared to the on-line reading at the time of sampling (see section 3.2.3).		

Recommended Method Sources	
MOECC	E3218
AWWA	2510 B
USEPA	102.1 SW-846, 9050A
ASTM	D1125-14

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	n/a	n/a	n/a	Applicable *
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	Applicable *	

* not required for on-line analyzers

9.8 ATG #8 – Solids

The term “Solids” refers to matter suspended or dissolved in an effluent or receiving body.

9.8.1 Total Suspended Solids (TSS) – ATG 8

This is the portion of total solids that is retained by a filter of a specified pore size. It may also be known as non-filterable matter.

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	500 mL	None	7 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate and filtration using glass fibre filter with approximately 1.5-2 micrometers particle retention (934 AH or equivalent)	Drying of filter and particulates at 103°C ± 2°C followed by gravimetry	3 mg/L

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	Use of a filter having particle retention less than nominal 1.5–2 micrometers of the recommended 934AH filter may lead to elevated results. The same filter size/model must be used for suspended solids and dissolved solids. Balance accuracy should be confirmed by frequent checks with standard weights. All results of weight checks should be recorded and retained for the MOECC review. Weights should cover the entire analytical range (i.e., include crucible weight if applicable).		

Recommended Method Sources	
MOECC	E3188
AWWA	2540 D
USEPA	160.2
ASTM	D5907-13

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	n/a	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	Applicable	

9.8.2 Volatile Suspended Solids (VSS) – ATG 8

The weight loss of the material on the TSS after igniting the sample is known as volatile solids.

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	500 mL	None	7 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene,	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs	n/a	

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
		polystyrene, PET		and analyze all applicable QC samples		
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Perform TSS analysis (see section 9.8.1)	Ignite filter at 600°C ± 50°C for 1 hour, followed by gravimetry	3 mg/L
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	Balance accuracy should be confirmed by frequent checks with standard weights. All results of weight checks should be recorded and retained for the MOECC review. Weights should cover the entire analytical range (i.e. include crucible weight if applicable).		

Recommended Method Sources	
MOECC	E3188
AWWA	2540 E
USEPA	160.4 (use temperature specified above)
ASTM	n/a

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	n/a	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	Applicable	

9.8.3 Total Dissolved Solids (TDS) – ATG 8a

This is the portion of total solids that passes through a 2.0 µm filter or smaller.

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	100 mL	None	7 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate and filtration using glass fibre filter with approximately 2 micrometers particle	Gravimetry after drying at 103°C ± 3°C.	10 mg/L

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
	retention (934 AH or equivalent)		
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	Use of a filter having particle retention less than nominal 1.5–2 micrometers of the recommended 934AH filter may lead to elevated results. The same filter size/model must be used for suspended solids and dissolved solids. Balance accuracy should be confirmed by frequent checks with standard weights. All results of weight checks should be recorded and retained for the MOECC review. Weights should cover the entire analytical range (i.e. include crucible weight if applicable).		

Recommended Method Sources	
MOECC	E3188
AWWA	2540 C (use temperature specified above)
USEPA	160.1 (use temperature specified above)
ASTM	D5907-13 (use temperature specified above)

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	n/a	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	Applicable	

9.8.4 Total Solids (TS)

"Total solids" is defined as the material residue left in a container after evaporation of the sample and drying in an oven at a specified temperature. It includes both the material that passes through a 1.5-2.0 µm filter and the material retained on the filter. It may be determined directly, as described in the methods below, or as a sum of the results from determining the "suspended" and "dissolved" solids in a sample.

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for	100 mL	None	7 days

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
			new containers			
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.				

Analytical Procedures	Sample Preparation	Instrumental Measurement	Reporting Units
Recommended	None	Gravimetry after drying at 103°C ± 3°C.	mg/L
Alternate	Prepare as for suspended and dissolved solids.	Sum of results from analysis for suspended and dissolved solids.	
Not Recommended	n/a	n/a	
Precautions/Notes	Balance accuracy should be confirmed by frequent checks with standard weights. All results of weight checks should be recorded and retained for the MOECC review. Weights should cover the entire analytical range (i.e., include crucible weight if applicable).		

Recommended Method Sources	
MOECC	E3188
AWWA	2540 B (use temperature specified above)
USEPA	160.3 (use temperature specified above)

ASTM	D5907-13 (use temperature specified above)

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	n/a	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	Applicable	

9.9 ATG #9 – Metals(including ATG 9a)

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Plastic	Soak overnight in 5% HNO_3, followed by distilled water rinses, if necessary	500 mL	HNO_3 (containing <1 mg/L of total metals) to pH <2	30 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, glass	Use new containers	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil If boron analysis is required, glass containers must not be used due to the potential for sample contamination.				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.			Adding Acid to a PET bottle before sampling will score the PET bottle and result in Antimony being leached from the bottle, giving false positive results.	Once properly preserved (pH<2) samples can be stored at room temperature. Prior to acidification of the sample, it must be kept <10°C.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Nitric acid digestion	Flame AA ICP DCP ICP-MS Uranium: fluorescence spectroscopy, ICP or ICP-MS	See Table 1
Alternate	Other acid digestion as appropriate	Graphite furnace AAS Polarography by method of standard addition in the presence of a suitable electrolyte Magnesium: EDTA titration	
Not Recommended	n/a	n/a	
Precautions/Notes	Regulated industries or sewage treatment plants may be required to report only a partial list of the parameters included in this group.		

Recommended Method Sources			
MOECC	E3094		
AWWA	3030 D	3030 E	3030 F
	3030 G	3030 K	3111 B
	3111 C	3111 D	3111 E
	3113 B	3120 B	3125 B
	3130 B	4500-B B	4500-B C
	Individual metals are listed as 3500-n		
USEPA	200.2 Rev 2.8	200.5 Rev 4.2	200.7 Rev 4.4
	200.8 Rev 5.4	200.9 Rev 2.2	200.15 Rev 1.2
	1637	1638	1639
	1640		
	SW-846, 3005A	SW-846, 3010A	SW-846, 3015A
	SW-846, 3020A	SW-846, 6010C	SW-846, 6020A
	SW-846, 6800	SW-846, 7000B	SW-846, 7010
	Older versions of EPA methods include separate methods for individual elements. The use of these methods is acceptable as long as the laboratory demonstrates that the method		

Recommended Method Sources			
	LMDL meets or exceeds the RMDLs in Table 1.		
ASTM	D511-09	D1068-10	D1687-12 C
	D1688-12	D1691-12	D1886-08
	D1971-11	D1976-12	D3082-09
	D3372-12	D3373-12	D3557-12
	D3558-08	D3559-08	D3645-08
	D3866-12	D3919-08	D3920-12
	D4190-08	D4309-12	D4691-11
	D5174-07 (2013)	D5673-10	D6800-12
	D6919-09	D4191-08	D4192-08
	D4382-12		

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	Applicable	Applicable	Applicable
NOTE: Spiked blank analysis must include the entire analytical procedure, including evaporation or digestion.				
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

The following metals may also be analyzed using the principles and techniques listed above:

Parameter	**CAS Number**	**Reporting Units**
Barium	7440-39-3	mg/L
Calcium	7440-70-2	mg/L
Manganese	7439-96-5	mg/L
Potassium	7440-09-7	mg/L
Sodium	7440-23-5	mg/L

9.10 ATG #10 – Hydrides (Antimony, Arsenic, Selenium)

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Soak overnight in 5% HNO_3, followed by distilled water rinses, if necessary	50 mL	HNO_3 (containing <1 mg/L of total metals) to pH <2	30 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene	Use new containers	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.			Adding Acid to a PET bottle before sampling will score the PET bottle and result in Antimony being leached from the bottle, giving false positive results.	Once properly preserved (pH<2) samples can be stored at room temperature. Prior to acidification of the sample, it must be kept <10C.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Acid digestion	Hydride generation in conjunction with atomic absorption or ICP	0.005 mg/L

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
		ICP-MS	
Alternate	n/a	Graphite furnace AAS Polarography by method of standard addition in the presence of a suitable electrolyte Colourimetry	
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources			
MOECC	E3089		
AWWA	3030 F 3113 B 3120 B 3500-Se B	3111 B 3114 B 3125 B 3500-Se C	3111 D 3114 C 3500-As B
USEPA	200.5 Rev 4.2 200.9 Rev 2.2 206.3 270.3 SW-846, 3005A SW-846, 3020A SW-846, 6800 SW-846, 7061A SW-846, 7741A	200.7 Rev 4.4 200.15 Rev 1.2 206.5 SW-846, 3010A SW-846, 6010C SW-846, 7000B SW-846, 7062 SW-846, 7742	200.8 Rev 5.4 206.2 270.2 SW-846, 3015A SW-846, 6020A SW-846, 7010 SW-846, 7063
ASTM	D1976-12 D3859-08 D5673-10	D2972-08 D3919-08 D4309-12	D3697-12 D4691-11

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.11 ATG #11 – Chromium (Hexavalent)

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass with plastic lined cap	Soak overnight in 5% HNO_3, followed by distilled water rinses, if necessary	200 mL	None	Unpreserved: 5 days
Alternate	MANUAL 1 or 2	Teflon®, with plastic lined cap	Use new containers	Volume required to meet RMDLs and analyze all applicable QC samples	Buffer solution (see below) designed to a pH of 9.3 to 9.7	Preserved: 28 days
Not Recommended		Contact with metallic foil, paper or cardboard				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.			Use ammonium sulphate buffer solution [i.e., $(NH_4)_2SO_4/NH_4OH$] or $(NH_4)_2SO_4/NH_4OH/NaOH$ + NaOH] as specified in EPA Method 218.6 (revision 3.3, 1994), EPA Method 218.7 (version 1.0, 2011), Standard Methods 3500-Cr C or ASTM D5257-11.	Unless ATG 11 is specifically required, analyze for ATG11 only if the total chromium result is >1 mg/L and ensure adherence with the 5-day storage time specified for ATG11.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	None	Colourimetry Ion chromatography Ion chromatograph/mass spectrometry	0.01 mg/L
Alternate	Solvent extraction	Polarography by method of standard addition in the presence of a suitable electrolyte	
Not Recommended	n/a	n/a	
Precautions/Notes	Unless ATG 11 is specifically required, analyze for ATG11 only if the total chromium result is >1 mg/L and ensure adherence with the 5-day storage time specified for ATG11.		

Recommended Method Sources			
MOECC	E3056	E3510	
AWWA	3500-Cr B	3500-Cr C	3500-Cr (2009)
USEPA	218.4 218.7 SW-846, 7196A SW-846, 7199	218.5 1636 SW-846, 7197 SW-846, 6800	218.6 Rev 3.3 SW-846, 7195 SW-846, 7198
ASTM	D5257-11	D1687-12 A	

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.12 ATG #12 – Mercury

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Teflon®, with plastic lined cap	Use new containers	200 mL	Add HCl to pH<2	28 days
Alternate	MANUAL 1 or 2	Glass with plastic lined cap	Soak overnight in 5% HNO_3, followed by distilled water rinses, if necessary	Volume required to meet RMDLs and analyze all applicable QC samples	Add 1–2 mL HNO_3 per 250 mL sample followed by at least 0.5 mL $K_2Cr_2O_7$ solution to produce definite, lasting yellow colour; or Add $KMnO_4$ solution until pink; or Add HNO_3 alone to pH<2.	14 days
Not Recommended		Contact with metallic foil				
Precautions/ Notes		No sample contact with metal except carbon steel or stainless steel.		Samples containing coloured materials, reducing agents and highly alkaline substances may require larger volumes of potassium dichromate solution and nitric acid as preservatives. The amounts of preservatives to obtain coloured acidic samples should be determined and these volumes noted on the	It is recommended that preservatives be stored in glass containers and away from mercury and its salts. A periodic test for mercury should be made to ensure preservatives are uncontaminated.	Preserved samples may be stored at an ambient temperature of 20°C or less.

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
				sample bottles so that an appropriate blank compensation can be done.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Oxidative acid digestion	Cold vapour generation in conjunction with AA, ICP, ICP-MS or fluorescence detector	0.0001 mg/L
Alternate	None	Hydride generation in conjunction with AA, ICP, ICP-MS or fluorescence detector	
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources			
MOECC	E3060	E3526	
AWWA	3112 B		
USEPA	245.1 Rev 3.0 200.8 Rev 5.4 SW-846, 7472	245.2, 1631E	245.7 Rev 2.0 SW-846, 7470A
ASTM	D3223-12		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.13 ATG #13 – Total Alkyl Lead (Inorganic Ligand)

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass amber with plastic lined cap	Soak overnight in 5% HNO_3, followed by distilled water rinse	1 L	None	4 days at <4°C
Alternate	MANUAL 1 or 2	Teflon®		Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metallic foil				
Precautions/ Notes				Fill slowly to the top, no air space, avoid turbulence.		Unless ATG 13 is specifically required, analyze for ATG13 only if the total lead is >1 mg/L and ensure adherence with the 4-day storage time specified for ATG13.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Liquid/liquid extraction	Colourimetry using dithizone reagent GC/AA	0.005 mg/L as lead
Alternate	Derivatization		
Not Recommended	n/a	n/a	
Precautions/Notes	Unless ATG 13 is specifically required, analyze for ATG13 only if the total lead is >1 mg/L and ensure adherence with the 4-day storage time specified for ATG13.		

Recommended Method Sources	
MOECC	n/a
AWWA	n/a
USEPA	n/a
ASTM	n/a

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.14 ATG #14 – Phenolics (4AAP)

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	MANUAL 1 or 2	Glass with phenolic-free cap	Generally none for new containers	250 mL	H_2SO_4 to pH between 1.5 and 2	30 days
Alternate	AUTO 1 or 2 or MANUAL 3	Teflon®, with phenolic-free cap	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	1 mL of (3N H_3PO_4 + 120 g/L $CuSO_4$*$5H_2O$) solution for each 250 mL sample, especially where high chloride is suspected to prevent interference.	
Not Recommended		Contact with metallic foil				
Precautions/ Notes	It is recommended that Manual sampling techniques be used for phenolics to avoid contamination from silicone rubber parts in automated samplers. If an automated sampler is used, sample contamination may be avoided by using the last bottle in the sequence for the phenolics (ATG14) sample.				For AUTO 1 or 2, sampler bottles must be pre-charged with preservative. Remove any oxidizing agents as soon as possible after sampling, but no later than 48 hours after sampling, by adding ferrous sulphate or sodium arsenite.	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate followed by distillation of acidified sample.	Colourimetry of buffered sample	0.002 mg/L as phenol
Alternate	n/a	Colourimetry of chloroform extract.	
Not Recommended	n/a	n/a	
Precautions/Notes	High chloride content in samples may cause severe interference problems in the analysis of phenolics.		

Recommended Method Sources			
MOECC	E3179		
AWWA	5530 B	5530 C	5530 D
USEPA	420.2 420.3 SW-846, 9067	420.4, Rev 1.0 SW-846, 9065	420.1 SW-846, 9066
ASTM	D1783-01 (2012)		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.15 ATG #15 – Sulphide

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	MANUAL 3 collected as Grab 2	Glass or Plastic	Generally none for new containers	250 mL	0.5 mL per 250 mL sample of 2N zinc acetate followed by drop wise addition of 5% sodium hydroxide to pH >9	7 days
Alternate	MANUAL 3 collected as Grab 1	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	Zinc acetate with sodium carbonate instead of sodium hydroxide	
Not Recommended						
Precautions/ Notes	If sampling by MANUAL 3 technique, preservative should be added after each fraction is collected.	Fill slowly, avoiding excessive air space and turbulence prior to preservation. All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only.				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Dissolution of precipitate	Methylene blue colourimetry Specific ion electrode Ion chromatography	0.02 mg/L
Alternate	Decantation if needed	Polarography by method of standard addition in the presence of a suitable electrolyte	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Not Recommended	n/a	n/a	
Precautions/Notes	The three grab samples may be combined in the lab immediately prior to analysis, or the three samples may be analyzed separately and an arithmetic mean reported.		

Recommended Method Sources			
MOECC	E3100		
AWWA	4500-S^{2-} D 4500-S^{2-} G	4500-S^{2-} E 4500-S^{2-} I	4500-S^{2-} F
USEPA	376.2	SW-846, 9215	
ASTM	D4658-09		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.16 ATG #16 – Volatiles,Halogenated and ATG #17 – Volatiles, Non-Halogenated

Volatile organic compounds (VOCs) include a number of compounds with low boiling points. Regulated facilities may only be required to report a subset of these parameter groups.

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	MANUAL 3 collected as Grab 2	Glass with Teflon® -lined septum cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	25 or 40 mL; no headspace	When samples contain residual chlorine, preserve with 80 mg $Na_2S_2O_3$ per 1 L and store in the dark	Unpreserved:7 days
Alternate	MANUAL 3 collected as Grab 1 or On-line analyzer	Glass with foil-lined cap		Volume required to meet RMDLs and analyze all applicable QC samples	2 to 4 drops HCl or sodium bisulphate	Preserved: 14 days
Not Recommended		n/a				
Precautions/ Notes		Fill slowly, avoiding excessive air space and turbulence prior to preservation. All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Purge and trap	GC-MS, capillary column	See Table 1
Alternate	n/a	GC-ECD or ELCD, capillary column GC-FID or PID, capillary column Headspace – GC-MS	
Not Recommended	n/a	n/a	
Precautions/Notes	The three grab samples should be analyzed separately and an arithmetic mean reported or they may be combined in the lab immediately prior to analysis.		

Recommended Method Sources			
MOECC	E3132		
AWWA	6040 B 6200 C	6200 B 6232 B	
USEPA	502.1 Rev 2.0 524.2 Rev 4.1 601 1624 C SW-846, 8260C	502.2 Rev 2.1 524.3 Ver 1.0 602 SW-846, 5030C SW-846, 8261	503.1 Rev 2.0 551.1 Rev 1.0 624 SW-846, 5032 SW-846, 8021B
ASTM	D3973-85 (2011) D5790-95 (2012)		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable, may use duplicate sample
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	Applicable	Applicable	

9.17 ATG #18 – Volatile Organic Compounds, Water Soluble

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	MANUAL 3 collected as Grab 2	Glass with Teflon® -lined septum cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	25 or 40 mL; no headspace	When samples contain residual chlorine, preserve with 80 mg $Na_2S_2O_3$ per 1 L and store in the dark	Unpreserved:7 days
Alternate	MANUAL 3 collected as Grab 1 or On-line analyzer	Glass with foil-lined cap		Volume required to meet RMDLs and analyze all applicable QC samples	2 to 4 drops HCl or sodium bisulphate	Preserved: 14 days
Not Recommended		n/a				
Precautions/ Notes		Fill slowly, avoiding excessive air space and turbulence prior to preservation. All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Purge and trap	GC-MS, capillary column	See Table 1
Alternate	n/a	GC-FID or PID, capillary column	
Not	n/a	n/a	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended			
Precautions/Notes	The three grab samples should be analyzed separately and an arithmetic mean reported or they may be combined in the lab immediately prior to analysis.		

Recommended Method Sources			
MOECC	n/a		
AWWA	n/a		
USEPA	603 SW-846, 8260C SW-846, 8031	SW-846, 5031 SW-846, 8261 SW-846, 8315A	SW-846, 5032 SW-846, 8015C SW-846, 8316
ASTM	D3695-95 (2013)		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable, may use duplicate sample
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	Applicable	Applicable	

9.18 ATG #19 – Extractables, Base Neutral

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon®-lined cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	800 mL	None	30 days
Alternate	MANUAL 1 or 2	Teflon® with Teflon®-lined cap	Instead of baking, rinse with acetone (or other water soluble solvent), distilled-in-glass hexane and/or dichloromethane, air dry	Volume required to meet RMDLs and analyze all applicable QC samples	Add first aliquot of extraction solvent on arrival at lab, prior to storage	
Not Recommended		n/a				
Precautions/ Notes		All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Liquid/liquid extraction; clean-up if necessary	GC-MS, capillary column	See Table 1
Alternate		High performance liquid chromatography (HPLC), ultraviolet or fluorescence detection for PAHs and biphenyl	
Not Recommended	n/a	n/a	
Precautions/Notes	N-nitrosodiphenylamine breaks down to diphenylamine in the injector. A single result is reported as diphenylamine.		

Recommended Method Sources			
MOECC	E3265		
AWWA	6040B	6410B	6440B
USEPA	506	525.1 Rev 2.2	525.2 Rev 2.0
	550	550.1	606
	607	609	610
	611	612	625
	1625C	SW-846, 3510C	SW-846. 3520C
	SW-846, 3535A	SW-846, 3610B	SW-846, 3611B
	SW-846, 3630C	SW-846, 3640A	SW-846, 3650B
	SW-846, 8100	SW-846, 8270D	SW-846, 8310
	SW-846, 8325	SW-846, 8410	
ASTM	D5241-92 (2011)	D6520-06 (2012)	

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable, may use duplicate sample
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	Applicable	Applicable	

9.19 ATG #20 – Extractables, Acid (Phenolics)

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon®-lined cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	800 mL	None	30 days
Alternate	MANUAL 1 or 2	Teflon® with Teflon®-lined cap	Instead of baking, rinse with acetone (or other water soluble solvent), distilled-in-glass hexane and/or dichloromethane, air dry	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Foil-lined caps				
Precautions/ Notes		All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics and phenolic resins (e.g., Bakelite® caps)		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Liquid/liquid extraction, pH adjusted to <2; derivatization if appropriate; clean-up	GC-MS, capillary column	See Table 1
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources			
MOECC	E3265		
AWWA	6410 B	6420 B	6420 C
USEPA	526 Rev 1.0 625 SW-846, 3520 C SW-846, 3640A SW-846, 8410	528 Rev 1.0 1625 C SW-846, 3535A SW-846, 8041A NCASI Method CP-86.07	604 SW-846, 3510C SW-846, 3650B SW-846, 8270
ASTM	D2580-06 (2012) D5241-92 (2011)	D6520-06 (2012)	

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable, may use duplicate sample
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	Applicable	Applicable	

9.20 ATG #21 – Extractables, Phenoxyacid Herbicides

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon®-lined cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	800 mL	None	30 days
Alternate	MANUAL 1 or 2	Teflon® with Teflon®-lined cap	Instead of baking, rinse with acetone (or other water soluble solvent), distilled-in-glass hexane and/or dichloromethane, air dry	Volume required to meet RMDLs and analyze all applicable QC samples		
Not Recommended		n/a				
Precautions/ Notes		All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Acidify prior to extraction. Liquid/liquid extraction; clean-up if necessary	GC-MS, capillary column	See Table 1
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources			
MOECC	E3119		
AWWA	6640 B		
USEPA	515.1 Rev 4.0 515.4 Rev 1.0 1658 SW-846, 3535A	515.2 Rev 1.1 555 Rev 1.0 SW-846, 3510C SW-846, 8151A	515.3 Rev 1.0 615 SW-846, 3520 C SW-846, 8321B
ASTM	D5317-98 (2011)	D6520-06 (2012)	

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable, may use duplicate sample
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	Applicable	Applicable	

9.21 ATG #22 – Extractables, Organochlorine Pesticides

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon®-lined cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	800 mL	None	30 days
Alternate	MANUAL 1 or 2	Teflon® with Teflon®-lined cap	Instead of baking, rinse with acetone (or other water soluble solvent), distilled-in-glass hexane and/or dichloromethane, air dry	Volume required to meet RMDLs and analyze all applicable QC samples		
Not Recommended		n/a				
Precautions/ Notes		All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Liquid/liquid extraction; clean-up if necessary	GC-MS, capillary column	See Table 1
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	Analysis may be combined with ATG 23, if both ATGs are required.		

Recommended Method Sources			
MOECC	E3400		
AWWA	6410B 6630D	6630B	6630C
USEPA	505 Rev 2.0 525.2 Rev 2.0 608.1 1656 SW-846, 3535A SW-846, 3650B SW-846, 8081B	508 Rev 3.1 527, Rev 1.0 608.2 SW-846, 3510C SW-846, 3620C SW-846, 3660B SW-846, 8085	508.1 Rev 2.0 608 617 SW-846, 3520C SW-846, 3630C SW-846, 8270D
ASTM	D5175-91 (2011)	D6520-06 (2012)	

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable, may use duplicate sample
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	Applicable	Applicable	

9.22 ATG #23 – Extractables, Neutral-Chlorinated

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon®-lined cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	800 mL	None	30 days
Alternate	MANUAL 1 or 2	Teflon® with Teflon®-lined cap	Instead of baking, rinse with acetone (or other water soluble solvent), distilled-in-glass hexane and/or dichloromethane, air dry	Volume required to meet RMDLs and analyze all applicable QC samples		
Not Recommended		n/a				
Precautions/ Notes		All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Liquid/liquid extraction; clean-up if necessary	GC-MS, capillary column	See Table 1
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	Analysis may be combined with ATG 22, if both ATGs are required.		

Recommended Method Sources			
MOECC	E3400		
AWWA	6410B	6040B	
USEPA	505 Rev 2.0 525.2 Rev 2.0 SW-846, 3510C SW-846, 3620C SW-846, 3660B SW-846, 8121 SW-846, 8410	508 Rev 3.1 612 SW-846, 3520C SW-846, 3630C SW-846, 8081B SW-846, 8270D	508.1 Rev 2.0 1656 SW-846, 3535A SW-846, 3650B SW-846, 8085 SW-846, 8270D
ASTM	D5241-92 (2011) D5790-95 (2012)	D6520-06 (2012)	

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable, may use duplicate sample
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	Applicable	Applicable	

9.23 ATG #24 – Chlorinated Dibenzo-p-Dioxins and Furans

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon® -lined cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	1 L	None	30 days
Alternate	MANUAL 1 or 2	Clear glass with Teflon® -lined cap	If needed, 3 rinses with distilled-in-glass methanol and/or dichloromethane, air dry. Cap: no pre-treatment	Volume required to meet RMDLs and analyze all applicable QC samples		
Not Recommended		n/a				
Precautions/ Notes		All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Liquid/liquid extraction and clean-up. Sample container must be rinsed with extraction solvent. If TSS >15 mg/L: filter sample, extract solids by Soxhlet using toluene, extract filtrate normally, combine both extracts prior to clean-up.	GC-HRMS, capillary column Low resolution MS acceptable with effective clean-up, if RMDL achieved	See Table 1 LMDL must be calculated for each congener listed in Table 1
Alternate	n/a	GC-MS/MS	
Not Recommended	n/a	n/a	
Precautions/Notes	The laboratory must be able to demonstrate that all glassware and equipment is free of contamination. The method requires that all samples be spiked with ^{13}C-labelled surrogates of the congeners listed in Table 1 and with labelled internal standards to aid recovery checks. The spikes must include at least one representative from each congener group, preferably one for each congener. Analysis must be done for the 17 dioxin and furan congeners listed in Table 1 and results recorded for each individual congener. Highest possible concentration assumptions are to be made where full chromatographic resolution does not occur. Analysis must be done in accordance with USEPA method 1613, Environment Canada reference method EPS 1/RM/19, USEPA SW-846 8280B, SW-846 8290A, or MOECC method E3418, current versions, as amended from time to time. The presence/concentration of 2,3,7,8-TCDF need not be confirmed on a second column unless: i) Its concentration is at or above the limit for this congener, or ii) The 2,3,7,8-TCDF contribution pushes the total TEQ value above the limit. In addition, it is recommended that total congener group concentrations be recorded to ensure continuity/comparability with any historical data. For the purpose of calculating a toxic equivalent concentration (TEQ) for a congener listed in Table 1, Section 8.0, the positive concentration value obtained for that congener shall be multiplied by the respective International Toxicity Equivalent Factor (TEF), as amended from time to time, listed in Table 2 below, for that congener, with suitable adjustments to yield a result in pg/L. If a positive result is not obtained for an individual congener, half of the laboratory method detection limit (LMDL) shall be used for the TEQ calculation. The total TEQ concentration is the sum of the TEQ concentrations for each congener listed in Table 2. The source of the TEF must be identified.		

Table 2: International Toxicity Equivalent Factors for Dioxins and Furans		
	TEF	TEF
	(NATO)	(WHO, 2005)
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1	1
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	0.5	1
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	0.1	0.1
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	0.1	0.1
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	0.1	0.1
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	0.01	0.01
Octachlorodibenzo-p-dioxin	0.001	0.0003
2,3,7,8-Tetrachlorodibenzofuran	0.1	0.1
2,3,4,7,8-Pentachlorodibenzofuran	0.5	0.03
1,2,3,7,8-Pentachlorodibenzofuran	0.05	0.3
1,2,3,4,7,8-Hexachlorodibenzofuran	0.1	0.1
1,2,3,7,8,9-Hexachlorodibenzofuran	0.1	0.1
1,2,3,6,7,8-Hexachlorodibenzofuran	0.1	0.1
2,3,4,6,7,8-Hexachlorodibenzofuran	0.1	0.1
1,2,3,4,6,7,8-Heptachlorodibenzofuran	0.01	0.01
1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.01	0.01
Octachlorodibenzofuran	0.001	0.0003

Table 2a: Example of a TEQ Calculation						
	Conc. pg/L	**LMDL**	**TEF (NATO)**	**TE/congener pg/L (1/2 LMDL)**	**TEF (WHO, 2005)**	**TE/congener pg/L (1/2 LMDL)**
2,3,7,8-Tetrachlorodibenzo-p-dioxin	2.3	0.1	1	2.3	1	2.3
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	1.4	0.1	0.5	0.7	1	1.4
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	0.23	0.2	0.1	0.023	0.1	0.23
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	1.2	0.3	0.1	0.12	0.1	0.12
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	ND	0.3	0.1	0.015	0.1	0.05
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	3.8	0.5	0.01	0.038	0.01	0.038
Octachlorodibenzo-p-dioxin	14	0.9	0.001	0.014	0.0003	0.0042

Table 2a: Example of a TEQ Calculation						
	Conc. pg/L	**LMDL**	**TEF (NATO)**	**TE/congener pg/L (1/2 LMDL)**	**TEF (WHO, 2005)**	**TE/congener pg/L (1/2 LMDL)**
2,3,7,8-Tetrachlorodibenzofuran	11	0.2	0.1	1.1	0.1	1.1
1,2,3,7,8-Pentachlorodibenzofuran	2.2	0.2	0.05	0.11	0.03	0.066
2,3,4,7,8-Pentachlorodibenzofuran	5.2	0.3	0.5	2.7	0.3	1.56
1,2,3,4,7,8-Hexachlorodibenzofuran	0.34	0.4	0.1	0.034	0.1	0.034
1,2,3,6,7,8-Hexachlorodibenzofuran	0.55	0.5	0.1	0.055	0.1	0.055
1,2,3,7,8,9-Hexachlorodibenzofuran	ND	0.6	0.1	0.03	0.1	0.03
2,3,4,6,7,8-Hexachlorodibenzofuran	0.50	0.6	0.1	0.05	0.1	0.05
1,2,3,4,6,7,8-Heptachlorodibenzofuran	ND	0.8	0.01	0.004	0.01	0.004
1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.11	0.8	0.01	0.0011	0.01	0.0011
Octachlorodibenzofuran	0.17	1	0.001	0.00017	0.0003	0.000051
Total TEQ 2,3,7,8-TCDD (0.5 DL)				**7.29**		**7.04**

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable [1]	n/a [2]	n/a [3]	n/a
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	Recommended in case re-analysis is needed	

1. Blank sample (method blank) need not be analyzed if ^{13}C-labelled compounds are used for spiked blank analysis.
2. A separate method blank must be analyzed if native dioxins and furans are used for spiked blank analysis.
3. A separate spiked sample need not be analyzed because method requires that ^{13}C-labelled standards representing each congener group be added to each sample prior to extraction.

9.24 ATG #25 – Solvent Extractables

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	MANUAL 3 collected as Grab 2	Clear glass with Teflon® or foil-lined cap	Generally none for new containers	800 mL	None	Unpreserved: 7 days
Alternate	MANUAL 3 collected as Grab 1 or 3 AUTO 1 or 2	n/a	Wash with detergent if necessary, distilled water and solvent rinses.	Volume required to meet RMDLs and analyze all applicable QC samples	Acidification with HCl to approximately pH 2	Preserved: 30 days
Not Recommended		Amber glass, plastic				
Precautions/ Notes		Sample should be collected directly into the laboratory container. All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics. Do not rinse containers.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Acidify with a mineral acid to approximately pH 2. Liquid/liquid extraction with n-hexane, plus solvent rinsings of sample containers. Silica gel chromatography when speciation into animal/vegetable and mineral/synthetic materials is needed.	Gravimetry Infrared spectroscopy is recommended to confirm the nature of the extracted materials.	1 mg/L
Alternate	Same as above, using dichloromethane instead of n-hexane.	n/a	

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Not Recommended	Use of Freons.	n/a	
Precautions/Notes	Entire sample must be analyzed; method requires that sample container be rinsed with extraction solvent.		

Recommended Method Sources	
MOECC	E3401
AWWA	5520B 5520G 5520C (using n-hexane or dichloromethane as the solvent)
USEPA	1664A SW-846, 9070A
ASTM	n/a

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	n/a	n/a	Applicable, may use duplicate sample
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	Recommended in case re-analysis is needed	

9.25 ATG #26 – Fatty and Resin Acids

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon®-lined cap	If needed, wash in hot water, detergent, water, distilled water rinse. Bake at 300°C for 4 hours. Cap: no pre-treatment	800 mL	None	7 days
Alternate	MANUAL 1 or 2	Teflon® with Teflon®-lined cap	Instead of baking, rinse with acetone (or other water soluble solvent), distilled-in-glass hexane and/or dichloromethane, air dry	Volume required to meet RMDLs and analyze all applicable QC samples		
Not Recommended		Foil-lined caps				
Precautions/ Notes		All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Liquid/liquid extraction with dichloromethane, neutral pH; methylate with (trimethylsiyl)diazomethane	GC-MS, capillary column	See Table 1
Alternate	pH adjusted to 9, Liquid/liquid extraction with t-butyl ether; methylation	GC-FID, capillary column	
Not Recommended	n/a	n/a	
Precautions/Notes	When analyzing using GC-FID, quantitation should be done relative to the response of dehydroabietic acid. The total ion count of the chromatographic peaks should be used for quantitation. Compound identity should be confirmed against the mass spectrum of the methylated acid with a match >80%.		

Recommended Method Sources			
MOECC	E3166		
AWWA	5560 D		
USEPA	SW-846, 3510C	SW-846, 3520 C	SW-846, 3535A
ASTM	n/a		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable, may use duplicate sample
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	Applicable, to contain dehydroabietic acid only	Applicable	

9.26 ATG #27 – Polychlorinated Biphenyls (PCBs), Total

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon®-lined cap	If needed, wash in hot water, detergent, water, distilled water rinse. Bake at 300°C for 4 hour. Cap: no pre-treatment	800 mL	None	30 days
Alternate	MANUAL 1 or 2	Teflon® with Teflon®-lined cap	Instead of baking, rinse with acetone (or other water soluble solvent), distilled-in-glass hexane and/or dichloromethane, air dry	Volume required to meet RMDLs and analyze all applicable QC samples		
Not Recommended		n/a				
Precautions/ Notes		All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Liquid/liquid extraction	GC-ECD, single capillary column GC-MS, capillary column	0.05 µg/L
Alternate	clean-up if necessary	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	Report as individual Aroclors or as a mixture of Aroclors, as appropriate.		

Recommended Method Sources			
MOECC	E3400	E3488	
AWWA	6410B	6630B	
USEPA	508 Rev 3.0	508A Rev 1.0	608
	608.1	608.2	617
	1656	SW-846, 3510C	SW-846, 3520C
	SW-846, 3535A	SW-846, 3620C	SW-846, 3630C
	SW-846, 3650B	SW-846, 3660B	SW-846, 8270D
	SW-846, 8082A		
ASTM	D5175-91 (2011)		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable, may use duplicate sample
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	Applicable	Applicable	

9.27 ATG #28a – Open Characterization – Volatiles

When required, this ATG is to be used to give an indication of the presence of Volatile organic compounds (VOCs) which might not otherwise be suspected to be present in the waste water stream.

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	MANUAL 3 collected as Grab 2	Glass with Teflon® -lined septum cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	25 or 40 mL; no headspace	None	7 days
Alternate	MANUAL 3 collected as Grab 1 or On-line analyzer	n/a		Volume required to meet RMDLs and analyze all applicable QC samples		
Not Recommended		n/a				
Precautions/ Notes		Fill slowly, avoiding excessive air space and turbulence prior to preservation. All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	Limit of Characterization
Recommended	Purge and trap	GC-MS, capillary column	10 µg/L against 1,2-dichlorobutane
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	The three grab samples should be analyzed separately and an arithmetic mean reported or they may be combined in the lab immediately prior to analysis.		
	Analysis must be performed according to the principles in MOECC publication *Techniques for the Gas Chromatography – Mass Spectrometry Identification of Organic Compounds in Effluents*, July 1989, Revised December 1990, Reprinted June 1991, PIBS 477e		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	n/a	n/a	n/a
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Recommended, in case re-analysis is needed	

9.28 ATG #28b – Open Characterization – Extractables

When required, this ATG is to be used to give an indication of the presence of organic compounds which might not otherwise be suspected to be present in the waste water stream.

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon® -lined cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	800 mL	None	30 days
Alternate	MANUAL 1 or 2	Glass with Teflon® -lined cap	Instead of baking, rinse with acetone (or other water soluble solvent), distilled-in-glass hexane and/or dichloromethane, air dry	Volume required to meet MDLs and analyze all applicable QC samples		
Not Recommended		n/a				
Precautions/ Notes		Fill slowly, avoiding excessive air space and turbulence prior to preservation. All sample contact surfaces should be Teflon®, glass, or stainless steel only. Avoid contact with plastics and metallic foil.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for re-analysis if needed.		

Analytical Procedures	Sample Preparation	Instrumental Measurement	Limit of Characterization
Recommended	Liquid/liquid extraction at pH >12 (base/neutral) followed by liquid/liquid extraction at pH <2 (acid)	GC-MS, capillary column; co-injection of base/neutral and acid fractions	10 µg/L against D_{10}-Phenanthrenene
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	Analysis must be performed according to the principles in MOECC publication *Techniques for the Gas Chromatography – Mass Spectrometry Identification of Organic Compounds in Effluents*, July 1989, Revised December 1990, Reprinted June 1991, PIBS 477e		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	n/a	n/a	n/a
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Recommended, in case re-analysis is needed	

9.29 ATG #29 – Elemental Characterization

When required, this ATG is to be used to give an indication of the presence of trace elements which might not otherwise be suspected to be present in the waste water stream.

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Teflon®	Soak overnight in 5% HNO_3, followed by distilled water rinses, if necessary	500 mL	HNO_3 (containing <1 mg/L of total metals) to pH <2	30 days
Alternate	MANUAL 1 or 2	polypropylene, high or low density polyethylene, polystyrene, PET	Use new containers	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil If boron analysis is required, glass containers must not be used due to the potential for sample contamination.				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only and Teflon® lined caps.			If any speciation is to be carried out on these samples then alternative preservatives maybe required.	

Analytical Procedures	Sample Preparation	Instrumental Measurement	Limit of Characterization
Recommended	Nitric evaporation or other acid digestion as appropriate	Flame AA and/or ICP DCP or ICP-MS	50 µg/L
Alternate		n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	Analysis must be performed in accordance with the principles in MOECC publication *Guidance Document for the Elemental Characterization of Liquid Waste Samples*, July 1989, second revision March 1991, Reprinted June 1991, PIBS 476e Hyphenated techniques that support the speciation of ions/metalloids may include HPLC or IC coupled to appropriate analytical instrument (AAS, AAF, ICP-OES, ICP-MS). EPA 6800 is an Elemental and Speciated Isotope Dilution Mass Spectrometry technique that may be applicable to many elements and molecular species.		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	n/a	n/a	n/a
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	n/a	

9.30 ATG #30– Anions

9.30.1 Chloride – ATG 30

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	50 mL	none	30 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate	Ion chromatography Colourimetry Titration	2 mg/L
Alternate	n/a		
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources			
MOECC	E3016		
AWWA	4110B 4500-Cl^- C 4500-Cl^- G	4110C 4500-Cl^- D	4500-Cl^- B 4500-Cl^- E
USEPA	300.0 Rev 2.1 325.2 SW-846, 9250 SW-846, 6500	300.1 Rev 1.0 SW-846, 9056A SW-846, 9251	325.1 SW-846, 9212 SW-846, 9253
ASTM	D512-12 D6508-10	D4327-11	

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.30.2 Sulphate – ATG 30

Sampling Procedures	**Sampling Type**	**Container**	**Container Pretreatment**	**Sample Volume**	**Preservation**	**Maximum Sample Storage time**
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	50 mL	none	30 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic				

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
		solvent content, use glass or Teflon® container only				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate	Ion chromatography	5 mg/L as sulphate
Alternate	n/a	Colorimetry	
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources			
MOECC	E3172		
AWWA	4110B 4500-SO_4^{2-} G	4110C	4500-SO_4^{2-} F
USEPA	300.0 Rev 2.1 SW-846, 9056A SW-846, 9038	300.1 Rev 1.0 SW-846, 9035 SW-846, 6500	375.2 Rev 2.0 SW-846, 9036
ASTM	D516-11 D6508-10	D4327-11	

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.30.3 Fluoride – ATG 30

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	50 mL	none	30 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate	Colourimetry Ion selective electrode Ion chromatography	0.1 mg/L
Alternate	n/a		
Not Recommended	n/a	n/a	
Precautions/Notes	High chloride content in samples may cause severe interference problems in the analysis of fluoride.		

Recommended Method Sources			
MOECC	E3172		
AWWA	4110B	4110C	4500-F^- B

Recommended Method Sources			
	4500-F⁻C 4500-F⁻ G	4500-F⁻ D	4500-F⁻ E
USEPA	300.0 Rev 2.1 340.2 Rev 1 SW-846, 9214	300.1 Rev 1.0 340.3 SW-846, 6500	340.1 Rev 2 SW-846, 9056A
ASTM	D1179-10	D4327-11	D6508-10

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.30.4 Bromide

Sampling Procedures	**Sampling Type**	**Container**	**Container Pretreatment**	**Sample Volume**	**Preservation**	**Maximum Sample Storage time**
Recommended	AUTO 1 or 2	Plastic	Generally none for new containers	50 mL	See notes	28 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes					Upon receipt at the lab, the sample should be sparged with N, He or Ar for 10 minutes.	

Analytical Procedures	Sample Preparation	Instrumental Measurement	Reporting Units
Recommended	Preparation for measurement system as appropriate	Ion chromatography	µg/L
Alternate	n/a	Ion selective electrode (ISE) Colorimetry	
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources			
MOECC	E3462	E3434 (Aug 2010)	
AWWA	4110B 4500-Br^- B	4110C 4500-Br^- C	4110 D
USEPA	300.0 Rev 2.1 326.0	300.1 Rev 1.0 SW-846, 9056A	317.0 Rev 2 SW-846, 9211
ASTM	D1246-10 D6581-12	D4327-11	D6508-10

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.31 ATG #31 – Total Residual Oxidants (Total Residual Chlorine)

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	On-line analyser	Amber glass with ground-glass stopper	None	1000 mL	None; protect from light	<1 hour
Alternate	GRAB 1, 2 or 3	Stopper or cap that will ensure headspace is eliminated.	n/a	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended						
Precautions/ Notes		Fill container completely, mount stopper to eliminate headspace.				Analysis of each grab sample should be initiated as soon as possible after sample collection.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	n/a	Amperometry Potentiometry	0.01 mg/L as chlorine
Alternate	n/a	Colourimetry	
Not Recommended	n/a	n/a	
Precautions/Notes	Each sample must be analyzed within the 1 hour storage time specified above.		

Recommended Method Sources			
MOECC	n/a		
AWWA	4500-Cl B 4500-Cl E 4500-Cl H	4500-Cl C 4500-Cl F 4500-Cl I	4500-Cl D 4500-Cl G
USEPA	330.1 330.4	330.2 330.5	330.3
ASTM	D1253-14		

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable, see note	n/a	Applicable	
Note: Travelling blank need not be analyzed if sample analysis occurs immediately after sampling at the sampling point.				

9.32 ATG #32 – Fibrous Chrysotile (Asbestos)

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Plastic container, never before been used	None; container must be new	1000 mL	None	2 days before filtration, unlimited after, dependent on reporting time requirement
Alternate	MANUAL 1 or 2	n/a	n/a	Volume required to meet RMDLs and analyze all applicable QC samples		
Not Recommended		n/a				
Precautions/ Notes		Wide-mouth containers are preferable. Do not agitate to avoid breaking clusters into fibres.				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Filtration onto membrane filter	Transmission electron microscopy with electron diffraction	0.04 million fibres/L
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources	
MOECC	n/a
AWWA	2570 B
USEPA	100.1 100.2
ASTM	n/a

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	n/a	n/a	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.33 ATG #33 – Adsorbable Organic Halide (AOX)

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon®-lined cap	Generally none for new containers	1000 mL	None	14 days
Alternate	MANUAL 1 or 2	Teflon® with Teflon®-lined cap	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	If analysis cannot be performed immediately upon arrival at laboratory, to 1 L of sample, add nitric acid to pH 2 then 1 mL of 0,1M sodium sulphite solution	
Not Recommended		n/a				
Precautions/ Notes						

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Carbon adsorption (column or shaker) at pH 2 followed by nitrate wash. Dohrmann 100-200 mesh charcoal, granular activated carbon or equivalent	Pyrolysis in an oxygen rich atmosphere followed by microcoulometric analysis	0.05 mg/L, based on 2,4,6-trichlorophenol
Alternate	n/a	n/a	
Not Recommended	n/a	n/a	
Precautions/Notes	Analysis should be carried out in an environment free of chlorinated solvents.		

Recommended Method Sources	
MOECC	E3225
AWWA	5320 B
USEPA	SW-846, 9020B 1650 C
ASTM	n/a

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	Applicable	Applicable	

9.34 ATG #34 – Miscellaneous Organics

9.34.1 Diethanolamine – ATG #34

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon®-lined cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	100 mL	None	30 days
Alternate	MANUAL 1 or 2	n/a	Instead of baking, rinse with acetone (or other water soluble solvent), distilled-in-glass hexane and/or dichloromethane, air dry	Volume required to meet RMDLs and analyze all applicable QC samples		
Not Recommended		n/a				
Precautions/ Notes		All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	None	Ion chromatography LC-MS/MS	0.1 mg/L

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Alternate	Liquid/liquid extraction; clean-up if necessary	LC-Thermal Energy analyzer (TEA)	
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources	
MOECC	n/a
AWWA	n/a
USEPA	n/a
ASTM	D7599-09e2

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	Applicable	Applicable	

9.34.2 N-nitrosodimethylamine (NDMA) – ATG #34a

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Amber glass with Teflon® -lined cap	If needed, wash in hot water, detergent, water, distilled water rinse. Heat at 105°C for 1 hour. Cap: no pre-treatment	1 L	None	14 days
Alternate	MANUAL 1 or 2	Teflon® with Teflon® -lined cap	Instead of baking, rinse with methanol, air dry	Volume required to meet RMDLs and analyze all	n/a	

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
				applicable QC samples		
Not Recommended		n/a				
Precautions/ Notes		All sample contact surfaces should be Teflon®, glass, metallic foil or stainless steel only. Avoid contact with plastics.		Collection of duplicate samples is recommended to fulfill QA/QC requirements and for reanalysis if needed.		Analysis must be initiated within 2 days for "Reactive" samples which contain precursors to NDMA and, upon chlorination, form NDMA during storage.

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Adsorption on Ambersorb® 572; desorption into dichloromethane	GC/HRMS, capillary column; quantification by isotope dilution	1.0 ng/L
Alternate	Liquid/liquid extraction with dichloromethane	GC/LRMS acceptable with effective clean-up if RMDL is achieved	
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources		
MOECC	E3388	
AWWA	6450 B	6450 C
USEPA	521 Ver 1.0	607
ASTM	n/a	

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	Applicable	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable, with each set of samples	n/a	Recommended, in case re-analysis is needed	

9.35 ATG #35 – Microbiological Parameters

9.35.1 *Escherichia coli* (*E. coli*) – ATG 35

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	Grab 2	Sterile Plastic or glass	Containers must be sterile	250 mL	Pre-charge container with sterile sodium thiosulphate to provide concentration of 100 mg/L in the sample volume collected. Chill on ice during transport to laboratory.	Unpreserved: 2 hours Preserved: 48 hours
Alternate	n/a					
Not Recommended		All non-sterile containers not specifically prepared for bacterial analysis			Samples must never be frozen.	
Precautions/ Notes	Sodium thiosulphate must be added as soon as possible after sample collection when chlorine or sodium hypochlorite has been used as a disinfectant. It is strongly recommended that suitable containers be used which are pre-charged with the preservative.					

Analytical Procedures	Sample Preparation	Culture Medium (Agar)	RMDL
Recommended	Membrane filtration	mFC-BCIG, incubate at 44.5 ±0.5°C for 24±2 hours (enzyme substrate)	1 CFU/100 mL
Alternate	n/a	mTEC agar plus urease; incubate at 44.5 ±0.2°C for 21±1 hours	
Not			

Analytical Procedures	Sample Preparation	Culture Medium (Agar)	RMDL
Recommended			
Precautions/Notes	Frozen samples must not be analyzed.		

Recommended Method Sources	
MOECC	E3371
AWWA	9222 9223
USEPA	1103.1 1603 1604 Enzyme substrate methods as approved by the EPA, 40 CFR Part 122, 136, et al, March 12, 2007.
ASTM	D5392-14

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable (media QC)	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	n/a	

9.35.2 Total Coliforms

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	Grab 2	Sterile Plastic or glass	Containers must be sterile	250 mL	Pre-charge container with sterile sodium thiosulphate to provide concentration of 100 mg/L in the sample volume collected. Chill on ice during transport	Unpreserved: 2 hours Preserved: 48 hours

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
					to laboratory.	
Alternate	n/a					
Not Recommended		All non-sterile containers not specifically prepared for bacterial analysis			Samples must never be frozen.	
Precautions/ Notes	Sodium thiosulphate must be added as soon as possible after sample collection when chlorine or sodium hypochlorite has been used as a disinfectant. It is strongly recommended that suitable containers be used which are pre-charged with the preservative.					

Analytical Procedures	Sample Preparation	Culture Medium (Agar)	Reporting Units
Recommended	Membrane filtration	mEndo LES agar; incubate at 36.0 ±1.0°C for 24±2 hours	CFU/100 mL
Alternate	n/a		
Not Recommended			
Precautions/Notes	Frozen samples must not be analyzed		

Recommended Method Sources			
MOECC	E3371		
AWWA	9222	9223	
USEPA	1604	SW-846, 9132	SW-846, 9131
	Enzyme substrate methods as approved by the EPA, 40 CFR Part 122, 136, et al, March 12, 2007.		
ASTM	n/a		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable (media QC)	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	n/a	

9.35.3 Fecal Streptococci

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	Grab 2	Sterile Plastic or glass	Containers must be sterile	250 mL	Pre-charge container with sterile sodium thiosulphate to provide concentration of 100 mg/L in the sample volume collected. Chill on ice during transport to laboratory.	Unpreserved: 2 hours Preserved: 48 hours
Alternate	n/a					
Not Recommended		All non-sterile containers not specifically prepared for bacterial analysis			Samples must never be frozen.	
Precautions/ Notes	Sodium thiosulphate must be added as soon as possible after sample collection when chlorine or sodium hypochlorite has been used as a disinfectant. It is strongly recommended that suitable containers be used which are pre-charged with the preservative.					

Analytical Procedures	Sample Preparation	Culture Medium (Agar)	Reporting Units
Recommended	Membrane filtration	mEnterococcus agar; incubate at 36.0 ±1.0°C for 48±3 hours	CFU/100 mL
Alternate	n/a		
Not Recommended			
Precautions/Notes	Frozen samples must not be analyzed		

Recommended Method Sources	
MOECC	E3371
AWWA	9230
USEPA	Enzyme substrate methods as approved by the EPA, 40 CFR Part 122, 136, et al, March 12, 2007.
ASTM	n/a

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	Applicable (media QC)	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	n/a	

9.35.4 *Pseudomonas aeruginosa*

Sampling Procedures	**Sampling Type**	**Container**	**Container Pretreatment**	**Sample Volume**	**Preservation**	**Maximum Sample Storage time**
Recommended	Grab 2	Sterile Plastic or glass	Containers must be sterile	250 mL	Pre-charge container with sterile sodium thiosulphate to provide concentration of 100 mg/L in the sample volume collected. Chill on ice during transport to laboratory.	Unpreserved: 2 hours Preserved: 48 hours
Alternate	n/a					
Not Recommended		All non-sterile containers not specifically prepared for bacterial analysis			Samples must never be frozen.	

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Precautions/ Notes	Sodium thiosulphate must be added as soon as possible after sample collection when chlorine or sodium hypochlorite has been used as a disinfectant. It is strongly recommended that suitable containers be used which are pre-charged with the preservative.					

Analytical Procedures	Sample Preparation	Culture Medium (Agar)	Reporting Units
Recommended	Membrane filtration	mPA agar; incubate at 36.0 ±1.0°C for 48±3 hours	CFU/100 mL
Alternate	n/a		
Not Recommended			
Precautions/Notes	Frozen samples must not be analyzed		

Recommended Method Sources	
MOECC	E3371
AWWA	9213 E
USEPA	Enzyme substrate methods as approved by the EPA, 40 CFR Part 122, 136, et al, March 12, 2007.
ASTM	D5246-13

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable (media QC)	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	n/a	n/a	n/a	

9.36 Toxicity Sample Collection and Analysis

9.36.1 Rainbow Trout

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	Grab 2	Polyethylene, polypropylene, polycarbonate, stainless steel, Nalgene® or Teflon®.	Containers must be non-toxic, preferably food-grade	40 litres (L) for single concentration (single concentration) rainbow trout acute lethality testing or pH stabilization testing	None	5 days
Alternate	n/a	Glass may be used but is not suitable for shipping large volumes.		60 L for multi-concentration (LC50) rainbow trout acute lethality or pH stabilization testing	None	
Not Recommended					Samples must never be frozen solid.	
Precautions/ Notes	Line sampling containers with food-grade plastic liners that have been quality control tested by the laboratory. Use wet-ice packs outside the liner but inside the sample container to keep the sample cool. Sample volumes are recommendations, but may vary depending on the size of the test fish. Sample volume must be sufficient to meet the loading density in Environment Canada method EPS 1/RM/13. Samples containing slush and/or ice chips may be analyzed but this condition must be recorded.					

Required analytical procedures:

Environment Canada, *Biological Test Method: Reference Method for Determining Acute Lethality of Effluents to Rainbow Trout*, EPS 1/RM/13, 2000, as amended from time to time

Environment Canada, *Biological Test Method: Procedure for pH Stabilization During the Testing of Acute Lethality of Wastewater Effluent to Rainbow Trout*. EPS 1/RM/50, 2008, as amended from time to time

9.36.2 *Daphnia magna*

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	Grab 2	Glass, polyethylene, polypropylene, polycarbonate, stainless steel, Nalgene® or Teflon®.	Containers must be non-toxic, preferably food-grade	1 litre	None	5 days
Alternate	n/a	Glass may be used but is not suitable for shipping large volumes.			None	
Not Recommended					Samples must never be frozen solid.	
Precautions/ Notes	If both rainbow trout and *Daphnia magna* testing is required, 1 L of sample may be used from the 40L collected for the rainbow trout test. Samples containing slush and/or ice chips may be analyzed but this condition must be recorded.					

Required analytical procedure:

Environment Canada, *Biological Test Method: Reference Method for Determining Acute Lethality of Effluents to Daphnia magna*, EPS 1/RM/14, 2000, as amended from time to time

9.36.3 Fathead Minnows

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	Grab 2	Polyethylene, polypropylene, polycarbonate, stainless steel, Nalgene® or Teflon®.	Containers must be non-toxic, preferably food-grade	≥ 28 litres or sufficient to meet the requirements of Environment Canada method EPS/1/RM/21	None	3 days
Alternate	n/a	Glass may be used but is not suitable for shipping large volumes.			None	
Not Recommended					Samples must never be frozen solid.	
Precautions/ Notes	Line sampling containers with food-grade plastic liners that have been quality control tested by the laboratory. Use wet-ice packs outside the liner but inside the sample container to keep the sample cool. Samples containing slush and/or ice chips may be analyzed but this condition must be recorded.					

Required analytical procedure:

Environment Canada, Biological *Test Method: Test of Larval Growth and Survival Using Fathead Minnows*, EPS 1/RM/22, 2nd edition, February 2011, as amended from time to time

9.36.4 *Ceriodaphnia dubia*

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	Grab 2	Polyethylene, polypropylene,	Containers must be non-toxic, preferably	Sufficient to meet the	None	3 days

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
		polycarbonate, stainless steel, Nalgene® or Teflon®.	food-grade	requirements of Environment Canada method EPS/1/RM/22		
Alternate	n/a	Glass may be used but is not suitable for shipping large volumes.			None	
Not Recommended					Samples must never be frozen solid.	
Precautions/ Notes	Line sampling containers with food-grade plastic liners that have been quality control tested by the laboratory. Use wet-ice packs outside the liner but inside the sample container to keep the sample cool. Samples containing slush and/or ice chips may be analyzed but this condition must be recorded.					

Required analytical procedure:

Environment Canada, Biological Test Method: Test of Reproduction and Survival Using the Cladoceran *Ceriodaphnia dubia*, EPS 1/RM/21, 2007, as amended from time to time

9.37 Additional Physical Analyses

9.37.1 Alkalinity

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	100 mL	none	14 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only				

Analytical Procedures	Sample Preparation	Instrumental Measurement	Reporting Units
Recommended	Preparation for measurement system as appropriate	Titration to fixed end-point of pH 4.5	mg/L as $CaCO_3$
Alternate	n/a	Colorimetry	
Not Recommended	n/a	n/a	
Precautions/Notes	Alkalinity may be analyzed from the same sample container as for ATG 3 (pH), ATG 7 (Specific Conductance) and/or ATG 8 (TSS/VSS/TDS/TS).		

Recommended Method Sources		
MOECC	E3218	
AWWA	2320 B	
USEPA	310.1 SW-846, 8203	310.2 SW-846, 8221
ASTM	D1067-11, A or B	

Laboratory QC	**Blank**	**Spiked Blank**	**Spiked Sample**	**Replicate**
	Applicable	n/a	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.37.2 Colour

Sampling Procedures	**Sampling Type**	**Container**	**Container Pretreatment**	**Sample Volume**	**Preservation**	**Maximum Sample Storage time**
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	100 mL	None	14 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples		
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only				

Analytical Procedures	Sample Preparation	Instrumental Measurement	RMDL
Recommended	Preparation for measurement system as appropriate	Colorimetry	True Colour Units (TCU)
Alternate	n/a		
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources			
MOECC	E3219		
AWWA	2120 C	2120 D	
USEPA	110.2	110.3	110.2
ASTM	n/a		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	n/a	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.37.3 Hardness

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	AUTO 1 or 2	Glass or Plastic	Generally none for new containers	50 mL	Nitric acid if analyzing by AAS or ICP	30 days if preserved
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC	None if analyzing by titration	

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
				samples		
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only				

Analytical Procedures	Sample Preparation	Instrumental Measurement	Reporting Units
Recommended	Preparation for measurement system as appropriate	Calculation from calcium and magnesium obtained as per ATG9	mg/L as $CaCO_3$
Alternate	n/a	Titration Colourimetry	mg/L as $CaCO_3$
Not Recommended	n/a	n/a	
Precautions/Notes	Calculation: mg equivalent $CaCO_3$/L = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]		

Recommended Method Sources		
MOECC	E3094	
AWWA	2340B	2340C
USEPA	130.2 SW-846, 8226	130.1
ASTM	D511-09 D6919-09	D1126-12
Also see ATG9 for recommended methods to determine calcium and magnesium.		

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	Applicable	Applicable	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

9.37.4 Turbidity

Sampling Procedures	Sampling Type	Container	Container Pretreatment	Sample Volume	Preservation	Maximum Sample Storage time
Recommended	On-line analyzer AUTO 1 or 2	Glass or Plastic	Generally none for new containers	100 mL	none	2 days
Alternate	MANUAL 1 or 2	Teflon®, polypropylene, high or low density polyethylene, polystyrene, PET	Wash with detergent if necessary, distilled water rinses	Volume required to meet RMDLs and analyze all applicable QC samples	n/a	
Not Recommended		Contact with metal foil				
Precautions/ Notes		If sample is expected to have high (>5%) hydrocarbon or organic solvent content, use glass or Teflon® container only				When the characteristics of the wastewater may lead to rapid changes in turbidity, an on-line analyzer must be used or grab samples must be collected and analyzed as soon as reasonably possible.

Analytical Procedures	Sample Preparation	Instrumental Measurement	Reporting Units
Recommended	None	On-line analyzer Nephelometry	NTU
Alternate	Preparation for measurement system as appropriate		
Not Recommended	n/a	n/a	
Precautions/Notes			

Recommended Method Sources			
MOECC	E3311		
AWWA	2130		
USEPA	180.1		
ASTM	D7315-12 D7725-12	D6855-12 D7726-11	D6698-14

Laboratory QC	Blank	Spiked Blank	Spiked Sample	Replicate
	Applicable	n/a	n/a	Applicable
Field QC	**Travelling blank**	**Travelling Spiked Blank**	**Duplicate**	
	Applicable	n/a	Applicable	

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Environment Canada, Biological Test Method: Test of Reproduction and Survival Using the Cladoceran *Ceriodaphnia dubia*, EPS 1/RM/21, 2007, as amended from time to time

Environment Canada, *Biological Test Method: Procedure for pH Stabilization During the Testing of Acute Lethality of Wastewater Effluent to Rainbow Trout*. EPS 1/RM/50, 2008, as amended from time to time.

Recommended Analytical Method Sources

MOECC Ontario Ministry of the Environment and Climate Change, Laboratory Services Branch; e-mail requests to LaboratoryServicesBranch@ontario.ca

AWWA American Waterworks Association, American Public Health Association, Water Environment Federation, *Standard Methods for the Examination of Water and Wastewater*, 22nd edition, 2012 or current published version

Note: methods from the 20th and 21st editions are also acceptable if the laboratory demonstrates that it meets the RMDL and recommended method principles.

USEPA United States Environmental Protection Agency; available electronically at EPA Methods

ASTM ASTM International, *Annual Book of ASTM Standards, Section Eleven, Water and Environmental Technology*, Volumes 11.01 and 11.02, 2014 or current published version. Also available online at ASTM International.